# Comparison of thermal and rheologic properties of Slovak mixed flower honey and forest honey

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**Abstract**

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The article deals with the comparison of thermal and rheologic properties of two types of honey – mixed flower honey and forest honey made in Slovak Republic. All honey parameters were measured during temperature manipulation in the temperature interval from 5 to 45°C. Two series of thermal and rheologic parameters measurements were done. Firstly samples of both types of fresh honey were measured at the beginning of storage and then the same samples of honey were measured again after one week of storage. The measuring of thermal parameters i.e. thermal conductivity, thermal diffusivity and specific heat was performed by the instrument Isomet 2104, which uses Hot Wire method, and the principle of measuring being based on the analysis of time-temperature relation. The measurements of dynamic viscosity were done by the viscometer Anton Paar (DV-3P), the principle of measuring being based on the dependence of the sample resistance on the probe rotation. Other rheologic parameters as kinematic viscosity and fluidity, were also determined. For the rheologic parameters measurements exponential relations are typical while for the thermal parameters linear relations were obtained.

**Keywords**: samples of honey; temperature; thermophysical properties; rheological parameters; time of storage

Controlled processes in manufacturing, handling, and holding require precise knowledge of physical quantities of materials. For the quality evaluation of food materials it is important to know their physical properties particularly, mechanical, rheologic and thermophysical (Božiková, Hlaváč 2010).

In this article are presented theoretical parts from thermophysics and rheology, thermophysical and rheologic measurement methods and the results of thermophysical and rheologic parameters measurements for different types of honey. Some rheologic and thermophysical properties of honey are mentioned in literature. Bhandari et al. (1999) examined rheologic properties of Australian honeys.

They found out that rheologic properties of honey depend on the composition of individual sugars, and the amounts and types of colloids present in honey. Zaitoun et al. (2000) examined rheologic properties of selected light-coloured Jordanian honeys. They found out that the viscosity of honey decreases with the water content. The water content is the major factor that influences the keeping quality or storability of honey. Chirife and Buera (1997) described a simple model for predicting the viscosity of sugar and oligosaccharide solutions. They found out that disaccharides, composed of two monomeric monosaccharides, give rise to a higher viscosity than monosaccharides when com-

pared in the same mass fraction. Junzheng and Changying (1998) were interested in the rheologic model of natural honeys in China. They and many other authors reported that honeys behave as Newtonian fluid. Honey viscosity was Newtonian, even in reduced-calorie varieties, and adhered to the Arrhenius equation, the viscosity exponentially decreasing with the temperature (Cohen, Weihs 2010). White et al. (1964) examined the effect of storage and processing temperature on the honey quality. In their investigation they found out that dark-coloured types of honey tend to be affected by heat faster than the light-coloured types. It is natural for many types of honey to granulate or crystallise upon storage. Since the retail honey market largely favours liquid honey, some types of processing are necessary to maintain the liquid state. This is most commonly done by straining, heating, or filtration (White 1999). In honey processing, heating is applied for the following reasons: to warm it sufficiently to facilitate straining, handling, and packing; to delay granulation. Other reason for honey heating is to destroy yeasts that may be present; hence, the keeping quality of the honey respective is assured (White 1975).

Generally, physical properties of honey are influenced by various factors such as: the type of flowers, way of processing and most of all area of origin, etc. The research of honey physical properties in Slovak Republic is at the beginning and particular properties are not known. Our research was oriented on measuring the rheological and thermophysical properties of honey.

## MATERIALS AND METHODS

According to Codex Alimentarius of the Slovak Republic (2004) honey is a natural sweet substance, produced by honeybees from the nectar of plants or from secretions of living parts of plants, or excretions of plant-sucking insects on the living parts of plants, which the bees collect, transform by combining with specific substances of their own, deposit, dehydrate, store and leave in honeycombs to ripen and mature.

Honey is the primary product of bees and belongs among natural sweeteners; it is also known for its health promoting effects. The main parts of honey are nectar and honeydew. Nectar is the secretion of the plant organs and it consists of concentrated solution of sugars (glucose, fructose, sucrose, and maltose).

Honeydew is plant juice, which passed through the part of the bee digestive tract. Its main ingredients are also sugars, but in more varied composition. Honey is a mixture of sugars, water, and other components. The specific composition of a honey depends mostly on the mixture of flowers visited by bees producing the honey and it is different in relation to locations, terms and particular colony of bees. Honey in general consists of fructose (approximately 38%), glucose (about 31%), sucrose (around 1%), other sugars (about 9%), water (approximately 17%), ash (around 0.17%), and other substances (Hlaváč 2010).

Two different types of honey were measured – mixed flower honey and forest honey. The general composition of both samples has been presented above; however there were some differences between the samples. For example, the colour of honey made the greatest difference, but it did not influence the thermophysical and rheological properties. The next difference was in the water content: forest honey had 17.86% and mixed flower honey had 16.33% of water.

All honey samples were analysed in laboratory settings (laboratory temperature 20°C, atmospheric pressure 1,013 hPa and relative air humidity 45%). Rheologic properties were measured in the temperature range (20–45°C), thermophysical properties were measured in the temperature range of (5–45°C). Temperatures higher than 20°C were obtained by heating in the water bath and lower temperatures were obtained by cooling in the refrigerator. The honey samples were without bubbles, lest the precision of the measurements should affected by them. The state of the samples during the measurements was different according to the sample temperature.

For the quality protection in practice, we need many series of measurements in a short time, so the current research prefers non stationary – dynamic methods for thermophysical and rheologic parameters measurements to the stationary methods which usually take a long time. On the basis of the facts presented, dynamic methods of thermophysical and rheologic parameters measurement were chosen and are described in the following text.

**Thermophysical parameters and method of measurement**. For thermophysical parameters measurements a dynamic method Hot Wire method (HW method) was used. HW method is a standard transient dynamic technique which is based on the measurement of the time – temperature relation in a defined distance from the heat source (hot wire) (Davis 1984). The heating wire as well

as the temperature sensor (thermocouple) is encapsulated in a probe that electrically insulates the hot wire and the temperature sensor from the test material (Wechsler 1992). Heat flux is generated for an appropriate time interval through a long thin uniform wire buried in the sample and the temperature response is measured by the change in the wire resistance. The response is analysed in accordance with a model characterised by the particular formula found by the solution of the partial differential equations using boundary and initial conditions corresponding to the experimental set up presented in the literature Božiková and Hlaváč (2010). By HW method, we can obtain the value of thermal conductivity and we can calculate the thermal diffusivity and specific heat.

According to Krempaský (1969), thermal conductivity λ, thermal diffusivity *a* and specific heat *c* belong among thermophysical characteristics.

Thermal conductivity λ is the property of a material which relates its ability to conduct heat. The heat transfer by conduction involves the transfer of energy within a material without any motion of the material as a whole. Conduction takes place when a temperature gradient exists in a solid (or stationary fluid) medium. Conductive heat flow occurs in the direction of decreasing temperature because higher temperature equates to higher molecular energy or more extensive molecular movement. Energy is transferred from the more energetic molecules to the less energetic ones when neighbouring molecules collide. This thermophysical parameter depends on many factors (Krempaský 1969). Thermal conductivity is defined by Fourier's law, Eq. (1):

$$\vec{q} = -\lambda \, \mathrm{grad}\, T \qquad (\mathrm{W/m}^2) \qquad (1)$$

where:
λ  – thermal conductivity (W/m.K)
$\vec{q}$  – vector of heat flow density (W/m$^2$)
*T*  – thermodynamic temperature (K)

Thermal diffusivity *a* characterises the velocity of temperature equalisation in the material during-non stationary processes. In numerical view it, equals the temperature change of unit volume caused by heat, which is transferred in unit time, by unit surface of the coat with unit thickness, in unit temperature difference on its facing side.

During the measurement of thermal diffusivity, it is estimated, how quickly a body can change its temperature; it increases with the ability of the body

to conduct heat and it decreases with the amount of heat needed to change the temperature the body.

$$a = \frac{\lambda}{c\rho} \qquad (\mathrm{m}^2/\mathrm{s}) \qquad (2)$$

where:
*a*  – thermal diffusivity (m$^2$/s)
*c*  – specific heat (J/kg.K)
ρ  – density of material (kg/m)

Specific heat *c* is defined as the heat which is necessary for a heating material of unit mass per 1 K; and by Eq. (3):

$$c = \frac{C}{m} = \frac{\partial Q}{m\,\partial T} \qquad (\mathrm{J/kg.K}) \qquad (3)$$

where:
*C*  – heat capacity (J/K)
*Q*  – heat (J)
*T*  – thermodynamic temperature (K)
*m*  – mass of material (kg)

This physical parameter is important for different technical and practical applications. The measuring of thermal parameters was performed with a digital instrument Isomet 2104 (Applied Precision SAS, Bratislava, Slovak Republic). Principle of measuring with this instrument is based on recording the time – temperature dependence during the sample heating. Thermal parameters of the measured sample are calculated from the dependence obtained. The measurement is based on the analysis of the temperature response of the analysed material to the heat flow impulses. If we use needle probe for the measurements of thermophysical parameters, the experimental arrangement is modelled by HW method, which is described by Liang (1995) and Assael et al. (2002).

**Rheologic parameters and method of measurement**. Dynamic viscosity is defined as the resistance of a fluid to flow. Viscosity changes with temperature. The difference between the effects of temperature on the viscosity of fluids and gases is related to the difference between their molecular structures. 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 Eyeing's theory, the molecules of liquids continuously move into the vacancies (Bird et al. 1960).

This process permits flow but requires energy. Activation energy is more readily available at higher temperatures and the fluid flows easily. The tem-

perature effect on viscosity can be described by an Arrhenius type equation:

$$\eta = \eta_0\, e^{-\frac{E_A}{RT}} \quad \text{(Pa.s)} \tag{4}$$

where:
$\eta$  – dynamic viscosity (Pa.s)
$\eta_0$ – reference value of dynamic viscosity (Pa.s)
$E_A$ – activation energy (J/mol)
$R$  – gas constant (J/mol.K)
$T$  – absolute temperature (Figura, Teixeira 2007) (K)

Liquid molecules are closely spaced with strong cohesive forces between them. The temperature dependence of viscosity can also be explained by cohesive forces between the molecules (Munson et al. 1994). As temperature increases, these cohesive forces between the molecules decrease and the flow becomes freer. As a result the viscosities of liquids decrease as the temperature increases. In liquids, the intermolecular (cohesive) forces play an important role. The viscosities of liquids show little dependence on the density, molecular velocity, or mean free path. In most liquids, viscosity is constant up to a pressure of 10,134 MPa, but at higher pressures it increases as the pressure increases (Sahin, Sumnu 2006).

Kinematic viscosity $\nu$ is defined as a ratio of dynamic viscosity $\eta$ to the density of the fluid $\rho$ at the same temperature:

$$\nu = \frac{\eta}{\rho} \quad \text{(m}^2\text{/s)} \tag{5}$$

Fluidity $\varphi$ is defined as the reciprocal value of dynamic viscosity $\eta$:

$$\varphi = \frac{1}{\eta} \quad \text{(1/Pa.s)} \tag{6}$$

The measuring of dynamic viscosity was performed with a digital viscometer Anton Paar DV-3P (Anton Paar GmbH, Graz, Austria). Digital viscosimeter Anton Paar DV-3P is a rotational viscometer, which measures the torque of a spinning probe embedded into the sample. The spinning cylinder or spindle is interconnected through a spring to the engine shaft, which is rotating at defined velocity. The angle of the angular rotation shaft is measured electronically. From the measured values, on the base of internal calculations are directly displayed the values of dynamic viscosity. This instrument works with several types of spindles and uses a wide area of velocity, which allows the measurement of viscosity in a large extent.

## RESULTS

### Results of thermophysical parameters measurements

Samples of mixed flower honey and forest honey were stored at laboratory temperature and were measured in different days during storage. The measurements were performed in the temperature interval ranking from laboratory temperature (22°C for rheologic measurements) respectively (from 5°C for thermophysical measurements) to 43°C. Dependencies of thermophysical and rheologic parameters on temperature and also on the storage time were examined. The graphical relations show two measurements: the first measurement (at the beginning of storage) and next measurement (after one week of storage). The results obtained with mixed flower honey are showed in Figs 1a–6a. As to the sample of forest honey the results are presented on Figs 1b–6b.

Temperature dependencies of thermal conductivity and specific heat can be described by linear increasing functions (Eqs 7 and 9) and in the case of temperature dependence of thermal diffusivity linear decreasing function (Eq. 8) can be used:

$$\lambda = A + B\left(\frac{t}{t_0}\right) \quad \text{(W/m.K)} \tag{7}$$

$$a = C - D\left(\frac{t}{t_0}\right) \quad \text{(m}^2\text{/s)} \tag{8}$$

$$c = E + F\left(\frac{t}{t_0}\right) \quad \text{(J/kg.K)} \tag{9}$$

where:
$t$                    – temperature (°C)
$t_0$                  – equals to 1°C
$\lambda$              – thermal conductivity (W/m.K)
$a$                    – thermal diffusivity (m$^2$/s)
$c$                    – specific heat (J/kg.K)
$A, B, C, D, E, F$     – constants dependent on kind of material, and on ways of processing and storing

In all cases were the coefficients of determination very high (Table 1).

Figs 1–3 demonstrate linear relations between thermophysical parameters and temperature during temperature stabilisation of honey samples. The study of the relationships between thermal conductivity, thermal diffusivity, specific heat and temper-
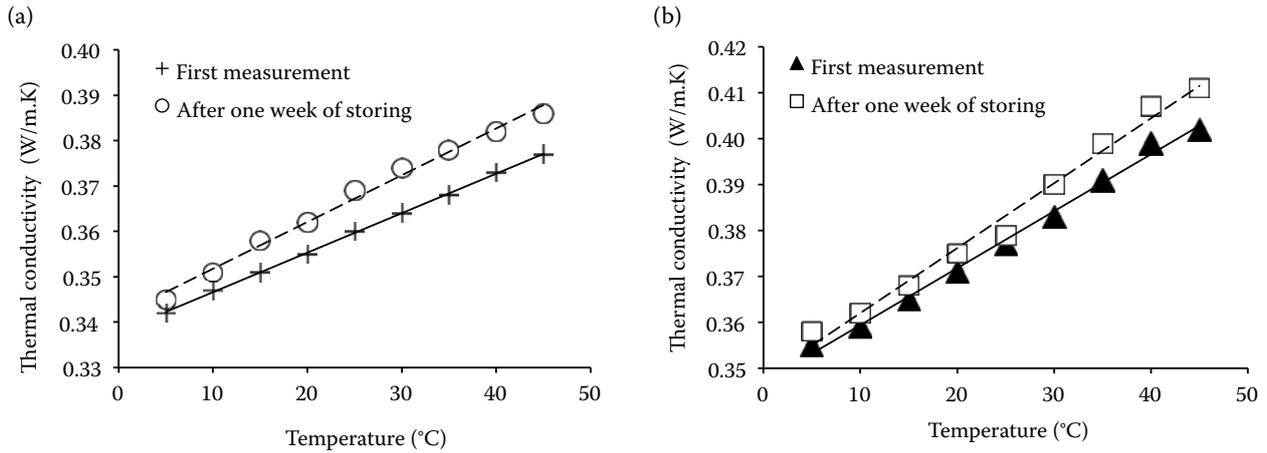
(a)



(b)

Fig. 1. Effect of temperature changes on thermal conductivity of (a) mixed flower honey and (b) forest honey
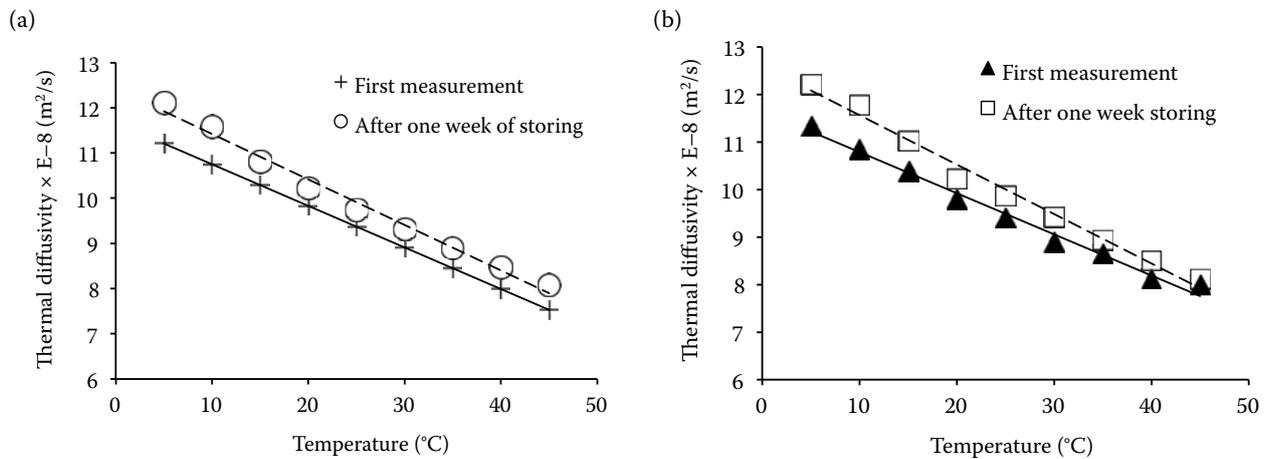
(a)

(b)

Fig. 2. Effect of temperature changes on thermal diffusivity of (a) mixed flower honey and (b) forest honey
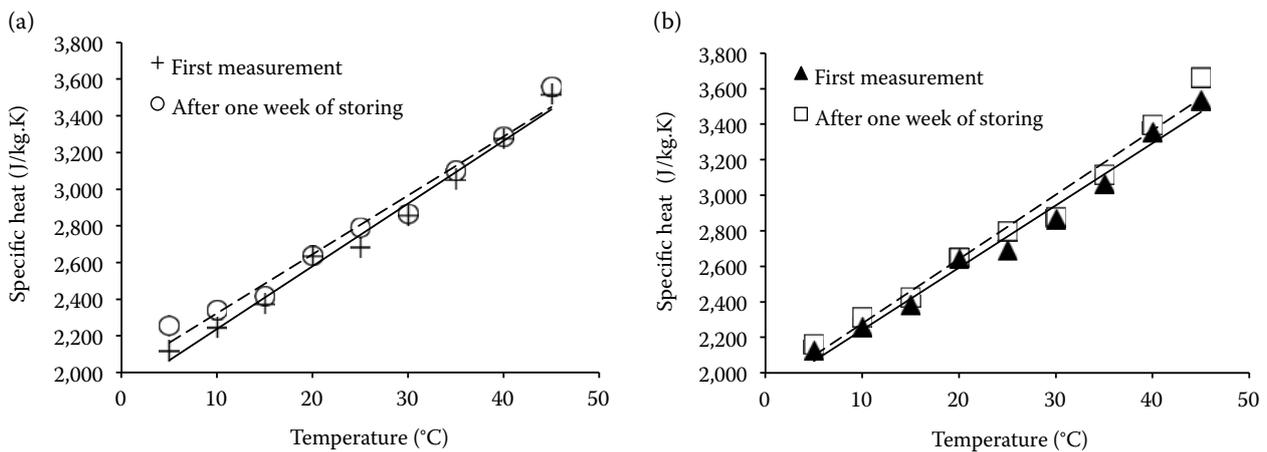
(a)

(b)

Fig. 3. Effect of temperature changes on specific heat of (a) mixed flower honey and (b) forest honey

ature showed that increasing temperature of the honey had a linear increasing effect on thermal conductivity and specific heat. The second measured thermal parameter – thermal diffusivity revealed linear decreasing progress during the temperature stabilisation process (Fig. 2). All results obtained for thermal conductivity and thermal diffusivity are in a good agreement with the literature Ginzburg (1985) and White (1975). From the presented results for thermophysical measurements it is clear that the thermal conductivity of high viscosity liquids or suspensoid materials can be measured with
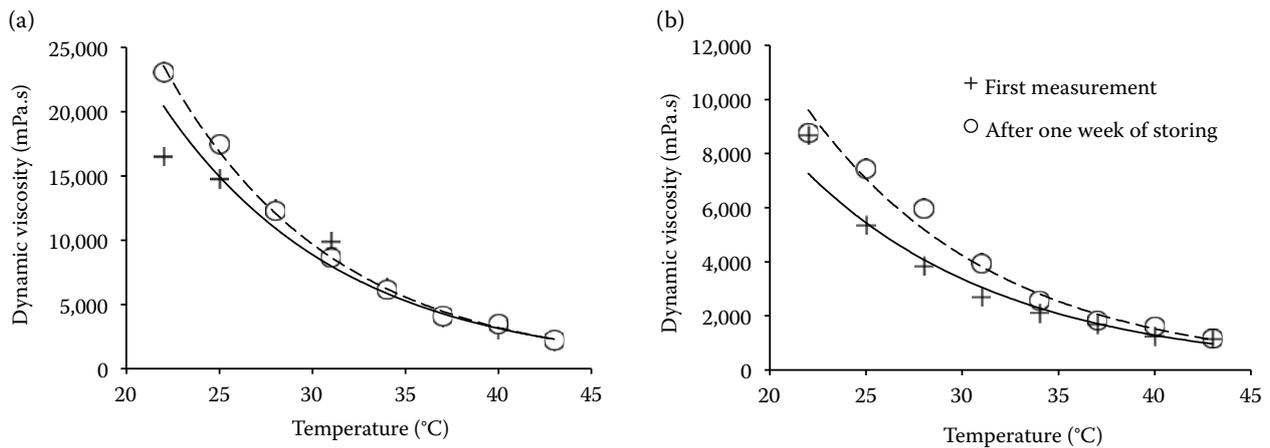
(a)



(b)



Fig. 4. Effect of temperature changes on dynamic viscosity of (a) mixed flower honey and (b) forest honey
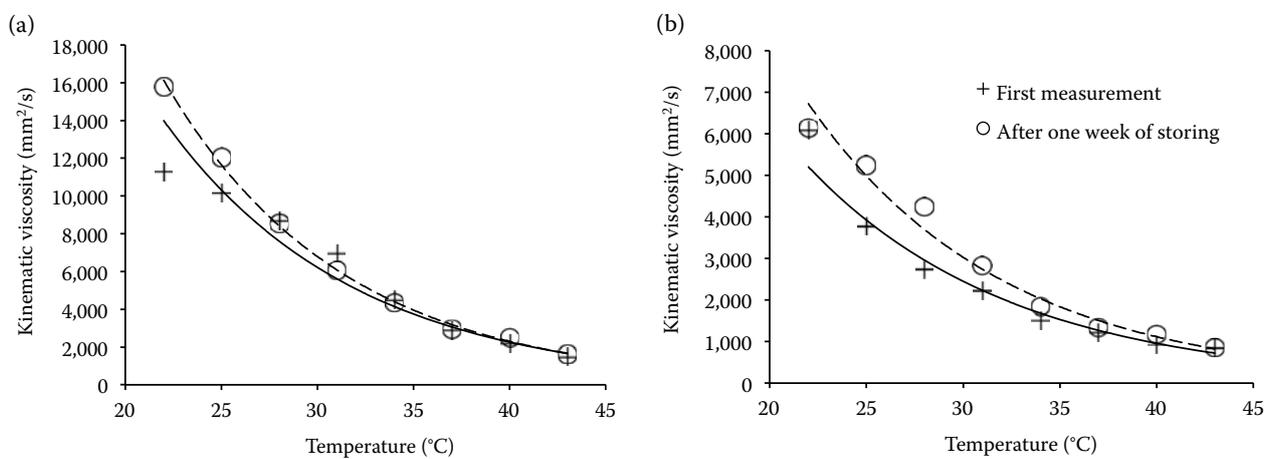
(a)



(b)



Fig. 5. Effect of temperature changes on kinematic viscosity of (a) mixed flower honey and (b) forest honey
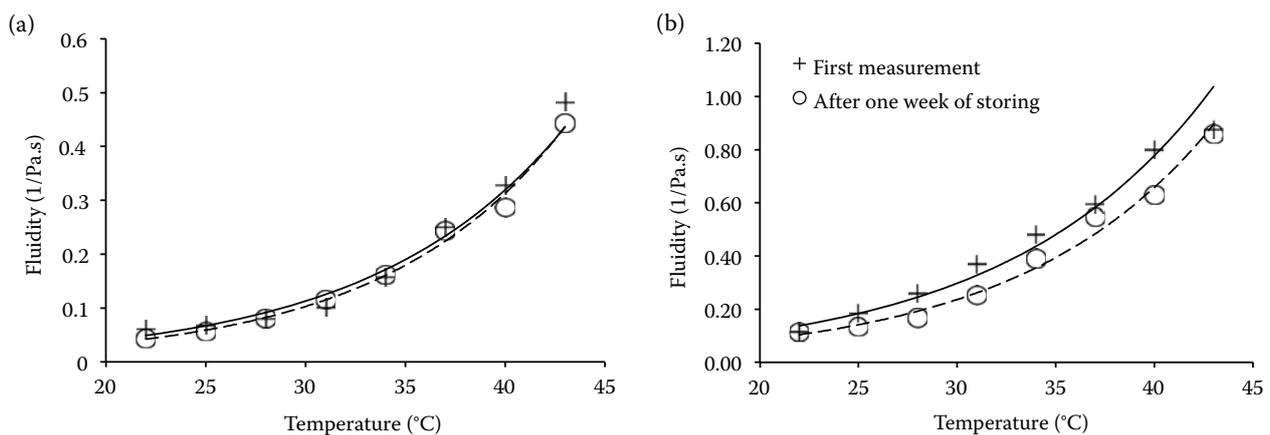
(a)



(b)



Fig. 6. Effect of temperature changes on fluidity of (a) mixed flower honey and (b) forest honey

HW method. For the data reliability protection, a series of one hundred measurements were done for every point in the presented graphic relations. Each point in the graphics characteristics was obtained as the average of the values measured.

**Results for rheologic parameters measurements**

The temperature dependencies of dynamic and kinematic viscosities can be described by decreas-

Table 1. Coefficients *A, B, C, D, E, F* of regression Eqs 7–9 and coefficients of determination ($R^2$)

|  | A (W/m.K) | B (W/m.K) | $R^2$ | C (mm²/s) | D (mm²/s) | $R^2$ | E (J/kg.K) | F (J/kg.K) | $R^2$ |
|---|---|---|---|---|---|---|---|---|---|
| **Flower honey measurement** | | | | | | | | | |
| First | 0.337917 | 0.00087 | 0.999428 | 0.1167 | 0.00092 | 1 | 1,895.35 | 34.21 | 0.985916 |
| Next | 0.341472 | 0.00103 | 0.991152 | 0.1242 | 0.00101 | 0.987847 | 2,001.91 | 32.13 | 0.976848 |
| **Forest honey measurement** | | | | | | | | | |
| First | 0.347000 | 0.00124 | 0.994138 | 0.1166 | 0.00087 | 0.988398 | 1,899.44 | 35.04 | 0.983495 |
| Next | 0.347889 | 0.00141 | 0.987057 | 0.1261 | 0.00104 | 0.987225 | 2,015.64 | 36.24 | 0.978808 |

Table 2. Coefficients *G, H, K, L, M, N* of regression Eqs 10–12 and coefficients of determination ($R^2$)

|  | G (mPa.s) | H (l) | $R^2$ | K (mm²/s) | L (1) | $R^2$ | M (1/Pa.s) | N (1) | $R^2$ |
|---|---|---|---|---|---|---|---|---|---|
| **Flower honey measurement** | | | | | | | | | |
| First | 202,185 | 0.104 188 | 0.969056 | 130,067 | 0.101353 | 0.967424 | 0.004975 | 0.104037 | 0.968316 |
| Next | 270,597 | 0.110 972 | 0.996520 | 174,024 | 0.108127 | 0.996333 | 0.003646 | 0.111313 | 0.996425 |
| **Forest honey measurement** | | | | | | | | | |
| First | 60,147.9 | 0.096 11 | 0.974692 | 41,287.8 | 0.09412 | 0.978836 | 0.016612 | 0.09614 | 0.974640 |
| Next | 91,376.4 | 0.102 37 | 0.984745 | 60,520.7 | 0.09983 | 0.984745 | 0.010924 | 0.10244 | 0.985470 |

ing exponential functions (Eqs 10 and 11) and in the case of temperature dependencies of fluidity increasing exponential functions (Eq. 12) can be used:

$$\eta = G\,e^{-H\left(\frac{t}{t_0}\right)} \quad \text{(Pa.s)} \tag{10}$$

$$\nu = K\,e^{-L\left(\frac{t}{t_0}\right)} \quad \text{(m}^2\text{/s)} \tag{11}$$

$$\varphi = M\,e^{N\left(\frac{t}{t_0}\right)} \quad \text{(1/Pa.s)} \tag{12}$$

where:
η — dynamic viscosity (Pa.s)
ν — kinematic viscosity (m²/s)
φ — fluidity (1/Pa.s)
$t$ — temperature (°C)
$t_0$ — equals to 1°C
*G, H, K, L, M, N* — constants dependent on kind of material, and on the ways of processing and storing

The influence of storage or storage time on rheologic properties of both types of honey was also examined.

The relations between the temperature and rheologic parameters like: dynamic viscosity and kinematic viscosity of the mixed flower honey and forest honey had a decreasing exponential shape which is in accordance with Arrhenius Eq. (4) while and temperature dependencies of fluidity had an increasing exponential shape for all measurements (Figs 4–6). The coefficients of determination were very high in all measurements, approximately in the range (0.97–0.99) (Table 2). Generally, the viscosity values of the mixed flower honey were higher than those of the forest honey sample and, on the contrary the values of fluidity were higher with the forest honey sample. The effect of the storage of the honey samples was also found.

From the presented results it is clear that dynamic and kinematic viscosity values were a little bit higher after storage due to the loosening of water during storage. The values of fluidity were a little bit smaller after storage, which was caused by the loosening of water respectively by crystallisation during the storage. Similar results were obtained by authors Sahin and Sumnu (2006), Figura and Teixeira (2007), and Cohen and Weihs (2010).

## DISCUSSION AND CONCLUSION

Very specific are food materials possessing variable chemical and physical properties depending

on the manipulation, external conditions and other factors which determine their behaviour. This article presents selected physical properties of honey. Out of many parameters of honey, mainly rheologic and thermal properties are very important in view of its mechanical and thermal manipulation. Based on facts presented, thermal and rheologic properties of selected Slovak honeys were examined, i.e. mixed flour honey and forest honey.

Thermophysical properties i.e. thermal conductivity, thermal diffusivity and specific heat and rheologic properties like dynamic viscosity, kinematic viscosity and also the fluidity of flower honey and forest honey were measured, analysed and also effects of temperature and storage time were examined. The results presented is clearly show that physical properties of all types of honey depend mostly on the temperature, time of storage, honey composition, and mixture of flowers visited by bees producing the honey and that they are different according to the locations, terms, and particular colony of bees.

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