RHEOLOGICAL PROPERTIES OF HONEY*

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Determination of rheological properties is very important for designing of devices for honey transportation or processing. The paper deals with rheological properties of three kinds of honey originating from the Czech Republic. The following rheological properties were described: dependence of viscosity on a sample temperature, dependence of shear stress on shear rate. Based on the measured values, the Arrhenius mathematical model was applied and subsequently used for determination of activation energy. Tests were carried out under the temperatures ranging 0–50°C. The measured values revealed Newtonian behaviour of the tested honey samples in the whole temperature range.

honey; rheological behaviour; Arrhenius model; activation energy

INTRODUCTION

Rheological measurements of substances are very important and applicable in many fields of human activity. Determination of rheological behaviour of substances is particularly important for designing of equipments for transport, pumping, and storage of substances. Application of rheology is commonly used for example in metallurgy (Zhou et al., 2001), polymer industry (Barker et al., 2008), building industry (Tregger et al., 2010), geology and mining industry (Burov, 2011), etc. Surveys of rheological properties also play an important role in food industry, where rheology relates with quality control or sensory properties (Yoo, 2004) of foods including honey (Popek, 2002). Bee honey is a natural product of saccharine character with a high nutritional and prophylactic value. It is a source of easily accessible sugars, organic acids, some amino acids, macro and microelements, and biologically active substances (Crane, 1976). The viscosity value depends on water content (14–24%) and temperature (Cubik et al., 1965; Abu-jdayl et al., 2002). In most papers, from the rheological viewpoint honey is presented as a Newtonian fluid (Bhandari et al., 1999; Zaitoun et al., 2001; Lazaridou et al., 2004; Juszczak, Fortuna, 2006). However, some kinds of honey were classified as non-Newtonian fluids with thixotropy behaviour (Witczak et al., 2011). According to Munro (1943) the presence of colloidal substances (0.18–0.8%) in some kinds of honey (heather, buckwheat, white clover) is related with thixotropy behaviour. According to Witczak et al. (2011) thixotropy can be caused by the content of substances with high molecular weight such as some proteins or dextran. When colloidal substances are removed, honey loses its thixotropy properties and its viscosity permanently increases (Bhandhari, 1999). The rheological behaviour was described for honeys coming from various countries worldwide (Kulmyrzaev, McClements, 2000; Juszczak, Fortuna, 2006; Cohen, Weihs, 2010). However, papers describing rheological properties of honeys from the Czech Republic are sporadic. Therefore, our objective was to extend the investigation in this field and deal with the rheological behaviour of selected Czech honeys.

MATERIAL AND METHODS

Honey samples

For determination of rheological properties three kinds of honey were selected: compound honey – blossom-honeydew honey (designated as Honey-1), compound honey – blossom-honeydew lime honey (Honey-2), and blossom honey – nectar from plants blooming in spring (Honey-3).

Firstly the honey samples were put into the thermostat heated to the temperature of 55°C. Warming-

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up took 1 h. During that time the crystals of honey melted down. Afterwards the temperature has been decreased to 30°C for the period of 48 h during which the air bubbles settled down. The water content in the samples was measured by refractive index at the temperature of 29°C with extrapolation to 20°C. The ABBE refractometer, type G (Carl Zeiss AG, Jena, Germany) was used for this purpose. The electrolytic conductivity was measured by the apparatus Mitronic MVM-1 (Germany) at a laboratory temperature of 24–25°C with the extrapolation to 20°C according to the correction factor of Szczęsna (Szczęsna, Rybak-Chmielewska, 2004).

All samples were strained through the mesh with pores of 1 mm within honey harvesting.

Rheological measurement

Rheological properties of the honey samples were measured by the rheometer MCR 102 (Anton Paar GmbH, Graz, Austria) with the use of cone-and-plate measuring geometry. The diameter of the cone was 50 mm, angle 1°. The following curves were evaluated: dependence of dynamic viscosity η on temperature and dependence of shear stress τ on shear rate . Dynamic viscosity is given by the equation

$$\eta = \frac{\tau}{\gamma} \qquad (1)$$

where:
τ = shear stress (Pa)
γ = shear rate (s^{-1})
Dynamic viscosity with fluidity was measured in a temperature range of 5–50°C and with the constant shear rate of 50 s^{-1}. The measurement of shear stress dependence on shear rate was performed in the range of 0–100 s^{-1}.

The Arrhenius mathematical model was used for the evaluation of the dependence of dynamic viscosity η on temperature and for the determination of activation energy E_A.

The Arrhenius mathematical model is given by the equation:

$$\eta = \eta_0 \cdot e^{-\frac{E_A}{RT}} \qquad (2)$$

where:
η_0 = constant, initial value of dynamic viscosity (Pa·s)
E_A = activation energy (J)
R = universal gas constant (J·K^{-1}·mol^{-1})
T = thermodynamic temperature (K)

All measurements were performed in three repetitions. Subsequently, arithmetic mean was calculated from the measured values.

RESULTS AND DISCUSSION

The water content in the samples is shown in Table 1. From the measured values it is evident that the sample Honey-3 had the maximum water content. The measured values are similar to those reported by other authors (Mossel et al., 2000; Yoo, 2004; Juszczak, Fortuna, 2006). Generally, the higher content of water in the honey means lower viscosity and higher fluidity (Yanniotis et al., 2007). But values of water content in the measured samples are very similar and differences in the values are within measuring device deviation. From this reason these values were not evaluated. The next value shown in Table 1 concerns electrolytical conductivity. According to Lachman et al. (2007) the chemical composition of honey is dependent on its origin and thus the composition of nectar and honeydew honeys differs. The concentration of mineral compounds ranges from 0.1 to 1.0% (Lachman et al., 2007). In comparison with nectar honeys, honeydew honeys are higher in minerals, resulting in higher electrolytic conductivity (Lachman et al., 2007). It is in accordance with the measured values, where honeydew honey (Honey-1) exhibits higher value of electrolytical conductivity than other honeys.

Fig. 1 shows the dependence of viscosity on increasing temperature. Exponential dependence was evaluated with the use of regression analyses. Coefficient of determination for the sample Honey-1 was $R^2 = 0.9866$, for Honey-2 it was $R^2 = 0.9858$ and for Honey-3 it was $R^2 = 0.986$.

Afterwards the dependence of increasing temperature on viscosity was put to further mathematical analyses. For these analyses the Arrhenius mathematical model shown in the equation (2) was applied. Logarithm of this equation is:

$$\ln \eta = \ln \eta_0 + \frac{E_A}{R \cdot T} \qquad (3)$$

From this equation activation energy E_A was determined by the use of regression analyses. Application of the Arrhenius model on the honey samples is shown in Fig. 2. Determination coefficients for the individual samples calculated using the regression analyses reached the following values: $R^2 = 0.995$ (Honey-1), $R^2 = 0.9945$ (Honey-2), and $R^2 = 0.9946$ (Honey-3). The values of activation energy were as follows: 104.85 kJ·mol^{-1} (Honey-1), 105.9 kJ·mol^{-1} (Honey-2), and 102.07 kJ·mol^{-1} (Honey-3). These values are in accordance with the results of other authors dealing with similar types of honey (Mossel et al., 2000; Juszczak, Fortuna, 2006). An exception is the honey with high content of macromolecular substances, which have thixotropic behaviour. Here the activation energy E_A is generally higher and can reach about 178 kJ·mol^{-1} (Bhandari

Table 1. Description of honey samples

Sample	Botanical and geographical description of sample	Water content (%)	Electrolytic conductivity (mS·cm^{-1})
Honey-1	Compound honey – blossom-honeydew honey: about 2/3 nectar namely from *Rubus idaeus, Leucosinapis alba, Phacelia tanacetifolia, Tilia* spp. and about 1/3 of honeydew. The sample was decrystallized before analysis. Date of harvesting: 10th July 2011. Geographical origin: CZ, Moravia	17.1	78.30
Honey-2	Compound honey – blossom-honeydew lime honey: nectar and honeydew namely from lime (*Tilia* spp.). The sample was decrystallized before analysis. Date of harvesting: 20th July 2011. Geographical origin: CZ, Moravia	17.7	66.73
Honey-3	Blossom honey – nectar from plants blooming in spring (*Salix* spp., *Acer* spp., *Prunus* spp., *Malus* sp., *Pirus* sp., and partially also *Robinia pseudacacia*, main part is represented by *Brassica napus*). This honey crystallized quickly after honey harvesting and the sample was decrystallized before analysis. Date of harvesting: 5th June 2011. Geographical origin: CZ, Moravia	17.9	17.62

et al., 1999). Furthermore, rheological properties of honey at various temperatures (0, 10, 15, 21, 30, 40 and 50°C) were studied. Results of the measurements for individual kinds of honey are shown in Figs. 3–5. From the rheograms it is evident that the shear stress dependence τ on the shear rate γ is linear for all kinds of honey tested and for all temperature values. The results show that the tested samples of honey are Newtonian fluids, most of them with Newtonian behaviour (as mentioned above). Exceptions are just the honeys with high content of macromolecular substances exhibiting thixotropic properties (W i c z a k et al., 2011).

CONCLUSION

Rheological behaviour of honey was determined with respect to water content in the individual samples. All the tested samples exhibited Newtonian behaviour. The honey samples were tested in the temperature range 0–50°C. The thixotropy and dilatancy behaviour was not observed in any sample of honey. Viscosity of samples depends on the kind of honey and also on temperature. The highest viscosity value had the sample Honey-2 (compound honey – blossom-honeydew lime honey), then the sample Honey-1 (compound honey – blossom-

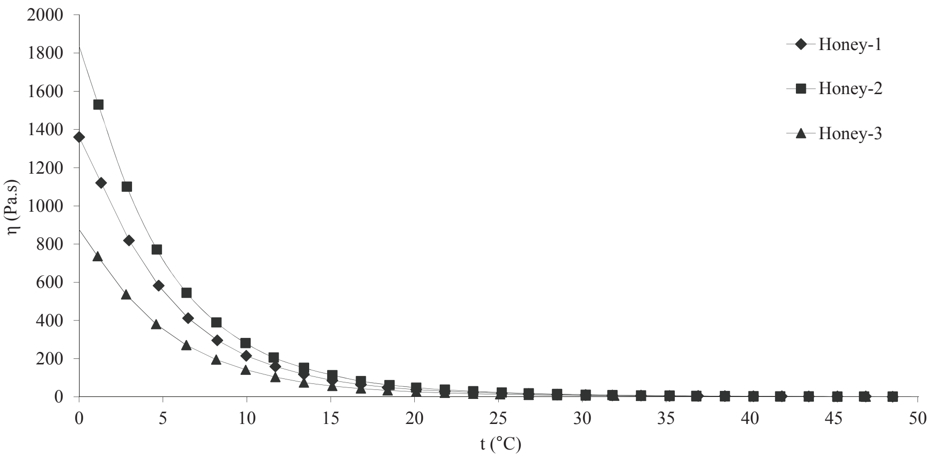

Fig. 1. Temperature dependence on viscosity of three kinds of honey

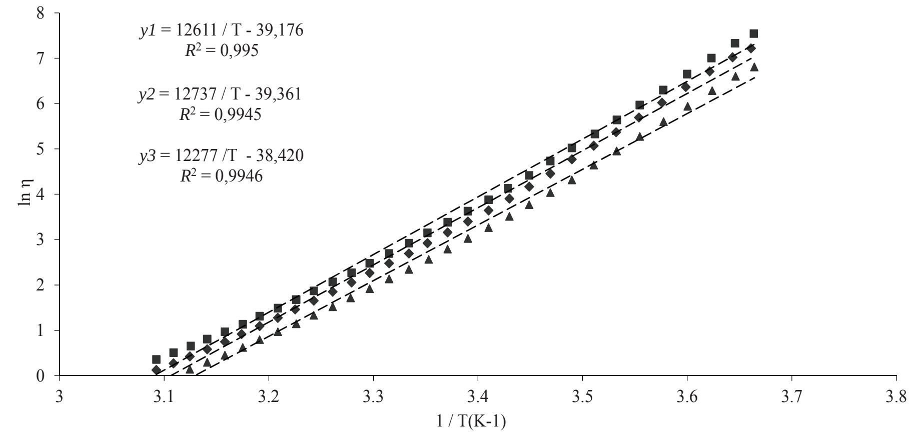

Fig. 2. Evaluation of the Arrhenius model for three kinds of honey

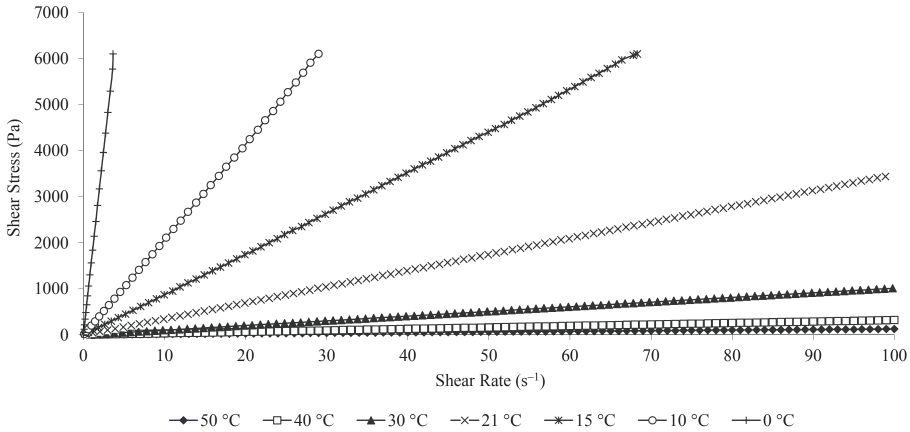

Fig. 3. Rheogram of the sample Honey-1 at various temperatures

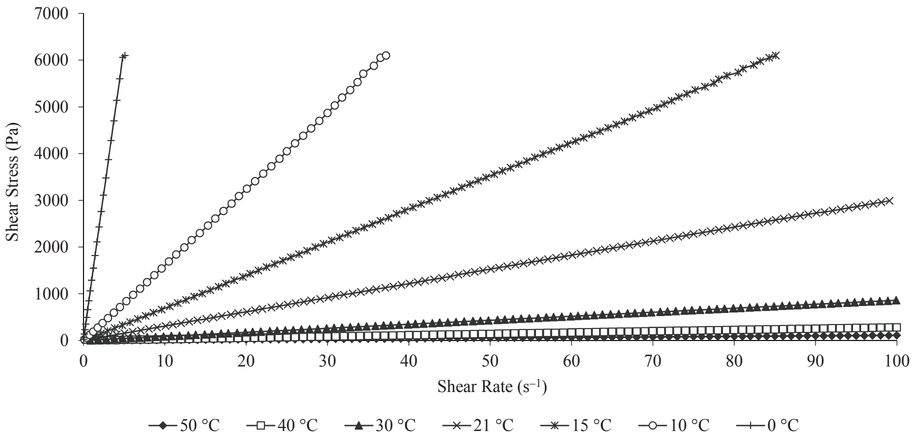

Fig. 4. Rheogram of the sample Honey-2 at various temperatures

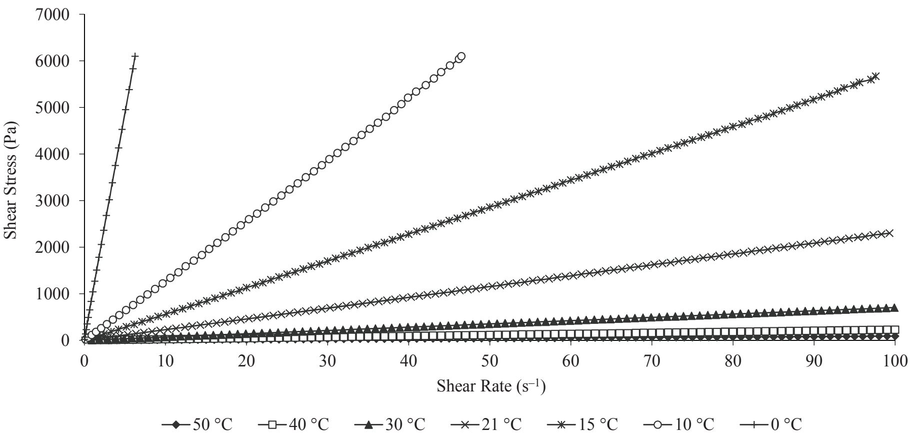

Fig. 5. Rheogram of the sample Honey-3 at various temperatures

honeydew honey), and the lowest viscosity value was found in the sample Honey-3 (blossom honey – nectar from plants blooming in spring with the designation). The honey with the highest value of activation energy displayed also the highest viscosity value.

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Reologické vlastnosti medu

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Určení reologických vlastností je důležité pro návrh a konstrukci zařízení, které jsou určené pro dopravu nebo zpracování medu. Práce se zabývá popisem reologických vlastností tří různých vzorků medů pocházejících z České republiky. V práci byly popsány následující reologické vlastnosti: závislost viskozity na teplotě vzorku a závislost smykové rychlosti na smykovém napětí. Na základě naměřených dat závislosti viskozity na teplotě byl aplikován Arrheniův matematický model. Pomocí tohoto modelu byla následně určena i aktivační energie. Testy probíhaly v teplotním rozsahu 0–50°C. Na základě naměřených hodnot bylo zjištěno, že testovaný med v celém teplotním rozsahu se chová jako Newtonská kapalina.

medy; reologické chování; Arrheniův matematický model; aktivační energie

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