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Original Article

RHEOLOGICAL PROPERTIES OF SOME HONEYS IN LIQUEFIED AND CRYSTALLISED STATES

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A b s t r a c t

The paper presents the results of rheological measurements conducted on three types of Polish honey: rape, multi-floral, and buckwheat honeys. The investigations involved identification of the properties of the honeys in both liquefied (by heating) as well as crystallised states. Both steady shear as well as dynamic rheological tests were performed. As a result, it was possible to show that the liquefied honeys behave like Newtonian fluids. Good agreement of the results between the rotary shear and oscillation rotary tests was observed, thus fulfilling the Cox-Mertz rule. The structure of the honeys was subjected to qualitative scrutiny by analysing photographs of the crystals taken in the conditions of shearing interferometry. The quantitative analysis was made by presenting a numerical distribution of crystal colonies with reference to the maximum dimensions of individual crystals. The geometric measurements of the crystals were carried out using analiSIS software. In the crystallised form, the media showed a thixotropic effect, and their apparent viscosity was many times higher than the dynamic viscosity in the liquid state. After plasticising by deformation with an increasing shear rate of up to 450s^{-1}, the equilibrium melting curves of the crystallised honeys were described by the Ostwald-de Waele model. One particular reason for the research was to show that the results obtained for the honeys crystallised by the steady shear method, were qualitatively different from the results obtained in the dynamic measurements. The Cox-Mertz rule cannot be applied for the crystallised honeys.

Keywords: crystallisation, crystallised structure, honey, rheological properties

INTRODUCTION

The rheological properties of honey constitute one of the most fundamental physical features determining the quality of the product and enable a number of technological operations on the product (Yanniotis et al., 2006). The influence of honey viscosity can be observed from the very moment the product is acquired from the honeycombs. The rheological properties of honey also play a significant role in such processes as: pumping, mixing, clarification, hydraulic transport, heating or batching (Sopade et al., 2004). The subject has been widely studied and there is extensive literature available on the rheological properties of the honey collected in different parts of the world (Bhandari et al., 1999, Gómez-Díaz et al., 2006, Kayacier & Karaman, 2008; Lazaridou et al., 2004; Mossel et al., 2000, Oh & Yoo, 2011; Trávníček et al., 2012; Yoo, 2004,).

Most of the reports on the subject maintain that honey is a Newtonian fluid whose viscosity depends on temperature and water content (Abu-Jdayil et al., 2002; Al-Malah et al., 2001; Bakier, 2007; Junzheng and Changying, 1998; Sopade et al., 2002; Yanniotis et al., 2006; Zaitoun et al., 2001). Some works indicate that liquid honey may have pseudoplastic properties (Gomez-Diaz et al., 2006; Mehryar et al., 2013) or thixotropic characteristics (White, 1978). To identify the rheological properties of honey, steady shear (Mossel et al., 2000; Recondo et al., 2006; Sopade et al., 2002; Yanniotis et al., 2006, Zaitoun et al., 2001) and dynamic measurements have been used (Ahmed et al., 2007; da Costa & Pereira, 2002; Kulmyrzeaev & McClements, 2000; Lazaridou et al., 2004; Mehryar et al., 2013; Oh & Yoo, 2011, Oroian et al., 2013; Sopade et al., 2004; Yoo, 2004).

All the above publications have one common characteristic – they make an attempt to analyse honey rheology in its liquid state. However, it is well known that almost all types of honey tend to crystallise when stored (Assil et al., 1991; Bhandari et al., 1999; Crane, 1975; Escuredo et al., 2014; White, 1978). The crystallisation process produces a series of significant changes in the product. The crystallisation of the solid phase releases water and enhances its water's activity (Bakier, 2009; Gleiter et al., 2006, Zamora & Chirife, 2006). However, the main effect of crystallisation is that it completely changes the product's consistency. Honey crystallising in small containers typically forms layers and creates coarse solid blocks. As such, crystallised honey has not been readily accepted by consumers (Cavia et al., 2002). At the same time, consumers have shown interest in fine grained or creamy honey characterised by a semi-liquid consistency (Bhandari et al., 1999). Already in the thirties of the last century, Dyce stated the honey preferences of consumers, and developed a special technology for production (Crane, 1975). There is relatively little to be found in the literature concerning the rheological properties of crystallised honey. A few papers just deal with the rheological identification of honey in its crystallised form - as one of the honey characteristics that changes after the crystallisation process (Mora-Escobedo et al., 2006; Conforti et al., 2006; Chen et al., 2009). Crystallised honey is a two-phase structure of a semi-solid type whose rheological behavior is determined by the mass fraction of both the solid phase and the morphology of the crystalline structure (Mora-Escobedo et al., 2006).

To shape the consistency of semi-liquid products is a complex problem that the food industry faces. There are a great number of different food products that show a semi-liquid consistency and constitute multiphase mixtures. This includes such products as chocolate, mayonnaise, mustard, ketchup, sweet sauces, and milk desserts (Bakier & Bakoniuk, 2013; Juszczak and Fortuna, 2006; Rao, 1999; Tárrega et al., 2005). Our research mainly dealt with the effect of the solid phase on the rheological properties of the analysed products. Only a small number of papers have dealt with the impact of the morphology of the solid phase on the consistency of the investigated products (Kulkarni et al., 2006). An effective tool for the analysis of the microstructure of food products is polarised light microscopy. This tool makes it possible to obtain clear images of the solid phase structure (Bakier, 2007; Kulkarni et al., 2006). This method uses an optical birefringence of organic substances and may be applied to honey (Bakier, 2004).

The present work is dedicated to the identification of the rheological properties of three selected types of honey characterised by a diverse crystalline structure. The same types of honey were analysed both in the liquid and crystallised states by means of rheological tests under the conditions of rotary rheometry. Oscillation rotary measurements were applied. The test results were compared and the influence of the crystalline structure morphology on the rheological properties of honey in the crystallised form was determined.

MATERIAL AND METHODS

Honey samples

The honey used for testing was collected in 2015. The investigated material included three types of honey: rape, multi-floral, and buckwheat. The test samples were chosen so they significantly differed from one another in both their natural crystalline structure and water content. The honey samples came directly from the author's own apiaries and were collected as follows: rape samples - May 25, multifloral samples - June 15, and buckwheat - June 29. Honey samples were 5 kg and were stored in an airtight opaque container at a temperature of 15 ± 2°C. The liquefaction process took place by heating a weighed portion of the crystallised medium in hermetically sealed containers for 24 hours at 55°C. After liquefaction, a thin film of white foam was removed from the surface of the liquid honey. Next, the honey was cooled to an ambient temperature and made ready for testing. A prolonged time of thermal treatment made it possible to conduct full honey liquefaction and remove any air bubbles. All the rheological measurements were carried out at a constant temperature of 25°C. At this temperature, the investigated honeys become "soft and plastic", making it possible to easily fill the rheometer cylinders and perform the necessary measurements.

Physico-chemical analysis

A detailed study of the physico-chemical properties, and a pollen analysis of the honey samples were carried out at the Bee Products Quality Testing Laboratory of the Apicultural Division of the Research Institute of Horticulture in Pulawy, Poland. The analysis involved chemical composition, i.e. the content of water, fructose, glucose, sucrose, maltose, turanose, trehalose, isomaltose, melezitose, erlose, raffinose, and hydroxymethylfurfural (HMF). The investigation also encompassed the diastase number (DN), pH, free acids, specific electrical conductivity as well as honey origin found out by pollen analysis. All analyses were performed in line with the Regulation of the Minister of Agriculture and Rural Development dated 14 January 2009. The water content was determined by refractometry, the carbohydrate content was determined by high performance liquid chromatography with refractive index detection (HPLC - RID), and the HMF content was analysed by high performance liquid chromatography with spectrophotometric detection (HPLC - UV). In turn, the diastase number was marked by the Phadebas method, ph by the potentiometric method, free acids - by potentiometric titration, and finally electrical conductivity was determined using the specific conductivity method.

Microstructural analysis

The structure of the crystallised honeys was subjected to qualitative analysis on the basis of photographs taken in the conditions of shearing interferometry (Bakier, 2003). The crystalline structure of the honeys was analysed quantitatively by measuring the geometry of the crystals photographed in the conditions of shearing interferometry using Biolar PI microinterfrometer. The samples for analytical observation were prepared on a microscope slide by spreading a small amount of crystallised honey in a drop of liquid honey of the same origin. Another slide was then placed on top. The thickness of the specimen suspension was about 0.1mm. Observations were carried out against a dark background with a crossed polariser and analyser. The acquisition was performed using a CCD camera with a resolution of 5 mil. pixels. The images were saved in the jpg format. Photographs were taken at a constant magnification of about 150X with a blocked camera zoom. For showing the exact magnification, the figures presented here show the photographic scale formed under the same conditions. The measurements were carried out using digital image analysis with the help of analiSIS software (SIS. 2003). Binarisation was performed based on the brightness histogram. The average of the maximum crystal size was adopted as a typical one whereas the morphological characteristics of the crystals were based on the quantitative distributions of crystal sizes with respect to the average maximum diameter.

Rheological measurements

Rheological measurements were conducted using the rheometer MCR 102 Anton Paar fitted with a Measuring System Data Sheet Anton Paar of co-axial cylinders operating in the Searle mode. The diameter of the inner cylinder was d_1=26.652 mm, and the external one was d_2=28.905 mm, which made the thickness of the measuring gap δ=1.127 mm. The rheometer with an ultrathermostat operating system made it possible to fully program the whole course of the experiment and also ensure their repeatability. The identification of the honeys was performed by applying rotary shear and dynamic rheological tests. The range of the shearing rate for rotary tests was $\dot{\gamma} \in \langle 0;450 \rangle s^{-1}$. The dynamic measurements were conducted within the angular oscillatory frequency of $\omega \in \langle 0;\ 250 \rangle s^{-1}$, and the oscillation angle was ±2°. These parameters made it possible to conduct research work in the field of linear viscoelasticity, which was verified in a preliminary study. The analyses were based on the averaged results obtained from three independent measurements.

Identification of the rheological properties of the liquid honeys in the rotary flow involved subjecting the media to shear stress in the range: $\tau \in (0;\ 500)$Pa. Shear rate increments were recorded every 5 Pa. The results are shown as flow curves $\tau = f(\dot{\gamma})$. As a result of a linear regression, it was possible to determine flow curve equations in the form of $\tau = \eta \cdot \dot{\gamma}$ in which coefficient η represents the value of dynamic viscosity. Measurements of liquid honey subjected to forced oscillation were carried out by measuring complex modulus G* and phase shift angle δ in the function of angular frequency of oscillation. Also based on the linear regression process, it was possible to determine the value of complex viscosity η^*. Next, both values of the dynamic and complex viscosity were compared to see whether the Cox-Merz relationship was fulfilled. Additionally, the relative difference between the obtained values of the dynamic and complex viscosity was calculated:

$$\Delta\eta = \frac{\eta - \eta^*}{\eta} \cdot 100\% \tag{1}$$

In the case of crystallised honeys, the rheological identification consisted of subjecting the honeys to the shearing process in a closed cycle within the shear rate $\dot{\gamma} \in \langle 0;450 \rangle$ s^{-1}. Initially, the shear rate was gradually increased every 50s^{-1} starting from the minimum value $\dot{\gamma}_{min} = 0.103$ s^{-1} and after the stabilisation of the shearing conditions, the values of steady shear stresses with the accompanying shear rates were recorded within the time of 180 s. As a result of the test, it was possible to obtain samples which had an identical deformation history. The samples were characterised by a damaged (broken) structure of the spatial colonies of the crystals. Next, having reached the maximum value of $\dot{\gamma}_{min} = 450$ s^{-1}, the stresses were gradually decreased every 50Pa to determine the values of the steady shear stresses with the accompanying decrease of shear rate. Thus, hysteresis loops characteristic of the thixotropic fluid were obtained. The steady stress values obtained in the rotary-balance cycle in the decreasing stress phase, were used to determine the balance flow curves that were approximated to fulfil the Ostwald-de Waele relationship. At this point, it was possible to calculate the values of the consistency coefficient and flow index as well as the dependence of apparent viscosity on shear rate $\eta' = f(\dot{\gamma})$. Oscillatory-dynamic measurements of crystallised honeys were carried out in the same way as for liquid ones, i.e. by measuring the values of complex modulus G* and the shift of phase angle δ in the function of the angular frequency of oscillation. Next, the value of complex viscosity was determined. Finally, the obtained values of the dynamic and complex viscosity were compared.

Statistical analysis

For the statistical analysis Statistica 12 software was used (StatSoft. 2014). The experimental results concerning liquid honeys characterised by Newtonian properties in the form of the dependence of shear stresses on the shear rate, were approximated to the linear form. In this way the regression equation was determined. In the case of crystallised honeys, the results of the experiments were approximated to the Ostwald-de Waele model. The calculation significance was at 5%. The evaluation of fitting the model to the experimental data was performed by calculating the coefficient of the root mean square error of calibration (RSM). Calculations were performed in Excel. If the value of RMS is below 5%, then it could be stated that fitting the model to the experimental data is very good. If that value is between 5 and 10% it is a good fitting. Also, the determination coefficient R^2 was calculated. It was used as the standard value to measure the congruity of the experimental results and the models assumed. Both the equations obtained from the approximations and the values of the determination coefficients and RSM, are shown in the figures presenting the experimental results.

Table 1

Physico-chemical and pollen characteristics of the honeys samples

No	Parameter	Unit	Rape honey	Multifloral honey	Buckwheat honey
1.	Water	%	18.2	18.5	19.2
2.	Fructose	g/100 g	38.1	37.3	38.8
3.	Glucose	g/100 g	39.7	32.2	34.3
4.	Sucrose	g/100 g	n.d.*	1.3	n.d.*
5.	Turanose	g/100 g	0.5	1.1	1.1
6.	Maltose	g/100 g	0.8	3.6	2.5
7.	Trehalose	g/100 g	<0.5**	0.9	1.0
8.	Isomaltose	g/100 g	n.d.*	<0.5**	<0.5**
9.	Melezitoze	g/100 g	n.d.*	n.d.*	n.d.*
10.	Erlose	g/100 g	n.d.*	1.3	n.d.*
11.	Raffinose	g/100 g	n.d.*	n.d.*	n.d.*
12.	Total sugar	g/100 g	79.1	77.7	77.7
13.	HMF	mg/100 g	0.7	0.9	9.9
14	Diastase (DN)	Schade	16.1	35.1	
15.	pH		4.17	5.80	
16.	Free acids	mval/kg	8.5	6.7	
17.	Specific electrical conductivity	mS/cm	0.14	0.50	
18.	Participation of four main plant pollens:	%	Rape 80.1 Plum 6.1 Willow 5.9 Cornflower 2.7	Rape 53.4 Buckthorn 12.2 Willow 10.3 Raspberry 7.6	Buckwheat 36.9 Rape 23.4 Melliot 9.3 Cornflower 8.3
19	Certification of honey origin specified by the manufacturer		Rape honey	Multifloral honey	Buckwheat honey
	Botanical origin according to pollen analysis		Rape honey beyond any doubt	Multifloral honey tinged with some rape pollen from bee bread	Buckwheat honey tinged with some rape pollen from bee bread

* Not detected at the limit of determination 0.5 g/100 g
** 0.5 g/100 g - limit of determination

RESULTS

The measurement results of the physico-chemical properties of the tested honeys including pollen analysis, are shown in Table 1. It should be noted, that of the three honey varieties, only rape honey yielded unequivocal results. Both the organoleptic characteristics, the ratio of glucose to fructose (G/F=1.04), as well as pollen analysis (rape pollen content 80.1%), are clear in this case. As concerns the second variety, i.e. multifloral honey, the organoleptic assessment and the G/F=0.86 ratio indicated that it is multifloral honey, while the result of pollen analysis shows the domination of the rape pollen with the presence of buckthorn and raspberry pollen that is characteristic of the honey harvested in June. In the third case, i.e. buckwheat honey, we observe the dominance of buckwheat pollen along with melliot and cornflower pollen. Surprisingly, the honey also contained up to 23.4% of rape pollen, which did not blossom at the time of this honey's collection. The last two cases show clearly that both the multifloral and buckwheat honey had been tinged with some rape pollen from bee bread. This is particularly evident in the case of buckwheat, which blooms a few weeks after rape. Rape pollen is very attractive to bees as it is readily available and contains a large amount of protein. As a result, bees gather the pollen in excess of their colony's actual needs and store the rape pollen as bee bread in their honeycombs. During centrifuging, the pollen falls into the honey.

The results of rheological identification of liquefied honeys in the rotary shear state are shown in Fig 1. They are presented as flow curves $\tau = f(\dot{\gamma})$ in Fig 1. As a result of approximation, it was possible to obtain linear equations with relatively high coefficients of determination R^2 and a value of the root mean square error of calibration between 1.96% and 7.31%. This means that fitting the model to experimental data is good. As can be seen, rape honey shows the highest value of dynamic viscosity amounting to $\eta_1 = 6.66$ Pas, multifloral honey η_1 = 5.02 Pas, whereas buckwheat honey shows the lowest dynamic viscosity equal to η_1 = 3.18 Pas.

Fig. 2 shows the research results of liquefied honeys under forced oscillations as dependence of the complex modulus on the angular frequency of oscillation. Even in these conditions the liquefied honeys show a linear dependence of the complex modulus on the frequency. Rape honey possesses the highest values not only of the complex modulus but of complex viscosity as well. Buckwheat honey is characterised by the lowest water content and the lowest complex modulus and complex viscosity.

The approximation results of the equation show high determination coefficients. The calculated numerical values (Fig. 2) constitute complex viscosity. The values of the dynamic viscosity of the honeys are similar to the complex viscosity. The relative differences between the average values of the dynamic and complex viscosities determined from the equation are as follows: 3.2% for rape honey, 4.7% for multifloral honey, and 9.4 % for buckwheat honey.

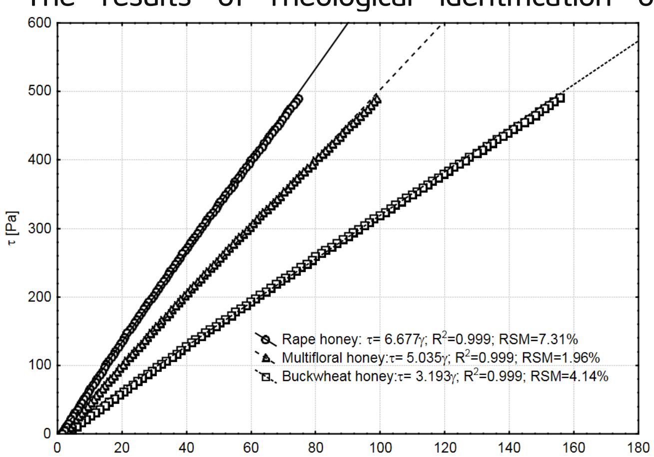

Fig.1. Flow curves of liquefied honeys

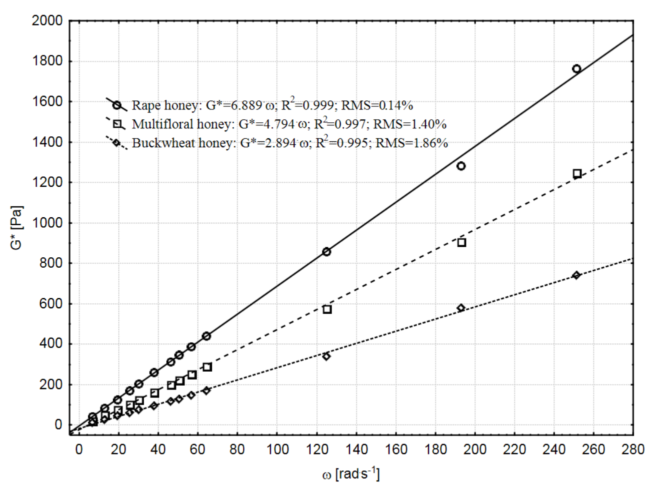

Fig. 2. Dependence of the complex modulus on the os cillation frequency of liquid honeys

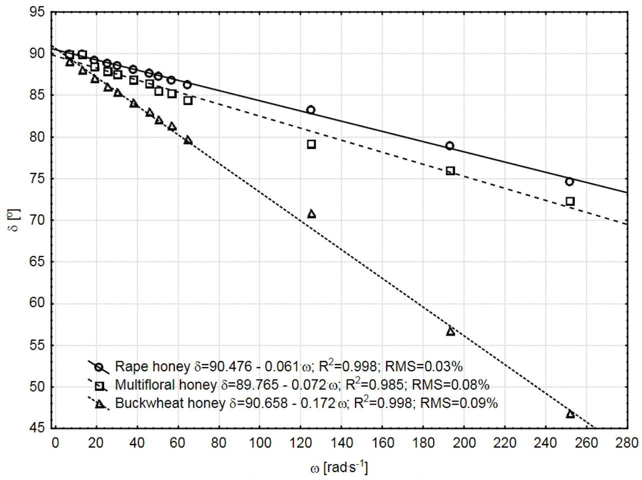

Fig. 3 Dependence of the phase shift angle on the oscillation frequency of liquid honeys

Fig. 3 shows the changes of the phase shift angle in the function of the angular frequency of oscillation. In all three types of the tested honeys, an increase in the frequency results in a linear decreased value of the phase shift angle. A characteristic feature in this case is the fact that the sample of rape honey shows the fastest decrease of the phase shift angle value. This means that an increase of oscillation frequencies in the medium is followed by the fastest increment of its elastic properties.
The next part of the paper deals with the study of the honeys in their crystallised state. First,

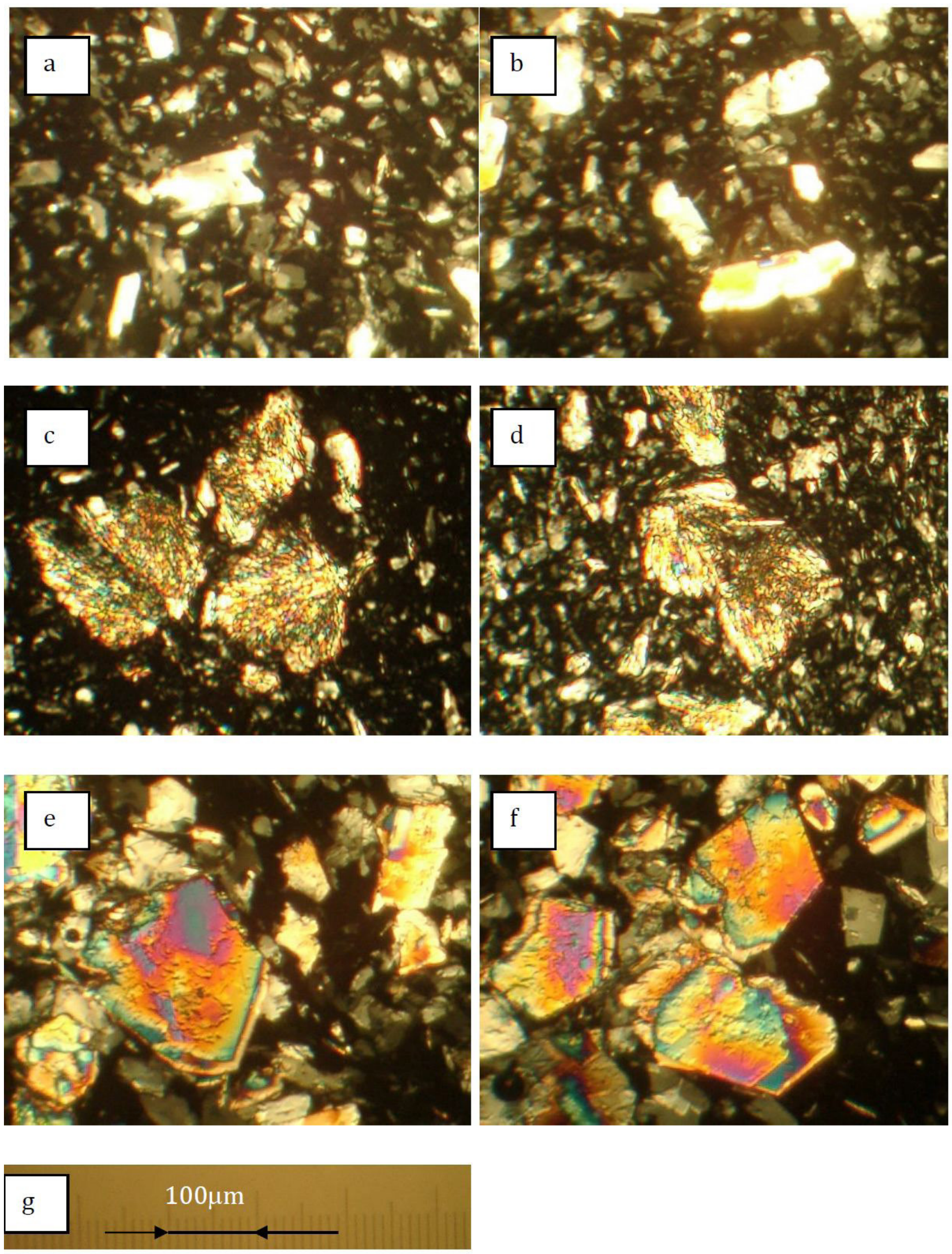

Fig. 4. Photographs illustrating the morphology of the crystalline structure of the investigated honeys: a) and b) rape honey, c) and d) multifloral honey, e) and f) buckwheat honey, g) scale photo 100 µm.

the results of crystalline structure characteristics of the honeys are given. The photographs in Fig. 4 show two pairs of images of the analysed honeys. Since the crystals are optical birefringence, the photographs taken using shearing interferometry show the crystals in the form of bright objects against a dark background. An initial analysis of their morphology allows us to see significant structural differences between the crystals. Rape crystals are small, oval, and have a regular "boundary line". Among small crystals, larger crystals can also be found with similar morphology. Multifloral honey is composed of irregular, ragged crystals both large and small in size with irregular shapes and thickness as well as sharp edges. (In birefringence measurements, thickness is interpreted by analysing color differences). Buckwheat honey is mainly composed of large crystals of noticeably regular and flat shapes, and considerable thickness, which is manifested by interferometric colors.

Figs 5, 6, and 7 give the quantitative characteristics of the crystal colonies forming each of the three types of honey. The figures show the computer analysis results for the images of individual crystals. This was done through the presentation of numerical distributions of crystal colonies composed of 2000 individual crystals relative to the maximum diameter of the crystals. The crystals clearly indicate that rape honey has the greatest number of crystals with d_{max}<10 μm. Multifloral honey has the most crystals with 10<d_{max}<30 μm. In contrast, buckwheat honey has relatively numerous crystals with dimensions of 30<d_{max}<70 μm. The number distribution of buckwheat honey crystals can be clearly distinguished from the rest by the characteristic extreme local fraction 30 <d_{max} <35 μm.

Fig. 8 shows the course of the test to which the three types of crystallised honeys were subjected under rotary shear, whereas Fig. 9 illustrates the final results of the test in the form of the dependence of shear stress on shear rate. The highest values of shear stress (both at increasing as well as decreasing shear rate) were observed for rape honey. Multifloral honey initially (at increasing values of shear

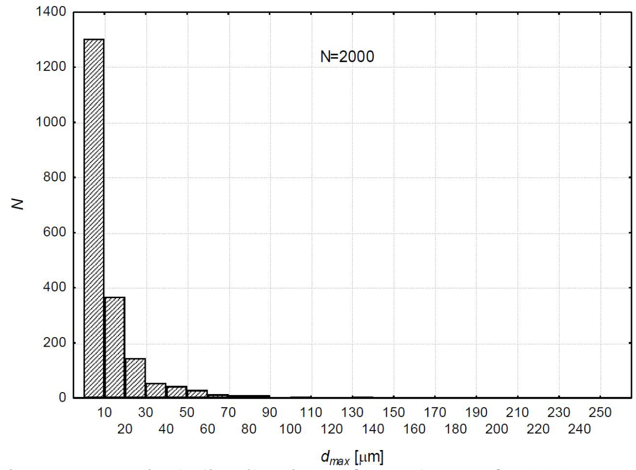

Fig. 5 Numerical distribution of a colony of 2000 rape honey crystals in relation to the maximum size average

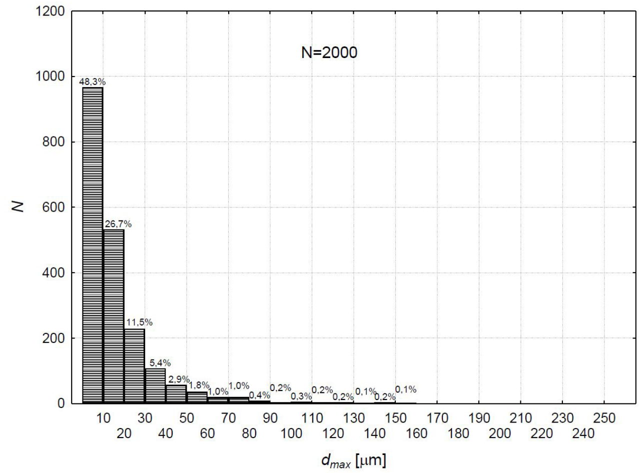

Fig. 6 Numerical distribution of a colony of 2000 multifloral honey crystals in relation to the maximum size average

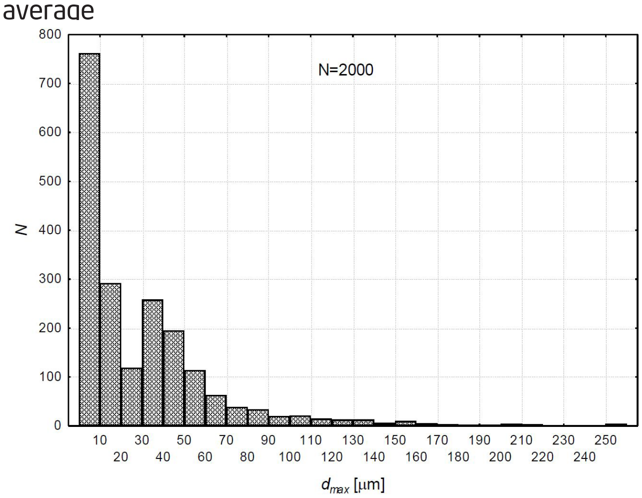

Fig. 7 Numerical distribution of a colony of 2000 buckwheat honey crystals in relation to the maximum size average

rate) at <150 s^{-1} had values similar to rape honey but at > 300 s^{-1} its values were more similar to buckwheat honey. With a drop of $\dot{\gamma}$, multifloral honey acted the same way as buckwheat honey during shearing. As a result of the experiment,

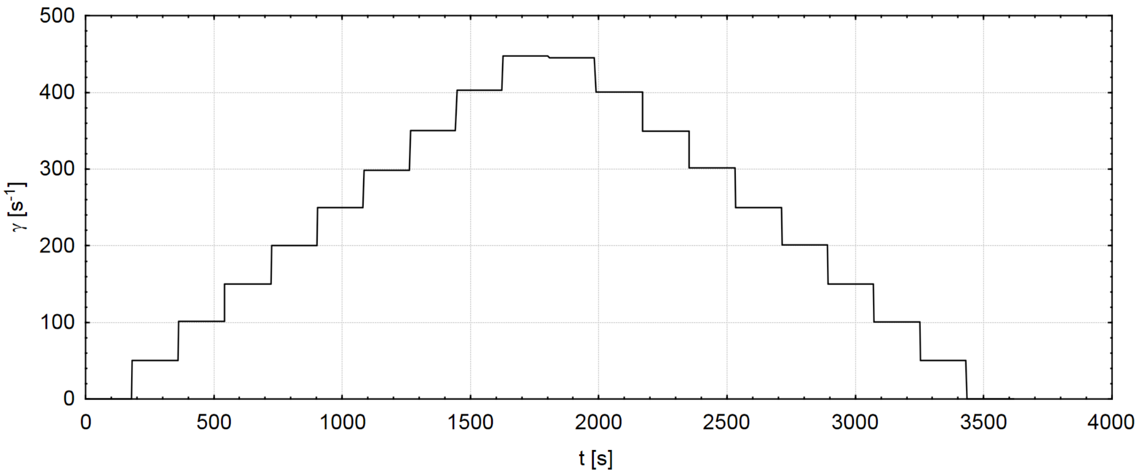

Fig. 8 Diagram of shear rate changes during the tests

it was possible to obtain hysteresis loops characteristic of the thixotropic fluid whose surface can be used to describe the thixotropic effect. The surface areas of the hysteresis loop of both multifloral and rape honeys, are relatively large compared with buckwheat honey. This effect is associated with destruction of crystalline agglomerates and the formation process of the velocity profile in the rheometric flow. Rape honey has a particularly high value of equilibrium stress at low shear rates $\dot{\gamma}$ <50 s^{-1}. With time, the values rise slightly, but quite regularly. Equilibrium stresses obtained for multi-floral honey initially grew rapidly with an increasing shear rate, and then decreased. Buckwheat honey acts much more regularly. The hysteresis loop is insignificant, and the curves are very regular both with the increasing and decreasing shear rate. It should be emphasised that the curves for the decreasing shear rate for all types of honey, are regular.

Fig. 10 shows the balance flow curves of the three types of honey, obtained from the experiment depicted in Fig. 5. These curves refer to the measuring points for the falling values of the shear rate. The approximation result shows that the curves satisfy the Ostwald-de Weale model, as evidenced by the value of RMS between 1.2% - 6.14 % and the coefficients of determination R^2>0.98. The flow curve of rape honey is clearly distinguishable from the other honeys. It is characterised by a much higher coefficient of consistency and a lower index of the flow value. While the differences between the flow curves of multifloral and buckwheat honeys are much smaller.

Fig. 11 shows the results of the same experiment, but as a dependence of apparent viscosity on shear rate. The values of apparent viscosity for rape honey are definitely higher than the rest of the media throughout the whole shear rate range. This effect is due to the morphology of

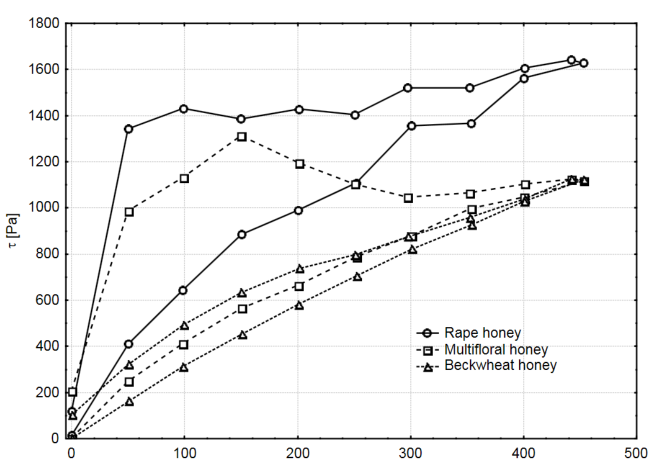

Fig. 9 Shear results for rising and falling shear rates

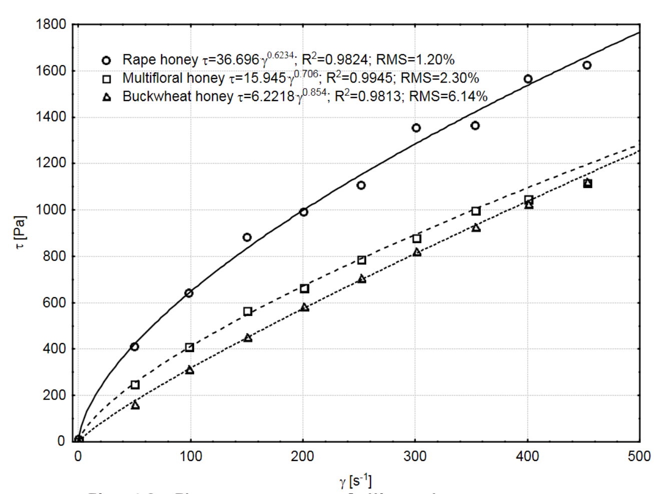

Fig. 10. Flow curves at falling shear rate

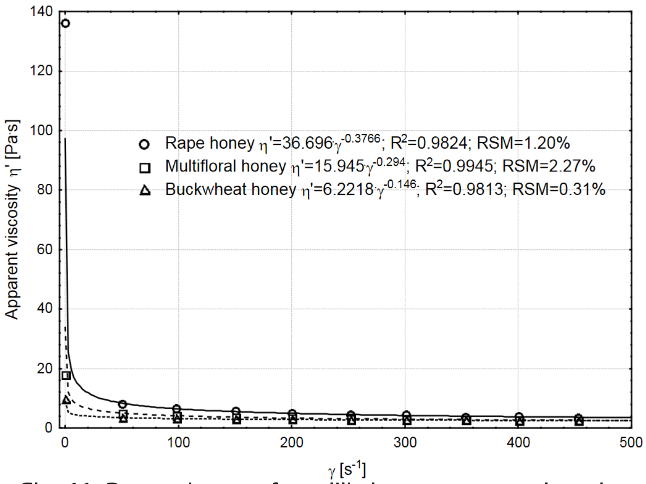

Fig. 11. Dependence of equilibrium apparent viscosity of crystallized honeys on shear rate

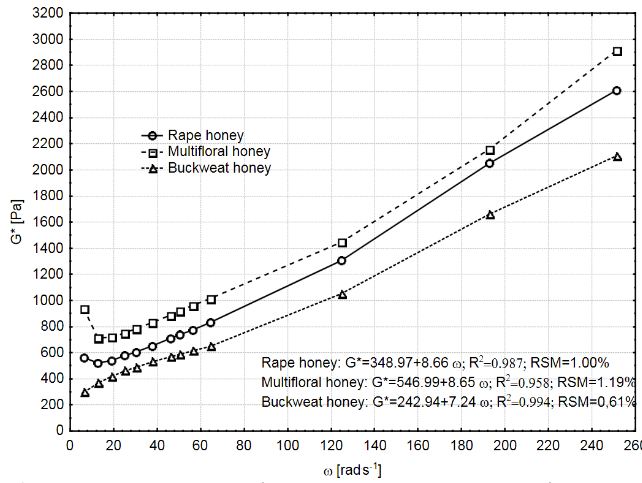

Fig. 12 Dependence of the complex modulus of crystallized honeys on the frequency of oscillation

the crystalline structure.

The remaining part of the paper presents the results of dynamic measurements. The dependence of the complex modulus as a function of the angular frequency of deformation is shown in Fig. 12. The highest value of the complex modulus was for multifloral honey, which was a surprise. Buckwheat honey (as expected), had by far, the lowest values. Rape honey in the whole range of variation, showed intermediate values between the multifloral and buckwheat honeys.

Fig. 13 shows the changes in the phase shift angle of the crystallised honeys as a function of the angular frequency of oscillation. All the honeys showed an increase in the value of the parameter with frequency. This increase was initially relatively strong and stabilised at $\omega>60$ rad·s^{-1}. At the value of $\omega\approx250$ rad·s^{-1}, all the media attained the value of δ=90°. At frequencies $\omega<100$ rad·s^{-1}, buckwheat honey had the highest values of the phase shift angle whereas multifloral honey had the lowest ones. At high frequencies the differences between the honeys decreased.

Fig. 14 shows the values of the complex viscosity of the crystallised honeys as a function of the angular frequency of oscillation and the regression equation. Here again, the values can be approximated to satisfy the power law. The resulting equations have lower coefficients of determination R^2, however the value of RMS was below 2.2 %, which shows a very good fitting model. It is significant that the resulting complex viscosity values for all three honeys were much higher than the apparent viscosity throughout the whole range of variability. The highest values of complex viscosity were shown by multifloral honey throughout the whole range shear stress angular velocity, with rape honey in the middle

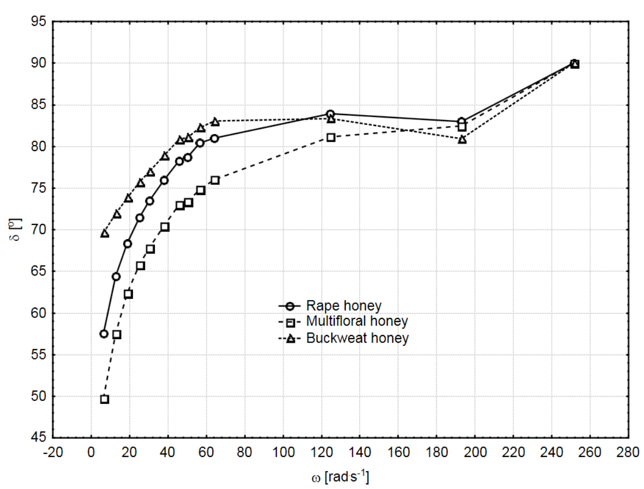

Fig. 13 Changes of the phase shift angle as a function of angular frequency of oscillation

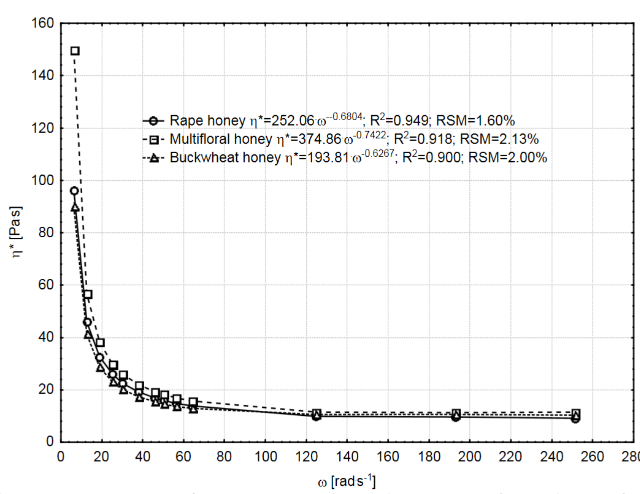

Fig. 14. Values of complex viscosity as a function of angular frequency of oscillation

and buckwheat honey with the lowest values. Consequently, there are significant qualitative differences between the results of apparent viscosity obtained from rotary measurements and the values of complex viscosity from oscillatory measurements. Thus, the Cox–Merz rule, in this case, was not satisfied.

DISCUSSION

Summarising the results of the research, it can be stated that in the case of liquid honeys the values of dynamic viscosity are correlated with the water content. The resultant values of dynamic viscosity are slightly lower than those obtained by other authors (Al-Malah et al., 2001; Lazaridou, 2004; Yonnitios et al., 2006). The differences may result from different chemical compositions of the analysed media. The determined values of complex viscosity are similar to the findings of other authors (da Costa & Pereira, 2002; Kulmyrzaev & McClements, 2000). Nominally, the dynamic viscosity values of liquid honeys are comparable with the values of complex viscosity, as shown by Lazaridou and other researchers (Lazaridou et al., 2004).

The result concerning crystallised honeys under rotary shear, shown in Fig. 9, unmistakably point out a strong thixotropic effect, similar to the one described by Conforti et al. for honey crystallised at -20° C (Conforti et al., 2006). The values of the apparent viscosity of the crystallised rape honey characterised by the finest structure (Fig. 11), are significantly higher than the other media within the whole range of shear rate. This effect must be a reflection of the morphology of the crystalline structure. The rheology of suspensions says that the narrowing of particle distributions increases the apparent viscosity of the suspension structure (Ferguson & Kembłowski, 1991). Multifloral honey that has a structure described as intermediate between rape and buckwheat honeys, also possesses intermediate values of apparent viscosity. At low shear rates, the values are significantly higher than for buckwheat honey. However, at high shear rates, the apparent viscosity of the two media are similar.

It is worth noting, that the results of complex viscosity obtained in the conditions of forced oscillation, differ qualitatively from the results for the liquid as well as crystalised honeys in rotary shear conditions. Literature sources on this issue confirm that the results of the measurements of steady shear equilibrium and dynamic analysis for crystalline suspensions, do not give such a representation of the problem (Ferguson & Kembłowski, 1991; Schramm, 1994). However, this phenomenon has not been previously described for crystalised honeys. The solution of the phenomenon should be looked for solely in the morphology of the crystalline structure. Multifloral honey has an irregular structure of crystals which in the course of oscillation may change location by performing slight rotational movements with respect to their temporary support points. The movements are caused by the rotor. Since the multifloral honey crystals are quite large, they have to overcome greater resistance when moving in the suspension. In contrast, rape honey morphology is characterised by fine, oval crystals which do not show the same effect when subjected to oscillation. Buckwheat honey on the other hand, is composed of large, flat crystals which do not change their position in the course of oscillation. They may merely slide with respect to one another.

Changes of the phase angle shift in Fig. 13, indicate that the crystallised media at low angular velocities had maximum elastic properties. The nature of these changes is opposite to the ones shown by the media in the liquid state. With an increase in the angular frequency, there is an increment of viscous properties that evidently dominate over the elastic ones. This is related to the destruction of the spatial structure of crystallised honey.

The presented results constitute crucial findings concerning the formation of honey consistency in its crystallised state. By controlling the crystallisation process assisted by mechanical treatment of the crystalising suspension, it is possible to purposefully shape the structure, and hence, in advance, develop desirable rheological properties of the end product. By creating a fine crystalline structure we can increase the consistency coefficient and "hide", for example, the water content. The research results also help us understand and analyse the perception of crystallised honey by human senses, since it is the effect arising in the process of chewing. Chewing is oscillatory in nature. However, the primary use of the results presented above is to provide data for the design of appliances for hydraulic transport of honey and machines which mix, press, etc.

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