TEMPERATURE AND STORING TIME EFFECT ON RHEOLOGIC PROPERTIES OF SELECTED TOMATO KETCHUPS

UTICAJ TEMPERATURE I VREMENA ČUVANJA NA REOLOŠKE OSOBINE ODABRANIH KEČAPA OD PARADAJZA

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ABSTRACT

This article is focused on monitoring and evaluation of rheological properties of tomato ketchups. The aim of the work was to show the importance of the knowledge about rheological properties of materials and determine qualitative changes in ketchup behaviour dependent on temperature changes and storage time. The measurements of all samples were carried out under the same conditions in approximate temperature range (5 – 30) °C. First measurements were performed at the beginning of storing, second measurements were done after two weeks of storing and last measurements were realised after four weeks of storing. There were constructed dependencies of rheologic properties on temperature and storage time and evaluated by the regression equations and the coefficients of determination. Ketchup is a non-Newtonian material, so apparent viscosity was measured. The measurements of apparent viscosity were performed on a digital rotational viscometer Anton Paar DV - 3P. Densities of measured samples were determined according to definition. We found out that apparent viscosity of samples decreased exponentially with increasing temperature, so the Arrhenius equation is valid. Ketchup's fluidity was increasing exponentially with the temperature. We also found out that apparent viscosity had decreased with storage time and on the other hand 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. 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.

Key words: ketchup, rheologic parameters, temperature, density, storing time, comparison.

REZIME

Ovaj rad je fokusiran na praćenje i procenu reoloških osobina kečapa od paradajza. Cilj rada bio je da se pokaže značaj poznavanja reoloških osobina materijala i odrede kvalitativne promene kečapa u zavisnosti od temperaturnih promena i vremena skladištenja. Merenja svih uzoraka obavljena su pod istim uslovima u približnom temperaturnom opsegu od 5 do 30°C. Prva merenja su obavljena na početku skladištenja, druga nakon dve nedelje skladištenja, dok su poslednja merenja obavljena nakon četiri nedelje skladištenja. Određene su funkcionalne zavisnosti reoloških osobina od temperature kečapa i vremena skladištenja. Zavosnosti su predstavljene regresionim jednačinama, a definisani su i koeficijenti determinacije. Kečap je nenjutnov fluid, tako da je izmerena prividna viskoznost. Merenja prividne viskoznosti vršena su na digitalnom rotacionom viskozimetru Anton Paar DV - 3P. Gustine izmerenih uzoraka su određene prema definiciji. Ustanovljena je da se prividna viskoznost uzoraka eksponencijalno smanjuje sa porastom temperature, tako da je Arrhenusova jednačina validna. Fluidnost kečapa eksponencijalno raste sa temperaturom kečapa. Takođe smo otkrili da je prividna viskoznost smanjena tokom vremena skladištenja, a sa druge strane fluidnost raste sa vremenom skladištenja, što može biti uzrokovano strukturnim promenama u uzorcima tokom skladištenja. Temperaturna zavisnosti gustine kečapa definisana je opadajućom linearnom funkcijom u izmerenom temperaturnom području. Izračunate reološke karakteristike mogu se koristiti za projektovanje tehnološke opreme ili pakovanja za distribuciju proizvoda krajnjim korisnicima. Poznavanje ponašanja protoka je takođe važno za razvoj novih recepata i direktnu kvalitativnu procenu proizvoda.

Ključne reči: kečap, reološke osobine, temperatura, gustina, vreme skladištenja, poređenje.

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 and Doležalová, 2014; Kubík et al., 2017), rheologic (Hlaváč and Božiková, 2011, 2012; Bikić et al., 2012; Bukurov et al., 2012; Glicerina et al., 2013; Diósi et al., 2014) and, thermophysical (Božiková and Hlaváč, 2010; Glicerina et al., 2013; Micić et al., 2014).

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 (Tan and

Kerr, 2015). 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 and 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). Changes of tomato powder during storage at different storage temperatures were evaluated during five months by Liu et al. (2010). Authors found out that higher storing temperatures had a significant effect on tomato powder qualities, while lower temperature had less

effect. Tomato powder has many advantages, including ease of packing, transportation and mixing. In addition, tomato powder can be used as an ingredient in many food products, mainly soups, sauces and ketchup (Liu et al., 2010). 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). Effect of temperature on dynamic and steady-state shear rheological properties of siriguela pulp was analysed by Augusto et al. (2012). Authors stated that the product flow behaviour can be well described by the Herschel-Bulkley model, and the parameters were modelled as a function of temperature. The relationship between electrostatic pectin-interactions and in vitro bioaccessibility of essential cationic minerals in selectively processed particulated tomato products was investigated by Kyomugasho et al. (2015). The effects of manothermosonication or thermal treatment on tomato pectic enzymes and tomato paste rheological properties were compared by Vercet et al. (2002). Quality parameters of tomato paste using guided microwave spectroscopy were determined by Zhang et al. (2014). 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 and 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). The concentrated tomato pastes are usually stored and used as an intermediate product with water and other ingredients to be reconstituted into final products, such as ketchups and sauces (Zhang et al., 2014). 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). Karaman et al. (2012) analysed linear creep and recovery of ketchup-processed cheese mixtures using mechanical simulation models as a function of temperature and concentration. Authors found out that effect of temperature on creep phase parameters (e.g. viscosity) could be successfully described by Arrhenius relationship. Authors had also determined the activation energies for analysed ketchup and had described the effect of temperature and concentration on activation energy (Karaman et al., 2012). Mert (2012) used high pressure microfluidization to improve physical properties and lycopene content of ketchup type products. 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. Effect of various hydrocolloids on the rheological properties of different formulated ketchups were examined by Sahin and Ozdemir (2004). Authors found out that all tested hydrocolloids can be used to improve consistency resp. viscosity of tomato ketchups. Apparent viscosity is defined as ratio of shear stress and corresponding shear rate and its physical unit is [Pa·s]. Viscosity changes with temperature. Viscosity of most of the liquids decreases with increasing temperature. Theories have been proposed regarding the effect of temperature on viscosity of liquids. According to Eyring 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 and 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 and Teixeira, 2007). The standard SI unit of density is [$\text{kg} \cdot \text{m}^{-3}$].

Reciprocal value of viscosity η is called fluidity φ and unit of fluidity is [$\text{Pa}^{-1} \cdot \text{s}^{-1}$] (Figura and Teixeira, 2007).

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

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

MATERIALS AND METHODS

Measurements were performed in laboratory settings (temperature 20 °C, atmospheric pressure 1013 hPa and relative air humidity 45 %) on three samples of tomato ketchup, purchased in local market. Analysed were these samples of ketchup: Heinz tomato ketchup, sweet ketchup Hamé and soft ketchup Snico. As ketchup is not Newtonian material, so apparent viscosity had to be measured. These other properties were determined: density and fluidity. 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) and measuring principle is based on dependency of sample resistance against the probe rotation. First measurements were performed at the beginning of storing, second measurements were done after two weeks of storing and last measurements were realised after four weeks of storing. Density of samples was determined according to definition (Eq. 2). Reciprocal value of viscosity (fluidity) was also determined (Eq. 3). There were constructed dependencies of rheologic 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 functions (4), in the case of temperature dependencies of fluidity can be used increasing exponential functions (5), and temperature dependencies of density were described by decreasing linear function (6).

$$\eta = A e^{-B \left(\frac{t}{t_0} \right)} \quad (4)$$

$$\varphi = E e^{F \left(\frac{t}{t_0} \right)} \quad (5)$$

$$\rho = -G \left(\frac{t}{t_0} \right) + H \quad (6)$$

where t is temperature, 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 viscosity values 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 (+), Heinz (Δ), Hamé (□)

Temperature dependencies of ketchup density are 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 and 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.

Fig. 2. Relations of ketchup density to the temperature Snico (+), Heinz (Δ), Hamé (□)

Fig. 3. Relations of ketchup fluidity to the temperature
Snico (+), Heinz (Δ), Hamé (□)

Fluidity dependencies on temperature are presented on Fig. 3. Increasing exponential character of dependency was used for all samples. Due to the fact that fluidity is defined as reciprocal value of viscosity, highest fluidities were found for Ketchup Hamé and lowest for Ketchup Snico.

Fig. 4. Relations of ketchup Heinz apparent viscosity to the temperature first measurement (+), next measurement (Δ), last measurement (□)

Regression coefficients and coefficients of determination for all dependencies are shown in Tab. 1.

Influence of storage time for sample of Ketchup Heinz could be seen on Fig. 4. It is clear from

Fig. 5 that highest apparent viscosity values were obtained in the beginning of storing, lower values were after two 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 two samples of ketchup. Karaman et al. (2012) obtained approximately

similar values of parameter in regression equation contributing with apparent viscosity. It can be seen from Tab. 1 that coefficients of determination reached very high values in the approximate range (0.965 – 0.998).

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

	Regression equations (4 – 6)		
	Coefficients		
Sample of ketchup	A [mPa.s]	B [1]	R^2
Snico	6 832.31	0.012 39	0.988 419
Heinz	5 147.80	0.009 54	0.980 328
Hamé	4 482.59	0.011 39	0.981 357
Sample of ketchup	E [$\text{Pa}^{-1} \cdot \text{s}^{-1}$]	F [1]	R^2
Snico	0.146 789	0.012 26	0.987 145
Heinz	0.193 872	0.009 61	0.978 436
Hamé	0.222 962	0.011 44	0.982 665
Sample of ketchup	G [$\text{kg} \cdot \text{m}^{-3}$]	H [$\text{kg} \cdot \text{m}^{-3}$]	R^2
Snico	1 136.59	1.031 33	0.991 941
Heinz	1 128.86	1.095 58	0.998 152
Hamé	1 122.73	1.061 75	0.997 124
Ketchup Heinz/ measurement	A [mPa.s]	B [1]	R^2
First	5 147.80	0.009 54	0.980 328
Next	4 834.27	0.008 38	0.965 453
Last	4 383.82	0.005 76	0.970 301

CONCLUSION

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. Rheologic properties of selected 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 fluidity was increasing exponentially with the temperature. We also found out that apparent viscosity had decreased with storage time and on the other hand 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 other authors (Kumbár and 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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