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Rheological Properties of Honey in a Liquid and Crystallized State

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Additional information is available at the end of the chapter

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Abstract

The rheological properties of honey are discussed separately for liquid and crystallized honey. The research methods used in both cases are characterized. The basic mathematical models are shown, which describe the viscosity of honey in its liquid form depending on temperature and water content. In the case of crystallized honey, the rheological properties were linked to morphological features and crystalline phase content. Results of characteristic experiments are presented, obtained during the shearing of crystallized suspension, that is, crystallized honey. Among other items, the dependency of equilibrium stress on shear rate, apparent viscosity on crystalline phase content, hysteresis loops as evidence that honey in its crystallized form is a rheologically unstable fluid. Results of measurements under forced oscillation conditions are included and compared with results of rotational measurements. It was shown that the research method influences the obtained results of rheological studies.

Keywords: viscosity, consistency, crystalline structure, rheology properties, cream honey, water activity

1. Introduction

The rheological properties describe the behaviours of matter under tensions resulting from external forces. Each real matter, whether a solid, liquid or gas, strains when exposed to external forces. We distinguish elastic, plastic and viscous strains. The behaviour of elastic bodies is described by Hook's law and is characterized by its disappearance once external forces are taken away. Plastic strain is permanent and remains even after the external force is gone. A perfectly plastic body is called a Saint-Venant's body. Viscous strain, also known as flow, is characterized by a constant increase in strain under constant stress. Perfectly viscous

fluids are described by Newton's law, which may be presented as a linear relation between shear stress and shear rate:

$$\tau = \eta \cdot \dot{\gamma}. \quad (1)$$

The η parameter in the equation above stands for dynamic viscosity. All fluids, which do not fulfil Newton's law, are called non-Newtonian fluids. Generally, non-Newtonian fluids are divided into rheologically stable, rheologically unstable and viscoelastic. They demonstrate partially viscous, elastic and plastic properties. Rheology is tasked with the description of these properties.

The rheological properties of honey are analysed mainly within the aspect of fulfilling the basic production processes such as hydraulic transport, mixing, heating or batching [1]. Viscosity is additionally one of the parameters of quality assessment of the product [2]. In multiple published reports on the rheological properties of honey, there is a common observation that it is in fact a Newtonian fluid [3–6]. A few publications hint at the existence of a clear thixotropic effect, although it is only seen in certain types of honey such as heather honey or the Manuka honey from New Zealand [5, 7]. It needs to be stressed, however, that such reports are with regard to honey in its liquid state also known as strained honey. The parameters, which significantly influence the dynamic viscosity of the analysed product, are temperature and water content [5, 8, 9].

Bee honey is a concentrated aqueous solution of sugars. Due to this, most of the obtained types of honey undergo crystallization when in storage [10]. The crystallization process results directly from the chemical composition, as in almost all types of honey glucose are present in its supersaturated state [5, 11]. Melezitose can also undergo crystallization in honeys. The resulting solid phase is a glucose monohydrate, which has various geometrical forms in crystallization [5, 12, 13]. Honey after crystallization is called set honey and is a two-phase structure, semi-solid, which substantially varies in its properties from the liquid state—strained honey [5, 14]. As a result of crystallization, the organoleptic properties undergo significant changes, mainly the honey's texture and water activity [15]. Literature regarding the rheological properties of crystallized honey is surprisingly modest. There are a few studies, which are just starting to analyse the issue [13, 14, 16, 17]. These studies only identify the specific rheological properties of crystallized honeys, as one of the characteristics which change after the crystallization process.

This analysis is an attempt at the identification of the rheological properties of honey both in its liquid state and in its crystallized form. The performance of this task has forced an analysis of additional issues, which determine the rheological characteristics. These are the measurement of the amount of solid phase formed after crystallization of the honey and its morphological characteristics. These issues are relatively seldom analysed in literature [14].

2. Research methods used in the identification of the rheological properties of honey

Rheological measurements can be conducted using two different measurement techniques: rotational rheometers and capillary rheometers. Due to the speed, comfort of use

and the possibility of measurement in wide spectrums of shear rate, rotational rheometers are in popular use at present. The used measurement systems are cone-plate, plate-plate or cylinder-cylinder in a Searle- or Couette-type rheometric flow. Modern-day rheometers are automated and allow obtaining information on the rheological properties relatively quickly, with relatively wide spectrums of shear rate in a precisely planned and repeatable way. The basic problem, which influences the choice of research method significantly, is the presence of the crystallized phase in the case of crystallized honey. The presence of crystals causes significant changes in the rheological properties, which in turn forces a choice of a proper measurement method. A wrong choice of measurement method for crystallized honey can result in unreliable results. As mentioned earlier, crystallized honey is a two-phase mixture, semisolid [5, 14]. It is a popular substance in the food industry. These can be products ready for consumption or half-finished products, which are undergoing processing in the form of solid-liquid mixtures [18]. Crystallized dispersions are also formed by metals in high temperatures. Semisolid media are usually characterized by non-Newtonian properties, and in order to identify them, complex rheological analysis methods are required [18–20].

Research methods regarding liquid and crystallized honeys are characterized below, separately. Additionally research aspects related to measurements of weight fraction and quantity morphological characteristics of the solid (crystallized) phase in crystallized honeys were noted.

2.1. Research methods used in the identification of the rheological properties of liquid honey

Liquid honey is a homogeneous fluid, a concentrated solution of sugars and other liquid substances. The majority of liquid honeys have characteristics of Newtonian fluids, which is why there are few limitations to research methods. From a researcher's point of view, the most beneficial measurement systems are the cone-plate or plate-plate ones. Such systems are easy to use and only a few millilitres of honey samples are required for rheological identification. The exchanging of the analysed medium in these systems is easy and the thermostating is satisfactory. Nevertheless, one may use the cylinder-cylinder measurement systems using the Searle or Couette flow. It is then necessary to have a larger amount of the pressure fluid and its exchange is more difficult. The identification of the viscosity of strained honey sample requires measurements to be conducted in at least a few or at best a few dozen measurement points, at which the shear stress for the assigned shear rates would be noted. The viscosity value is obtained by approximating the results to a linear function. The results of such an experiment are presented in **Figure 1**. Due to the fact that honey samples viscosity greatly depends on the temperature and water content, the values of these parameters are worth noting for every measurement. The viscosity value is a numeric coefficient in the obtained equation after the approximation of the experiment's results. In the example shown in **Figure 1**, the dynamic viscosity value is 12.95 Pas. Whether it is a Newtonian fluid is decided by the fact the points align themselves in a straight line. A fine measure of linearity (Newtonian properties) is the determination coefficient. If its value is greater than $R^2 > 0.95$ it may be stated that the fitting of the results to a Newtonian model is very good.

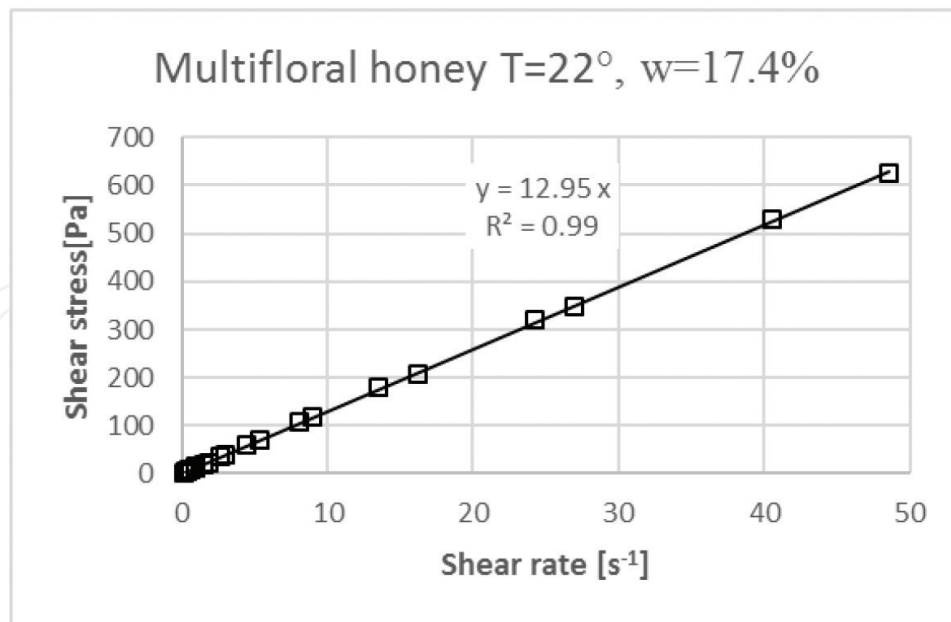


Figure 1. Method of determining the dynamic viscosity of liquid honeys.

A similar test can be conducted for any fluid of unknown rheological properties. It is the first effect of a rheological identification of a fluid. If the points do not align along a straight line, it serves as proof of the fluid being non-Newtonian, and a precise research methodology can be chosen.

There are numerous mathematical models used to describe rheological properties of honey in its liquid state [2, 21, 22]. Their main focus is on the description of the viscosity in the function of temperature. Arrhenius's equation is most often used for this purpose [8, 23]:

$$\eta = \eta_0 \exp\left(\frac{E_a}{RT}\right). \quad (2)$$

There is an opinion that this equation describes the dependency between viscosity and temperature relatively well, and the obtained results have an error margin no greater than 4.41% [23, 24].

In the literature analysing the issue, the William-Landel-Ferry (WLF) equation is also used to model the influence of temperature on honey viscosity [21]. This dependency uses glass-transition temperature and the viscosity in glass state to describe the dynamic viscosity of honey [22]. The mathematical equation is in the following form [21, 22]:

$$\ln\left(\frac{\eta}{\eta_g}\right) = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)}. \quad (3)$$

It is also noted that the WLF dependency describes honey viscosity in the function of temperature very precisely, while this description is very sensitive to changes of the composition of the medium [21, 22]. The usage of the WLF model is relatively valuable in a general rheological analysis of honey and the identification of glass-transition temperature, which is made possible based on rheological measurements.

The main drawback of the dependencies described above used to describe honey viscosity is the omitting of water content in the product. This is a parameter, which influences honey viscosity as significantly as temperature. This is why two-parametric models are used for practical purposes, which include both water content and temperature [1].

Dynamic measurements are also becoming more common in the analysis of rheological properties of honey [2, 22]. This also includes mixtures of honey and propolis as well as other food products [25]. The measurements are mainly connected with the identification of the value of the complex modulus G^* , storage modulus (elasticity) G' and viscosity modulus (loss) G'' , phase angle δ and complex viscosity η^* in relations to the frequency [20]. The results are also presented in the form of graphs showing the changes of the elasticity modulus, the loss modulus and the complex viscosity in the function of yaw rate [2, 22]. There is no uniform opinion on the range of frequencies used in the measurements. The results are characterized by a generally linear dependency of both the storage modulus and the loss from frequency. The determined complex viscosity values in dynamic measurements do not always correspond to the dynamic viscosity. The measurements of the complex modulus G^* and the phase angle yield a uniform assessment of the rheological behaviour of the medium and determine the storage modulus (elasticity) G' and the loss modulus (viscosity) as simple dependencies [20]:

$$G' = G^* \cdot \cos\delta \quad (4)$$

$$G'' = G^* \cdot \sin\delta \quad (5)$$

The value of the phase angle δ is determined by the division of energies in the deformed medium into stored energy and energy lost to induce flow [20]. The closer the value of the angle is to $\delta = 90^\circ$, the closer the properties of the substance are to a completely liquid state (Newtonian body). If $\delta = 0^\circ$, the substance is completely elastic and is a hook's body [19].

2.2. Research methods used in the identification of the rheological properties of crystallized honey

As a matter of fact, measurements of the rheological properties of crystallized honey samples should be conducted solely by the use of rotational rheometers, additionally with a cylinder-cylinder measurement system. This is due to the fact that systems characterized by narrow openings generate significant errors in research because of the dimensions of the crystals. It is believed that the openings should have a linear dimension of at least three times the size of the largest crystal.

An additional effect, which needs to be taken into account in rheological studies of suspensions with a high concentration of solid phase such as honeys, is the unstable behaviour during shearing [19]. In the case when this influence is reversible, the fluids are thixotropic or antithixotropic [19, 20]. Irreversible changes in rheological properties of fluid are called rheodestruction or rheomalaxis [20]. This is connected with the destruction of the crystalline structure during shearing. The characteristic of rheologically unstable fluids requires the use of different research methods and additional rheological parameters. An additional and important aspect is the method of preparation and placement of the analysed medium in the

measurement system, as the activities connected with filling the measurement cylinders significantly influence the results of the analyses.

In the case of suspensions with a high-weight concentration of solid body, which present non-Newtonian behaviour, apparent viscosity is commonly used for rheological characteristic [20]. The apparent viscosity η' is defined as a relation between the value of shear stress and shear rate:

$$\eta' = \frac{\tau}{\dot{\gamma}}. \quad (6)$$

Apparent viscosity is the simplest and often used parameter of rheological characteristic of crystalline suspensions as well as other non-Newtonian fluids [19]. A graphic representation of changes in the apparent viscosity in the function of shear rate allows also to create a precise rheological characteristic of rheologically stable fluids.

In the studies of rheological properties of suspensions, which are in most cases rheologically unstable, equilibrium viscosity η_{eq} is used [19]. This parameter can be identified as the relation of equilibrium stress τ_{eq} obtained during shearing at a constant rate $\dot{\gamma}$ for a period of time long enough for equilibrium in the deformed system to occur:

$$\eta_{eq} = \frac{\tau_{eq}}{\dot{\gamma}}. \quad (7)$$

The representation of equilibrium viscosity or equilibrium stress in the function of shear rate is commonly used for rheological characteristic of suspensions [19]. Experiments are usually conducted with shear speed increasing in increments [20]. Equilibrium stress in crystallized honey samples is usually described using the Ostwald-de Waele model [14]:

$$\tau_{eq} = k \cdot \dot{\gamma}^n. \quad (8)$$

Another aspect of analysing the properties of semisolid sets related with their instability is the determination of behaviour in a closed cycle of shearing with increasing and then decreasing shear rate. By using a constant tempo of increase and then decrease of shear stress, characteristic changes in time are obtained in the form of a hysteresis loop [20]. This constitutes a traditional quality test for the occurrence of thixotropia [19]. By repeating an identical shear cycle after a certain amount of time of the medium remaining dormant, an answer can be obtained to the influence of time on the rebuilding of the internal structure of the crystalline suspension. Conforti et al. used such a cycle: with an increasing shear rate from 0 to 320s^{-1} for 1.5 min, holding for 2 min at $\dot{\gamma} = 320\text{s}^{-1}$ and then decreasing with an identical shear tempo, for the rheological characteristic of honey samples in their crystallized state [13]. It was proven that all analysed honey samples presented with a hysteresis loop whose shape was determined by the crystalline structure of the analysed media.

Measurements which enable us to obtain a hysteresis loop need to be performed with caution, for the cylinder slip not to occur causing the syneresis effect [19, 20]. It needs to be mentioned that the possibility to compare the hysteresis loop is available only when the loops are obtained in an identical shear cycle with a constant increase of deformation rate and its consecutive decrease. Additionally, there is a strong influence of the human factor related to the method of introducing the sample into the measurement system of the rheometer [12].

The thixotropic effect is also analysed in the microstructural context, as stress changes during shearing are related with the transformations occurring in the internal structure of the fluid. The scalar value κ also called the structural parameter is used for this purpose [19]. Then, the thixotropic behaviour of the substance can be described using two constitutive equations:

$$\tau = f(\dot{\gamma}, \kappa); \quad (9)$$

$$\frac{d\kappa}{dt} = g(\dot{\gamma}, \kappa). \quad (10)$$

When the equilibrium stresses τ_{eq} are reached, that is, the shear rate of the structure equals its rebuild rate, then the growth $\frac{d\kappa}{dt} = 0$ and the structural parameter has the equilibrium value $\kappa = \kappa_{eq}(\dot{\gamma})$. Eq. (9) has the form [19]:

$$\tau = f[\dot{\gamma}, \kappa_{eq}(\dot{\gamma})] = \tau_{eq}(\dot{\gamma}). \quad (11)$$

This is the equilibrium flow curve, which as mentioned above for crystallized honey samples can have the form of relation (8). Nevertheless, one can find reports in the literature on the usage of the structural parameter defined in a different way [4, 20].

The complement of the empirical methods of the rheological analysis of crystallized honey samples is studies conducted using a dynamic rheological test. Such techniques are very useful to measure properties of suspensions, in which complex interactions between the ingredients take place. By determining the conditions of the decay of structures forming such sets during shearing, it is possible to obtain a precise rheological characteristic [20]. A classic method in this regard is to use oscillation measurements to identify the influence of temperature and pH of the environment on the blood coagulation process [26].

The values measured in dynamic measurements are usually complex modulus G^* and the phase angle (Eqs. (8) and (9)). Based on these two parameters, it is possible to conduct a uniform assessment of the rheological behaviour of the medium. Viscoelastic media are additionally characterized by a parameter called complex viscosity, which is defined as the ratio of the complex modulus to the angular frequency of oscillation [20]:

$$\eta^* = \frac{G^*}{\omega} \quad (12)$$

Attention is paid to the fact that between the complex and dynamic viscosity, there is a dependency called the Cox-Merz dependency [20]:

$$\eta^* = \eta \Big|_{\omega=\dot{\gamma}}. \quad (13)$$

Lazaridou et al. stated that in the case of Greek honey in liquid form, the value of dynamic viscosity is generally greater than that of complex viscosity [2]. Ferguson and Kemplowski (1991) noted that the Cox-Merz dependency has a limited range of use in the case of suspensions due to the structural differences of these fluids while dormant and while in set flow. In the case of semisolid food products, the Cox-Merz dependency is modified to the form of [20]

$$\eta^* = C \eta^\alpha \Big|_{\omega=\dot{\gamma}}. \quad (14)$$

There are, however, no data whether the above-mentioned rule can be used for crystallized honey.

2.3. Research methods used to measure the amount of solid phase in crystallized honey

Reports on the amount of solid phase formed in honey are relatively modest. Existing data point to this value being approximately 15% [12]. Meanwhile, this parameter defines, at a very basic level, the rheological properties of crystallized honey. It would seem that the answer to this question can be obtained by simply comparing the solubility of glucose in water (saturation concentration) at a given temperature with its content in the product. The result of this comparison is not, however, so obvious. Glucose can crystallize in an anhydrous form and as a monohydrate [5]. Data on the solubility of anhydrous glucose point to its saturation concentration (in an aqueous single component solution) at a temperature of 25°C being approximately 60% [27]. The solubility of glucose monohydrate is lower and in these conditions amounts to slightly above 50% [27]. Zamora and Chirife assume that the value of saturation concentration of glucose in water at 25°C is 103.3 g of glucose per 100 g of water [28]. By relating the glucose content to water content for various honeys, we can obtain a glucose concentration level of 1.5–2.5 g of glucose/g of water [28]. Glucose in almost all types of honey is present in a supersaturated state. Fructose, despite the fact that its content is higher in most honeys than that of glucose, never reaches its saturated state, which is 405.1 g per 100 g of water [5, 27, 28]. Nevertheless, there is an influence of fructose on the crystallization process of glucose and it is necessary to perceive honey as a ternary set of water, glucose and fructose. The results of studies by Lothrop and Kelley regarding the equilibrium of such sets show that they are sufficiently complex [5]. It is generally known that a high addition of fructose reduces the tendency to crystallize. Own research of model aqueous solutions of glucose and fructose allowed to make visible the significant influence of fructose on the crystallization process of glucose [29]. The increase of fructose concentration in a supersaturated glucose solution extended the time of crystallization changes the morphology of the crystals formed and reduces the amount of crystallized glucose [29]. Measurements using computer imagery analysis allowed to show that the formed crystals of glucose monohydrate in the presence of high concentration of fructose within the solution are characterized by larger size in comparison to crystals obtained from pure glucose solutions. There is, additionally, a linear increase in absorbance in the infrared spectrum of glucose suspension under the influence of an increased mass fraction of solid phase [12]. Lupano analysed changes in the absorbance of honey samples during crystallization at a wavelength of $\lambda = 660$ nm and stated that they depend on the crystallization temperature [30]. Conforti et al. searched for a dependency between the absorbance determined at $\lambda = 660$ nm, for various types of honey samples and the water content and parameters determined on the basis of chemical composition. The results of these comparisons did not yield uniform results [13].

A standard approach to determining the amount of solid phase, which melts in the mixture, is by using differential scanning calorimetry (DSC). In the case of honey, there are several reports on the use of DSC to analyse crystallized honey samples [2, 14, 17, 22, 30]. The results of these analyses show unarguably that DSC allows for a perfect identification of the glass-transition temperature together with the caramelization temperature and other changes occurring in carbohydrates in high temperatures [2, 14, 22]. Lupano reports that in the range of 20–50°C, changes occur on the DSC thermograms, which strongly depend on the conditions in which the crystallization of honey takes place and are characterized by a low value of enthalpy with a significant standard deviation of results [30].

Crystallization changes significantly the way of binding water within a product. Growth in water activity caused by the crystallization in honey samples is from approximately 0.012 even to as much as 0.12 with an average value of 0.027 [12]. Identical results obtained for 49 Argentinian honey samples yielded values from 0.014 to 0.056 with an average value of 0.034 [28]. Glieter et al. showed that the increase in water activity after crystallization depends on the origin and for nectar honey samples it has the value of approximately 0.04 and for honeydew honey samples of 0.02 [15]. Nevertheless, the literature lacks in a clear explanation of the factors determining the increase in water activity in honey samples after crystallization. Bhandari and Bareyre [31] showed on model glucose solutions that the dissolution of glucose monohydrate lowers the water activity proportionally to the weight of dissolved crystals. Basing on this, a conclusion was reached that through changes in water activity, the amount of crystallized solid phase can be determined. Own research conducted under similar conditions, but using honey samples, allowed to show that the explanation is not that obvious.

The measurement of mass fraction of solid phase in crystallized honey samples is possible using near-infrared spectroscopy (NIR). Near-infrared spectroscopy is an effective measurement technique enabling the conducting of complex analyses of the crystallization process [32]. The NIR spectroscopy is especially effective in analysing food product sets, which contain water. Own research showed a linear increase in the absorbance with an increase in the mass fraction of the crystalline phase in aqueous glucose suspensions. By using NIR spectroscopy, it is possible to analyse other occurrences in honey samples during crystallization [32].

The analysis procedure for determining the mass fraction of crystallized phase in crystallized honey comprises two stages [12]. The first stage is to determine the calibration equations using preparations with a known mass fraction of crystalline phase in a given honey samples (different honey samples show different absorbance values). In the second stage, measurement is possible of the mass fraction of crystalline phase in crystallized honey. The identification of solid phase has to be conducted for a wavenumber of $\nu \approx 4467 \text{ cm}^{-1}$ [12]. This results from the fact that for this value of the wavenumber there is an isobestic point in glucose solutions. In an isobestic point, the absorbance values of glucose solutions have a constant value, which is the same as the absorbance of water and does not depend on the concentration of glucose in the aqueous solution. For the value of $\nu \approx 4467 \text{ cm}^{-1}$, there occurs one of the local extremes on the differential spectrums of liquid and crystallized honey samples [12]. Fructose solutions do not have at this point an isobestic point. Nevertheless, the absorbance values of aqueous fructose solutions for $\nu \approx 4467 \text{ cm}^{-1}$ are also close to absorbance of pure water. By using this information, it is possible to state that the increase of absorbance in crystallized honey samples for a wavenumber of $\nu \approx 4467 \text{ cm}^{-1}$ is connected only to the presence of solid phase in the form of glucose monohydrate within the honey [12].

2.4. Quantitative measurement of the morphology of a crystalline structure

Crystals formed in honey during crystallization are most commonly presented as photographs made using ordinary optical microscopes [13, 14, 17, 30]. Unfortunately, such images are not very clear and troublesome in interpretation and in computer editing using software

for computer-aided image analysis. The literature suggests the existence of images of such crystals made in polarized light [33]. They enable a relatively effective presentation of morphology of the crystalline phase in the honey samples. A detailed analysis of the crystalline structure of honey samples under birefractive interferometry allowed to prove that it is an extremely effective research technique, as glucose monohydrate crystals are characterized by optical birefringence [12]. Measurements of the morphology of the crystalline structure conducted based on images obtained under birefractive interferometry in transition lighting in the so-called black background using a bipolar PI interfero-polarizing microscope are very effective [12, 34]. Takes is to place a drop of honey between two microscope slides. Due to the need for sharp images of the crystalline structure, the thickness of the medium layer cannot exceed 0.1–0.2 mm. It is difficult under these conditions to photograph the crystalline agglomerates occurring in honey samples, as they have a higher thickness. In order to minimize the phenomenon of interfusing of the crystals in own research, a method was devised of displaying the crystals through introducing a thin layer of crystallized honey onto the liquid honey. In this way, it was possible to minimize the occurrence of interfusion of crystals in images. Observations can be conducted with a magnification of approximately 150 \times using a charge-coupled device (CCD) camera. **Figure 2** shows two sample images of crystallized rape and buckwheat honey [12].

Quantity characteristics of the morphology of the crystalline structure of crystallized honeys can be obtained through determining the distribution of the number of crystals in reference to a characteristic dimension, for example, the maximum diameter (maximum linear dimension of crystals). In order to provide representative nature of the conducted analyses, a sufficiently large population needs to be taken into analysis, for example, one composed of 2000 crystals. The analysed images should be chosen at random. It was shown that crystals in crystallized honey samples demonstrate empirical distribution of exponential character in relations to maximum diameter:

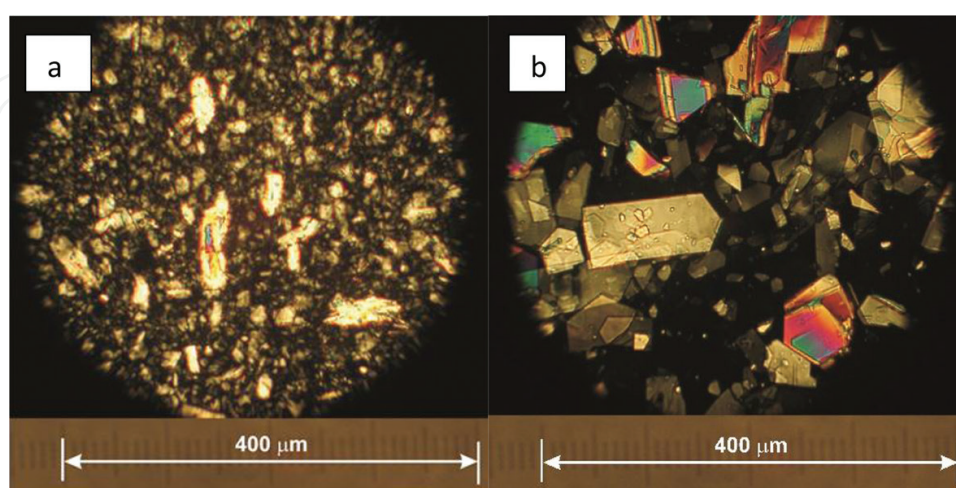


Figure 2. Images made under birefractive interferometry showing the structure of crystallized honey samples: (a) rape honey and (b) buckwheat honey [12].

$$N(d_{\max}) = \lambda \cdot \exp(-\lambda \cdot d_{\max}) \quad (15)$$

Due to the fact that exponential distribution is characterized by one parameter, there is a possibility of quantitative characteristic of the morphological crystalline structure the analysed honeys through a comparison of the λ values [12].

3. Rheological properties of liquid honey

As mentioned earlier, liquid honey has the properties of a Newtonian fluid with a high viscosity value, which strongly depends on temperature. **Figure 3** shows two sample flow curves obtained through rotational measurements (which in this case are straight lines—Newtonian fluid) of honey at a temperature of 298 and 308 K. A 10° increase in temperature caused a decrease of viscosity from 12.95 to 5.52 Pas, which is over 57%. It is worth noting that this viscosity value is a few (a few dozen) thousand times higher than that of water, which is 0.001 Pas. By expanding the range of temperatures, it can be easily shown that its influence in the lower values is even greater. **Figure 4** shows the results of viscosity measurements of buckwheat honey with a water content of 18.1% at a temperature range of 268–295 K. The results of this experiment can be approximated to the exponential curve, whose equation is shown in **Figure 4**.

Nevertheless, water content also significantly influences the viscosity of honey. Oppen and Schuett as early as in 1939 published an equation, which describes the relations between the viscosity logarithm and water content [35]:

$$W = (62,500 - 1567) [T(\log \eta_r + 1) - 2287(313 - T)]. \quad (16)$$

Junzheng and Changying developed a fairly simple dependency based on empirical studies [1]:

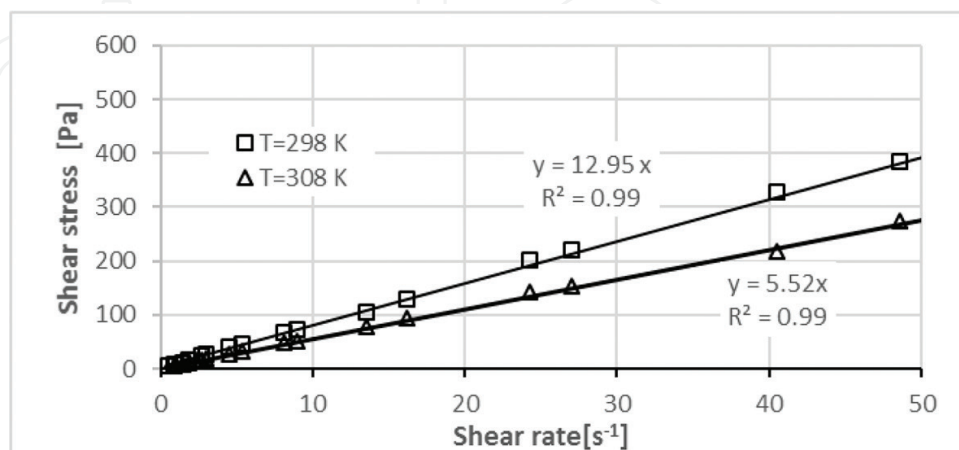


Figure 3. Sample results of rheological measurements—flow curves of multifloral honey $w = 17.6\%$ at a temperature of 298 and 308 K.

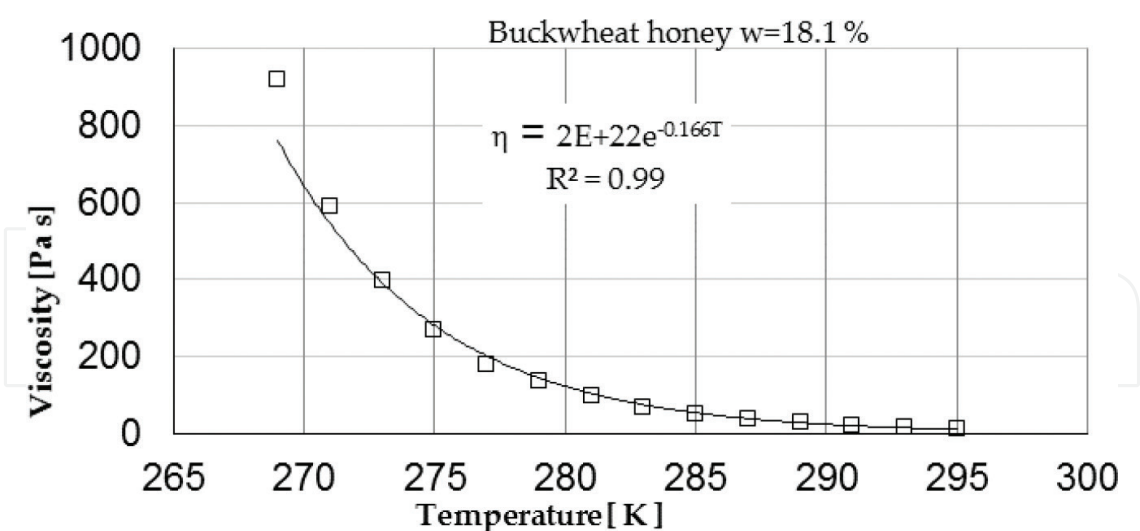


Figure 4. Dependency of buckwheat honey samples viscosity on temperature in the range of 268–295 K.

$$\eta = 14.2 \cdot 10^3 \cdot \exp(-0.31 \cdot w - 0.085 \cdot t). \tag{17}$$

A similar equation was used to describe the viscosity of Spanish honeys [9]:

$$\eta = 19.2 \cdot 10^3 \cdot \exp(-0.3 \cdot w - 0.087 \cdot t). \tag{18}$$

Eqs. (17) and (18) were formed for a relatively high water content percentage, which is in the range from 17.07 to 34.06% and a narrow range of temperature in Celsius [1, 9]. They show that it is relatively easy to describe the viscosity of liquid honeys—taking into account both the temperature and the water content.

Own research conducted on a few hundred samples of Polish honeys for a wide range of temperatures from 260 to 330 K allowed to determine that there is a dependency between water content and temperature expressed in absolute terms [29]:

$$\mu = 1.72 \cdot 10^{22} \cdot \exp(-38.363 \cdot W - 0.1398 \cdot T) \tag{19}$$

The difference in the values of numeral coefficients of the equation above in relations to dependencies (17) and (18) is mainly the results of the usage of temperature expressed in absolute terms and expressing water content by a mass fraction. A graphic illustration of the above-mentioned dependency is shown in Figure 5. It is interesting that for a temperature below 0°, all types of honey show high viscosity exceeding 1000 Pas.

The dependencies presented above (17–19) can be accepted as approximated mathematical models of viscosity of liquid honey samples. It needs to be kept in mind that honey shows changeability related to various environmental factors. However, for technological purposes, these dependencies allow for sufficient approximation of the viscosity value in relations to temperature and water content. These relatively simple relations allow to determine

the value of honey samples viscosity for a wide range of temperatures and water content and to perform calculations connected with hydraulic transport, mixing or heating of the honey.

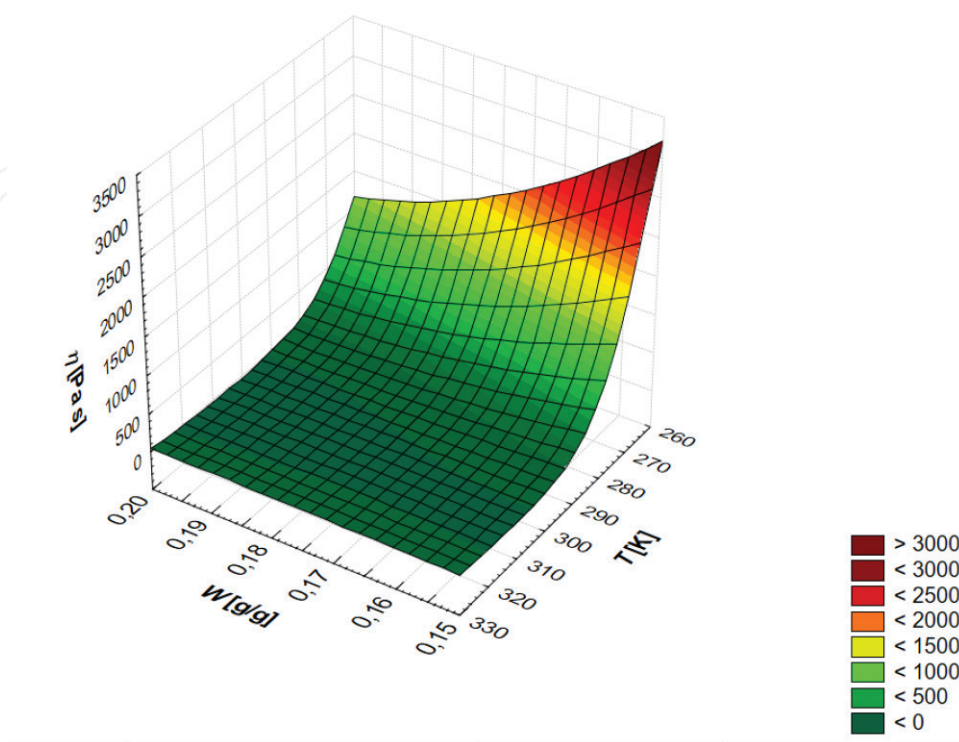


Figure 5. Relation of the viscosity of honey samples to temperature and water content [29].

To finish the discussion on the rheological properties of liquid honeys, attention must be paid to the fact that the measurement results in a dynamic rheological test are similar to rotational measurements. The values of complex viscosity of the analysed media are similar to the values of dynamic viscosity and the relative differences between the average values of dynamic viscosity and complex viscosity do not exceed 10% [12].

4. Rheological properties of crystallized honey

In the case of crystallized honey, the task of determining the rheological properties is more complicated. Honey is not a homogeneous body, it does not show Newtonian properties and additionally it becomes solid after longer periods of storage. In order to analyse such a medium, cylinder-cylinder systems seem to be the most appropriate. Even the filling of the measurement system with crystallized honey can be problematic, as the block needs to be crushed, which at a temperature below 20°C can be difficult. The method used to this end can later influence the results of the experiment, so it needs to be done in a repeatable fashion. Such a problem does not occur in the case of creamed honey, which is obtained (to put in plainly) by mixing of the crystallizing mass. Rheological properties of crystallized honeys can be influenced by the mass fraction and shaping (morphology) of the crystalline phase apart from temperature and water content.

The crystalline structure of different types of honey can vary significantly, which is a result of differences in chemical composition—mainly the content of glucose, fructose and water [36]. The morphology of crystals is also significantly influenced by crystallization conditions. **Figure 6** shows images of the crystalline structure of three types of honey: rape, multifloral and buckwheat. Even a superficial quality assessment conducted based on visual data allows to identify significant differences. The results of sample measurements, which allow to quantitatively characterize the populations of crystals of the individual types of honey samples, are shown in **Figures 7–9**. Rape honey is characterized by the largest crystal fraction with a d_{\max} of $<10\text{ }\mu\text{m}$ [12]. The multifloral honey has a large crystal fraction of $10 < d_{\max} < 30\text{ }\mu\text{m}$ in diameter [12]. Buckwheat honey has a large number of crystals with the dimensions of $30 < d_{\max} < 70\text{ }\mu\text{m}$ [12]. The numerical distribution of buckwheat honey crystals clearly distinguishes it from the other honeys through a characteristic local extreme for the $30 < d_{\max} < 35\text{ }\mu\text{m}$ fraction and is close to the results obtained by Mora-Escobedo et al. for the Mexican tajonal honey. The obtained results using the maximum diameter characterize the morphology of the crystalline structure more clearly than using the crystals' surface area [14]. Distributions characterizing the population of crystals have an exponential character and can be described unambiguously using the λ -parameter.

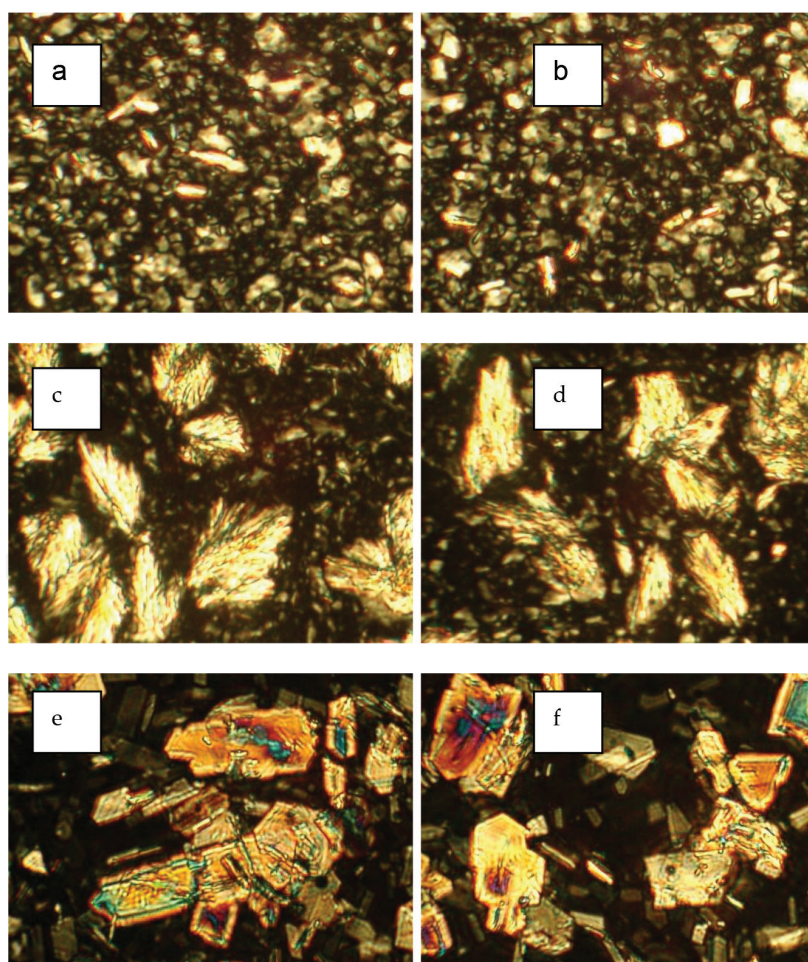


Figure 6. Images showing the morphology of the crystalline structure of honeys samples: (a) and (b) rape honey, (c) and (d) multifloral honey, (e) and (f) buckwheat honey.

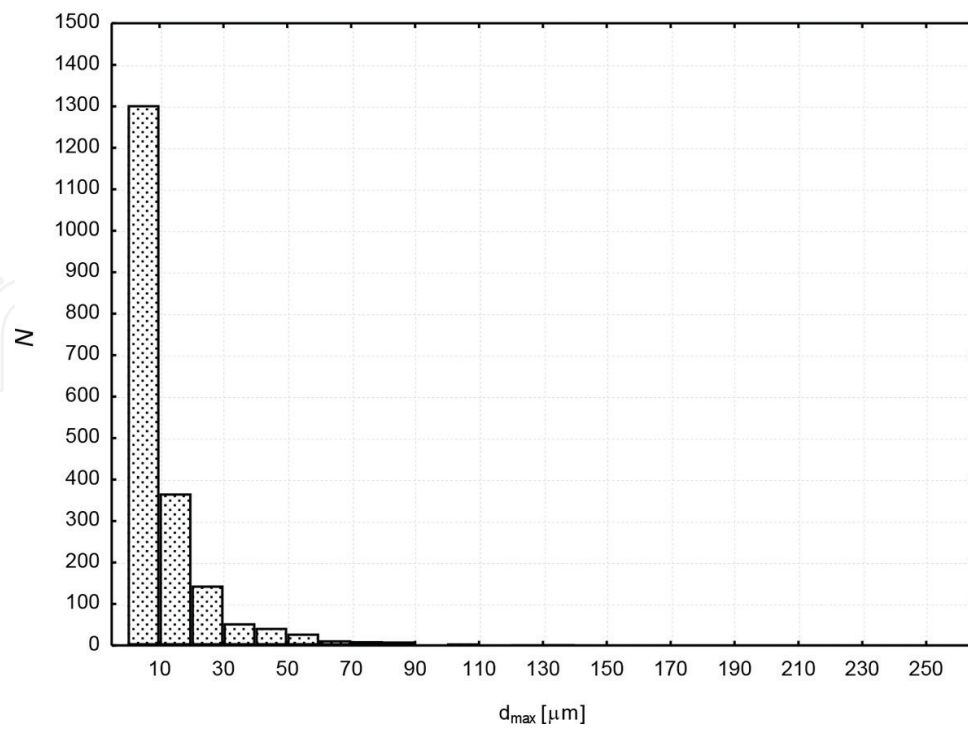


Figure 7. Numerical distribution of the population of 2000 crystals identified in rape honey samples according to maximum diameter.

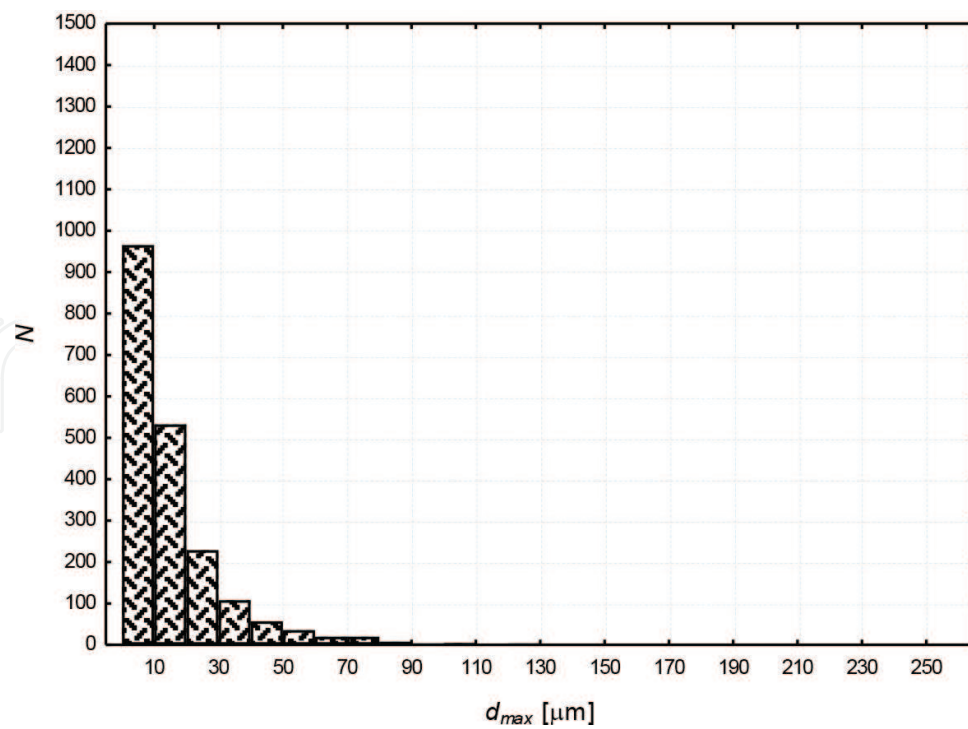


Figure 8. Numerical distribution of the population of 2000 crystals identified in multifloral honey samples according to maximum diameter.

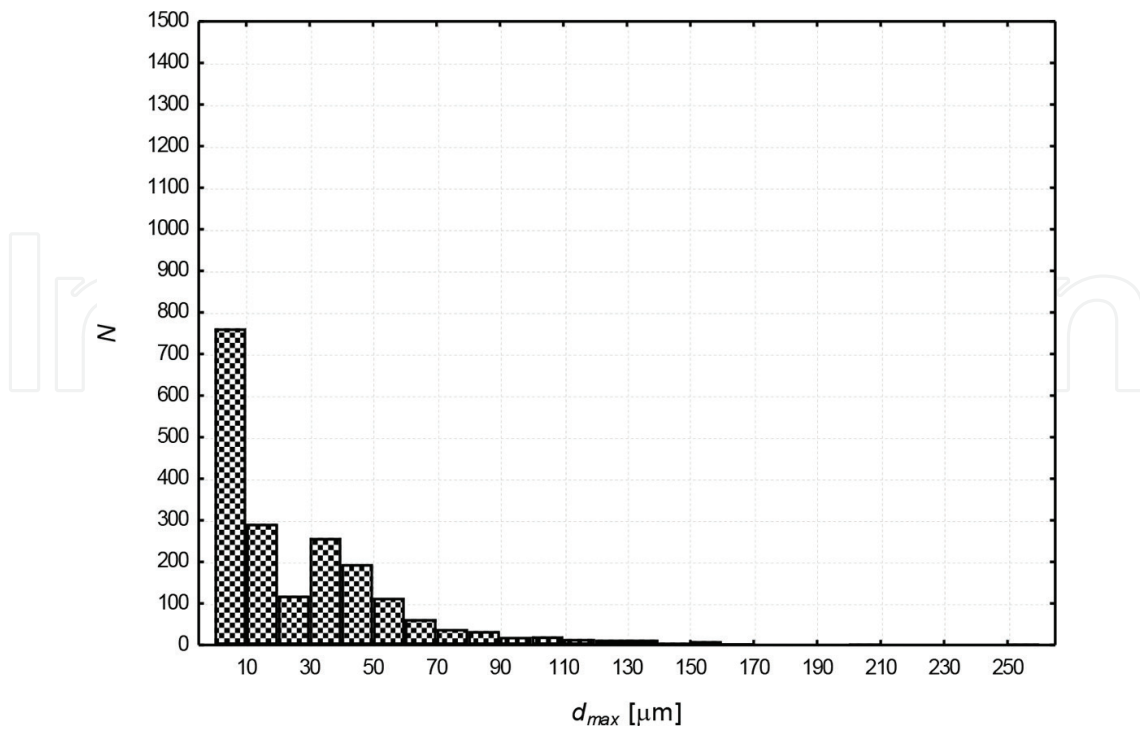


Figure 9. Numerical distribution of the population of 2000 crystals identified in buckwheat honey samples according to maximum diameter.

It is best to begin the rheological characteristic of crystallized honeys from the presentation of equilibrium flow curves (**Figure 10**). As a reminder, the equilibrium flow curve is obtained through assigning equilibrium stress values to shear rate values. The equilibrium stress values are read after stabilizing at a constant level with shearing at a constant shear rate. Next, the value of shear rate is increased in increments and the measurement is repeated.

Based on the flow curves shown in **Figure 10**, the influence of morphology of the crystalline structure on the rheological properties of the analysed suspensions can be estimated. It needs to be mentioned, however, that the content of solid phase in these media was rape 18.2%, multifloral 18.5% and buckwheat 19.2%. The rape honey curve is located the highest and the stress increases at the fastest rate in relation to the increase in shear rate despite the fact that the solid phase content is not the highest. Multifloral honey is characterized by a flow curve located below the rape honey, while the flow curve of buckwheat honey is located below the previous two [12, 36].

A large amount of small crystals causes a significant increase of the texture coefficient and causes the stress in the suspension to increase quickly with the increase of shear rate. Crystallized honeys with large and flat crystals show lower values of the texture coefficient as well as apparent viscosity [12]. The flow curves shown in **Figure 10** can have the following dependencies assigned to describe the apparent viscosity:

$$\text{rape honey } \eta' = 122.07 \times \dot{\gamma}^{-0.604} \quad (20)$$

$$\text{multifloral honey } \eta' = 56.54 \times \dot{\gamma}^{-0.466} \quad (21)$$

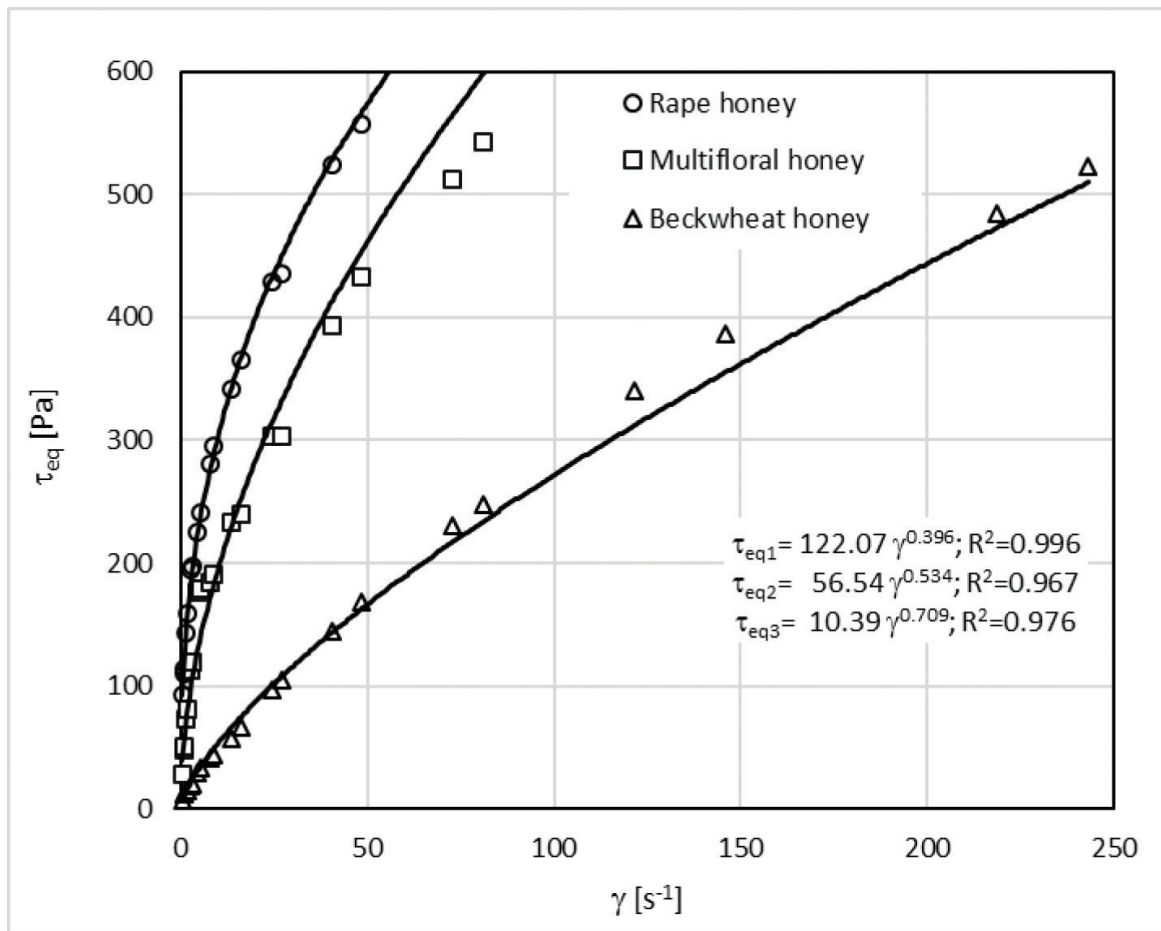


Figure 10. Equilibrium flow curves of media in crystallized state and at a temperature of $T = 30^{\circ}\text{C}$ [12].

$$\text{buckwheat honey } \eta' = 10.39 \times \dot{\gamma}^{-0.291}. \quad (22)$$

Based on the data above, it can be stated that honeys with a fine-scaled structure are characterized by a higher value of apparent viscosity. This effect is even more noticeable in the form of a graph presenting the dependency of apparent viscosity in the function of mass fraction of the crystalline phase with low values of shear rate of $\dot{\gamma} = 0.5 \text{ s}^{-1}$ (**Figure 11**). It needs to be remembered that shear rate is a parameter which is strongly influencing the value of apparent viscosity.

Another characteristic effect presented by crystallized honey samples is its rheological instability. **Figure 12** shows characteristic hysteresis loops obtained in a shearing cycle with an increasing and then decreasing shear rate to a shear stress value of 500 Pa. The obtained hysteresis loops are characteristic for thixotropic fluids [19, 20]. All honeys in their crystallized state show a strong thixotropic effect, which can be measured using the hysteresis surface area. Nevertheless, it needs to be stressed that this effect is to a great extent permanent (the fluid does not fully rebuild its dormant-state properties) and is also connected with the destruction of the crystalline structure. During shearing, the breaking of small crystals occurs, which can be attributed to rheodestruction [20].

Crystallized honey samples show interesting behaviour in a dynamic rheological test. **Figure 13** shows the results of measurements of the same honey samples, which were rheologically characterized under rotational shearing conditions in **Figure 10**. The values of the viscosity mod-

ulus are a few times higher than of the elasticity modulus. As a result, the rheological properties of crystallized honeys are similar to those of viscous fluids. It is noticeable that the highest values of both the viscosity modulus and the storage modulus fall to the multifloral honey, while buckwheat honey is characterized by the lowest values. The values G' and G'' for rape honey are located between the values obtained for multifloral and buckwheat honeys, respectively. This behaviour shows that in relations to measurements conducted under rotary shearing conditions (Figure 10), there is both a quality and quantity change in the behaviour of the media.

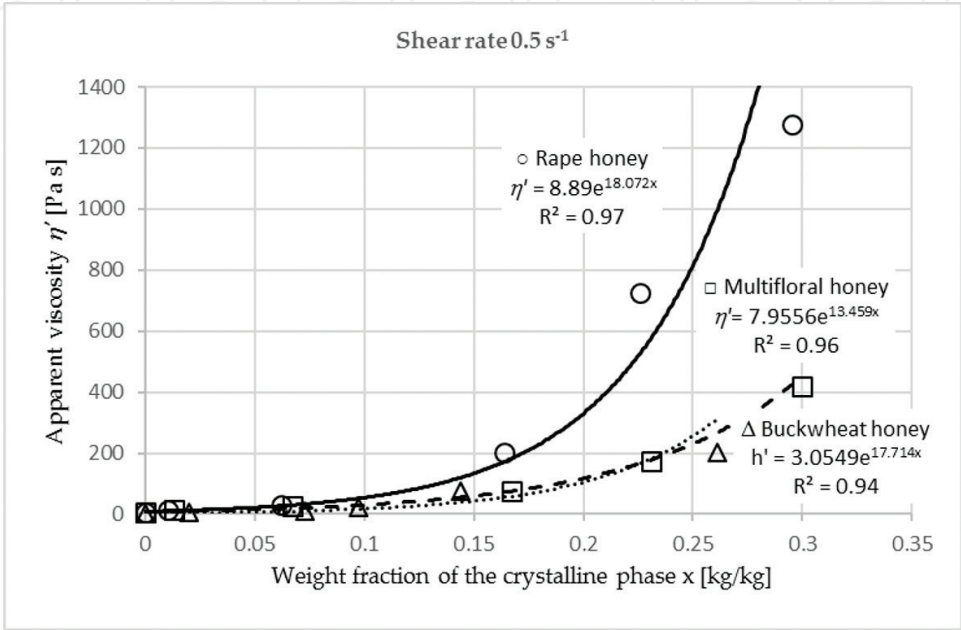


Figure 11. Dependency of apparent viscosity of crystallized honey on the mass fraction of crystallized phase for $\dot{\gamma} = 0.5 \text{ s}^{-1}$.

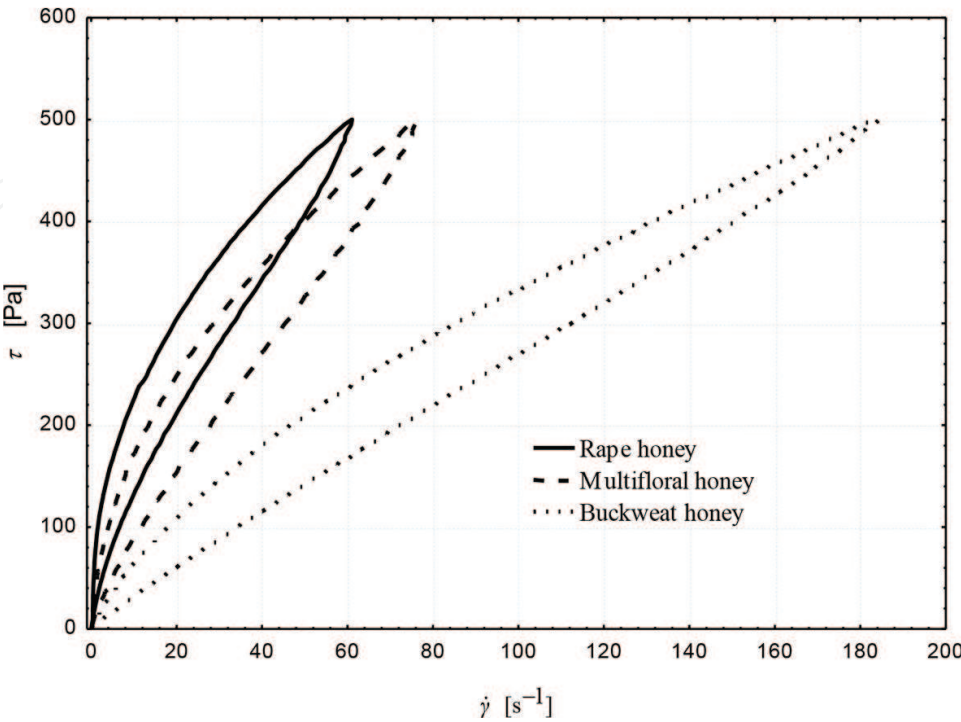


Figure 12. Characteristic hysteresis loops obtained for the analysed honeys for shearing with an increasing and then decreasing shear rate [12].

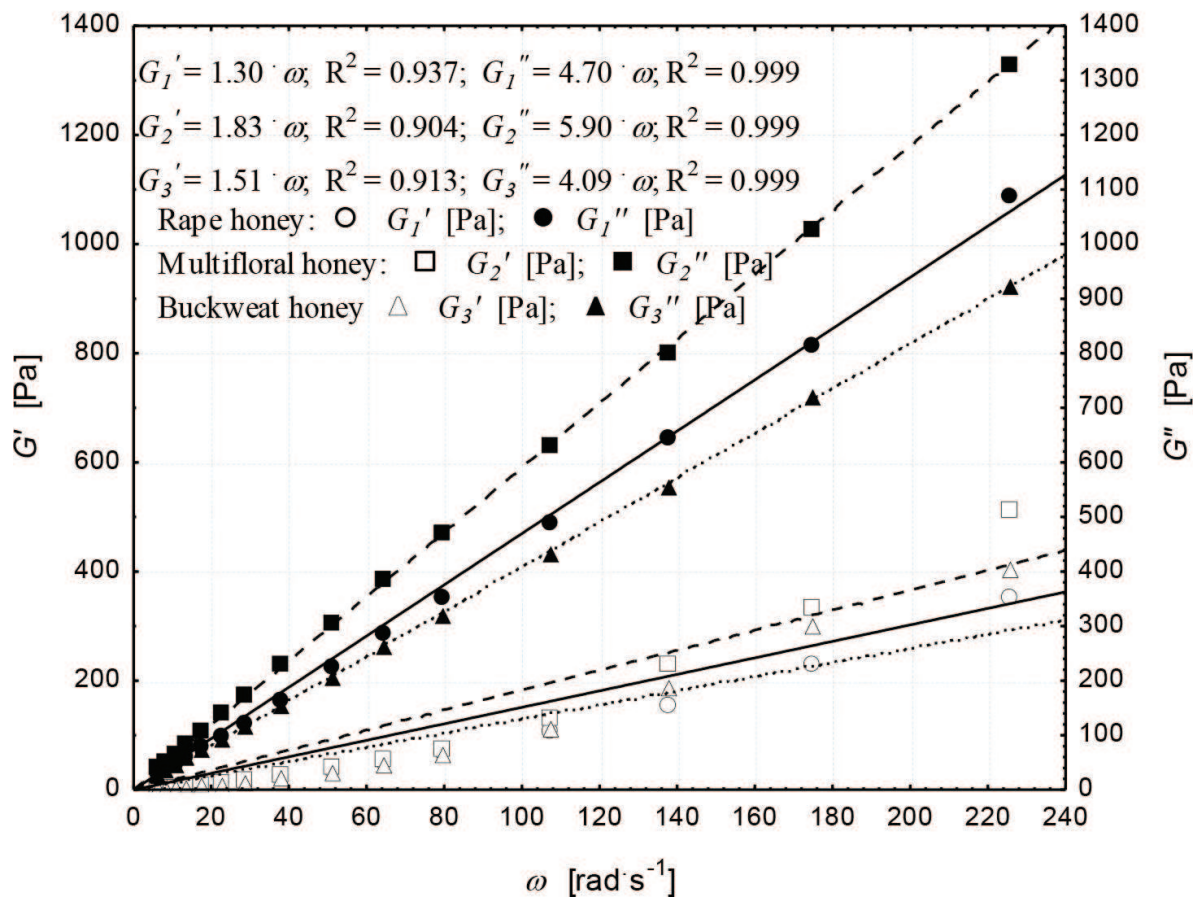


Figure 13. Values of the elasticity modulus and storage modulus of crystallized media in a function of angular oscillation frequency at a temperature of 30°C [12].

Differences in measurement results of rotational and oscillation measurements of crystallized honeys can be shown especially effectively by placing the values of apparent viscosity and dynamic viscosity on one graph. Such a graph is presented in **Figure 14**. Under oscillation shearing conditions, the highest values of complex viscosity were shown by crystallized multifloral honey samples, whereas under equilibrium shearing, the highest values of apparent viscosity were shown by rape honey samples (**Figure 10**). It needs to be stressed that both media were characterized by a similar water content and crystalline phase content. The parameter, which determined such behaviour, was mainly the morphology of the crystalline structure. The irregular shaping of crystals in multifloral honey samples under oscillation shearing (with constant shifts of the direction of deformation) generated higher movement resistance. It was thus noted that the manner of deformation of crystallized honey is a significant factor influencing the obtained rheological measurement results. Apparent viscosity of crystallized honeys decreases along with the increase of shear rate, whereas complex viscosity shows only slight changes with values close to constant.

Figure 14 clearly shows that crystallized honeys do not fulfil the Cox-Merz rule Coxa-Merza [20], since

$$\eta^* \neq \eta' \Big|_{\omega=\dot{\gamma}} \quad (23)$$

Nevertheless, there are such values of angular oscillation frequency and shear rate at which complex viscosity and apparent viscosity are equal to one another. These can be determined from **Figure 14**.

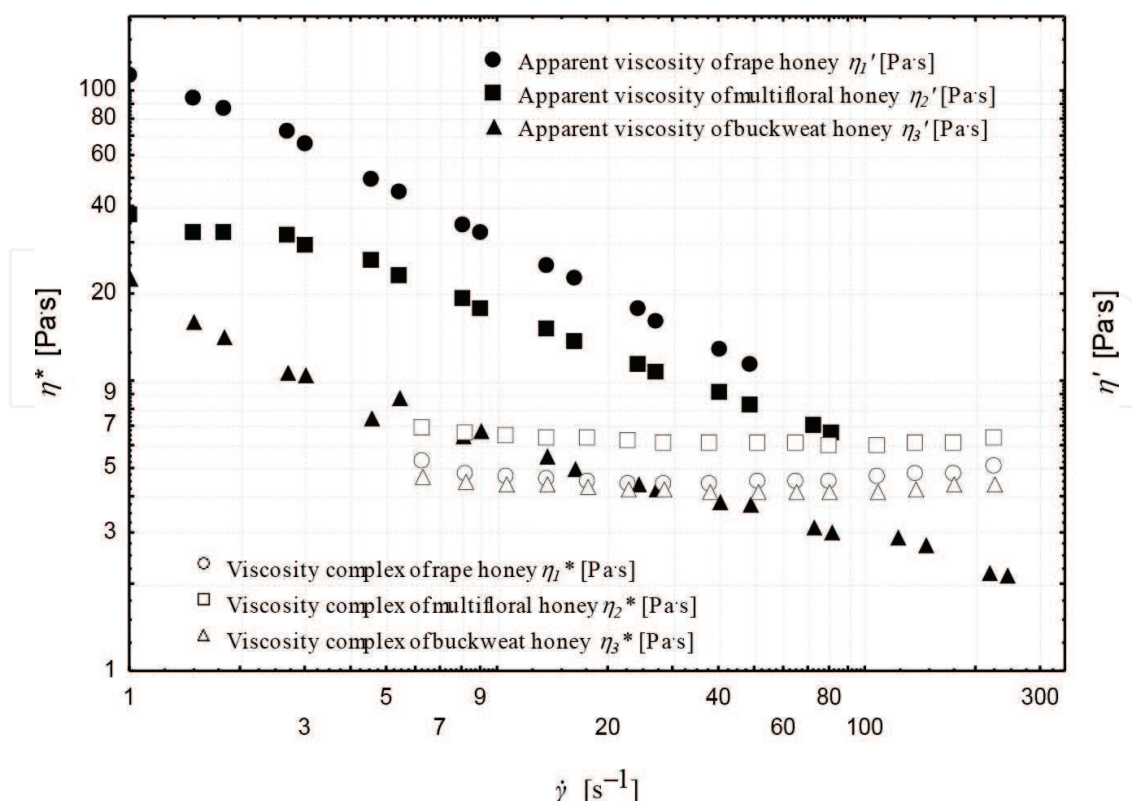


Figure 14. Presentation of the values of complex viscosity and apparent viscosity of crystallized honeys at a temperature of 30°C [12].

The results of rheological measurements of crystallized honey presented above do not exhaust the issue. The majority of the graphs shown in this text were obtained under specific conditions and it is hard to generalize them, as was the case with liquid honeys. Rheological studies of crystallized honey are extremely important in shaping the texture of the so-called creamed honeys. Creamed honey is obtained by the so-called direct crystallization with additional mixing during crystallization. This enables to deliberately shape the texture of crystallized honey to obtain characteristic features expected by consumers.

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