INFLUENCE OF CHEMICAL COMPOSITION AND TEMPERATURE ON HONEY PHASE ANGLE

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Abstract: *Honey is a complex material which exhibits a viscoelastic behavior under oscillatory testing. The rheological behavior of honey is influenced by moisture content, concentration and by the temperature (all the rheological parameters are decreasing with the increasing of the temperature). This article is about the influence of chemical composition (fructose, glucose, sucrose, moisture content) and temperature on the honey phase angle. The honey is meeting the Codex Alimentarius requirements regarding moisture content. The sum of fructose and glucose concentrations was 60 g/100 g in agreement with CE directive 2001/110/CE. The phase angle was measured at 30, 35, 40, 45 and 50 °C; the viscous component is maxim at low temperature (in the study case at 30 -45 °C). It can be observed that at 30 °C, 35 °C, 40 °C and 45 °C, the phase angle evolution is not influenced by the frequency applied; the phase angle is changing a little with the frequency. At 50 °C, the phase angle is strongly influenced by the frequency, is decreasing its value proportionally with frequency.The suitable precidtion of the phase angle with temperature and chemical composition has been observed using the 3rd grade polynomial model with variables; the model achivied has reached a regression coeffiecient (R^2) 0.9915.*

Keywords: *honey, sugar, polynomial model*

1. Introduction

Honey is a natural and nutritious food used by many people all over the world since ancient times, mainly because of its significant contribution to human health. However, the quality of honeys varies dependent on the climate and environmental conditions around the foraging area of honey bees. Further processing and improper storage condition also influent the quality of honeys indirectly [1].

Viscosity of honey is an important factor that concerns both processing parameters of honey production (e.g. velocity of centrifuging or filtering) and its sensory properties perceived by consumers. The majority of fluid honeys shows Newtonian behaviour and their viscosity strongly depends on temperature [2-4].

The viscoelasticity is the property of materials that exhibit viscous and elastic characteristics when underdoing deformation. Viscous materials, like honey, resist shear flow and strain linearly with time when a stress is applied [5]. The viscoelastical parameters of a viscoelastical materials are: elastic modulus (G'), viscous modulus (G''), complex modulus (G*), complex viscosity (η*) and phase angle (δ).

The rheological properties of honey have been investigated by some authors in the last decades [2-4, 6-8], however no other papers have been reported on the phase angle determination and the influence of different factors on it.

The aim of this study is to determine the phase angle of different honey types, to study the influence of the temperature on the magnitude of it, to model the chemical and temperature influence of the phase angle.

2. Materials and methods

2.1. Materials

For the rheological behaviour of honeys samples were purchased different 6 samples of different origins (floral, polyflorals and honeydew); the samples have been purchased from the Romanian market. The rheological properties of honeys can be influenced by the presence of crystals and air bubbles [8].
Before measuring the rheological properties, the samples were warmed to 55 °C to dissolve the crystals, and were kept at 30 °C to eliminate the bubble airs, which could interfere during the rheological studies.

2.2. Concentration (°Brix) and moisture content determination

The concentration of soluble solid content (°Brix) and refractive index were determined using a refractometric method. We used Leica Mark II Plus refractometre.

The moisture content was determined using the Chataway table [9]. The measurement were taken in duplicate

2.3. Sugar determination

The determination of glucose, fructose and sucrose in honey samples was made by a HPLC 10ADVP -SHIMADZU, with RI-detector, according to a method described by Bogdanov [9]. The compounds were separated on a Alltech type Alltima amino column, 250×4.6 mm i.d. and particle size 5 µm. The samples were prepared as: 5 g of honey were dissolved in water (40 ml) and transferred quantitatively into a 100 ml volumetric flask, containing 25 ml methanol and filled up to the volume with water. The solution was filtered through a 0.45 µm membrane filter and collect in sample vials. Flow rate 1.3 ml/min, mobile phase: acetonitrile/water (80:20, v/v), column and detector temperature 30 °C, sample volume 10 µl.

A calibration curve was made for each sugar using standard solutions of different concentrations (0.5–80 mg/ml). The linear regression factor of the calibration curves was higher than 0.9982 for all sugars. Sugars were quantified by comparison of the peak area obtained with those of standard sugars.

The results for each sugar were expressed as g/100 g honey. Values of parameters were expressed as the mean ± standard deviation to a confidence interval for mean of 95 %.

2.4. Phase angle determination (δ)

Phase angle determination was made using the device designed and realised at Food Engineering Faculty, at a frequency ranged between 0.1-10 Hz, and a amplitude of 2 dB.

2.5. Statistical analysis

The statistical analysis was made using the next software packs: Excel 2007 and Unscrambler X 10.1. The variables were weighted with the inverse of the standard deviation of all objects in order to compensate for the different scales of the variables.

3. Results and discussions

In this study have been analysed 6 honey samples, each one with a different chemical composition. The phase angle was measured at 5 temperatures 30 °C, 35

°C, 40 °C, 45 °C and 50 °C). In table 1 is presented the chemical composition of the honeys samples. The honey is meeting the Codex Alimentarius requirements regarding moisture content The sum of fructose and glucose concentrations was 60 g/100 g in agreement with CE directive 2001/110/CE [10].

Table 1
Chemical composition of honey

	Acacia	Dandelion	Honeydew	Polyfloral	Sun flower	Tilia
Moisture (g/100g)	18.6	16.9	17.7	19.2	19.3	19.0
°Brix	80.2	81.9	81.4	80.0	79.9	79.8
Fructose (g/100g)	47.3	40.2	35.9	35.3	38.6	43.3
Glucose (g/100g)	27.6	33.2	34.5	31.3	34.8	32.4
Sucrose (g/100g)	2.0	1.2	0	2.2	1.6	1.1
Fructose + glucose (g/100g)	74.9	73.4	70.4	66.6	73.4	75.7
F/G	1.7	1.2	1.0	1.1	1.1	1.3

The samples were analysed at a frequency ranging 0.1 – 10 Hz. In figure 1 is presented the evolution of phase angle with temperature and frequency. The phase angle ranged between 75,16 – 89,98°. The phase angle is ranging between 0 and 90°, the region between 0 – 45° corresponds to viscoelastical materials with elastic part dominant, and the region between 45-90° corresponds to viscoelastical materials with viscous part dominant. From phase angle point of view honey is a viscoelastical material with the viscous part dominant. The viscous component is maxim at low temperature (in the study case at 30 -45 °C). It can be observed that at 30 °C, 35 °C, 40 °C and 45 °C, the phase angle evolution is not influenced by the frequency applied; the phase angle is changing a little with the frequency. At 50 °C, the phase angle is strongly influenced by the frequency, is decreasing its value proportionally with frequency.

3rd grade multivariable polynomial modelling of the influence of chemical composition and temperature on phase angle of honeys

The data model regarding the prediction of phase angle (δ) of honey, measured at 1 Hz, in function of its chemical composition (fructose, glucose, sucrose, sugars (the difference between Brix concentration –reported as dry mater – and the sum of fructose, glucose and sucrose), non-sugars components (the difference, reported to 100 g, between 100 g and the sum of moisture content and Brix concentration), moisture content and temperature was been made using a 3rd grade polynomial equation with seven variables. The measured and predicted values have been compared to see the suitability of the model. The equation of the model is as given (eq. 1):

$$\delta = b_0 + \sum_{i=0}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n} b_{iii} x_i^3 + \sum_{i<j<k}^{n} b_{ijk} x_i x_j x_k + \sum_{i<j}^{n} b_{ij} x_i x_j + \sum_{i<j}^{n} b_{ij} x_i^2 x_j + \sum_{i<j}^{n} b_{ij} x_i x_j^2 \quad (1)$$

where δ the phase angle predicted, b_0 is a constant that fixes the response at point of the experiments, b_i – regression coefficient for the linear effect terms, b_{ij} – interaction effect terms, b_{ii} – quadratic effect terms and b_{iii} – cubic effect terms.

In table 2 are presented the correspondence between actual and coded values of design variables.

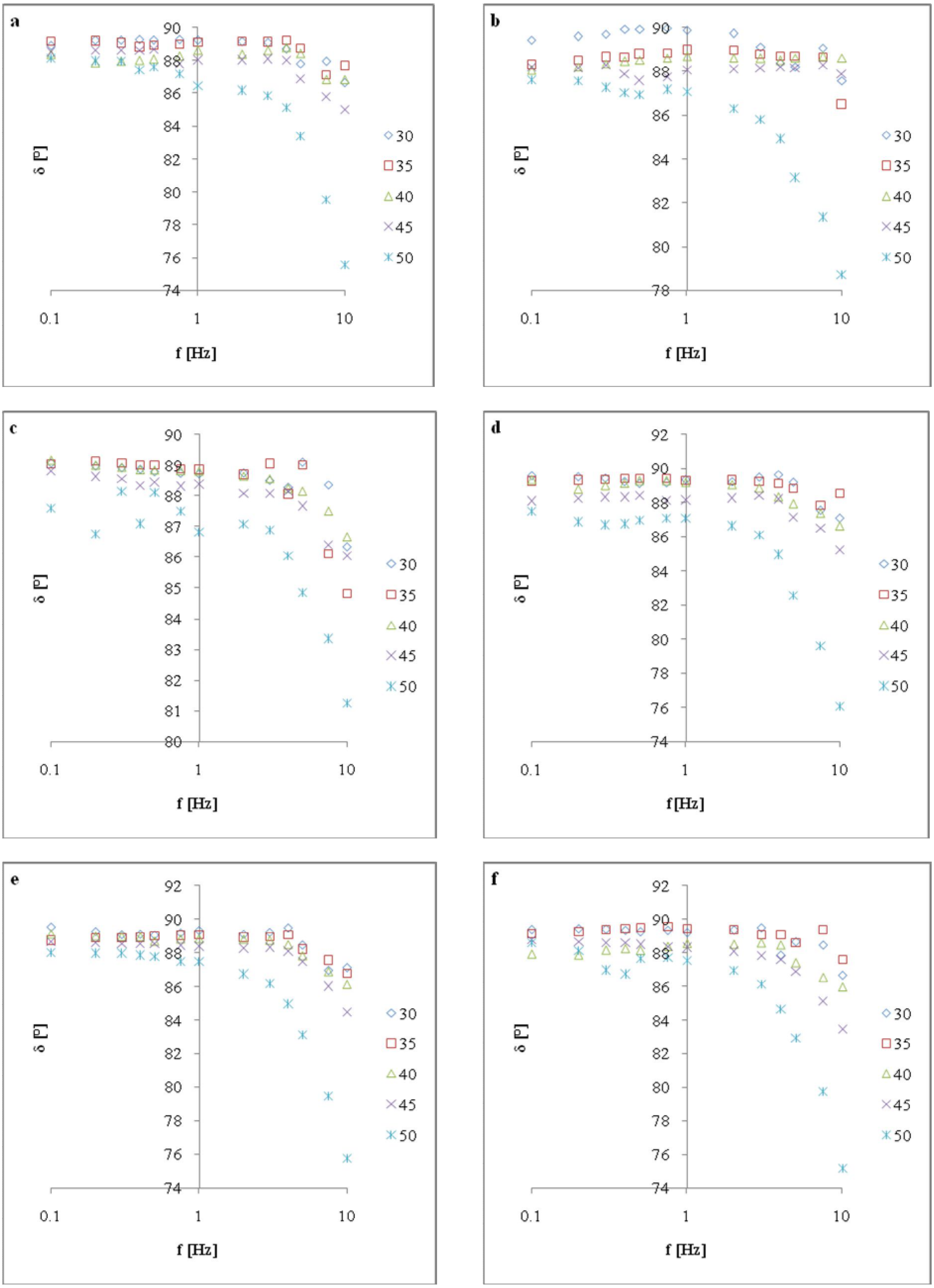

Fig. 1. Phase angle variation with temperature and frequency a. acacia, b. dandelion, c. honeydew, d. polyfloral, e. sun flower, f. tilia

Table 2
Correspondence between actual and coded values of design variables

Variable	Symbol	Actual values of coded levels	
		-1	+1
Temperature (°C)	X_1	30	50
Fructose (g/100g)	X_2	35,29	42,85
Glucose (g/100g)	X_3	27,65	35,36
Sucrose (g/100g)	X_4	0	2,22
Sugars (g/100g)	X_5	2,95	11,21
Non-sugar substances (g/100g)	X_6	1,64	1,76
Moisture (g/100g)	X_7	16,24	17,96

The design parameters (X_1-X_7) have been modeled in order to achieve the model. The model summary is presented in tabel 5.36. The coefficient of regresion of the proposed model represents 99.91 (R^2 adjustat 99.82) (Table 3).

Table 3
Model summary

Model	Standard deviation	R^2	R^2 adjusted	P
Cubic	0.19	0.9915	0.9812	0.0001

$$\delta = 89{,}90 - 0{,}84 \cdot X_1 + 0{,}70 \cdot X_2 + 0{,}25 \cdot X_3 + 0{,}21 \cdot X_4 + 0{,}51 \cdot X_5 + 0{,}15 \cdot X_6 - 0{,}86 \cdot X_1^2 - 0{,}60 \cdot X_1 \cdot X_2 - 0{,}74 \cdot X_1 \cdot X_3 + 0{,}04 \cdot X_1 \cdot X_4 - 0{,}37 \cdot X_1 \cdot X_5 + 0{,}25 \cdot X_1 \cdot X_6 - 0{,}32 \cdot X_1^3 - 0{,}22 \cdot X_1^2 \cdot X_2 + 0{,}27 \cdot X_1^2 \cdot X_3 + 0{,}15 \cdot X_1^2 \cdot X_4 - 0{,}62 \cdot X_1^2 \cdot X_5 - 0{,}17 \cdot X_1^2 \cdot X_6 \quad (2)$$

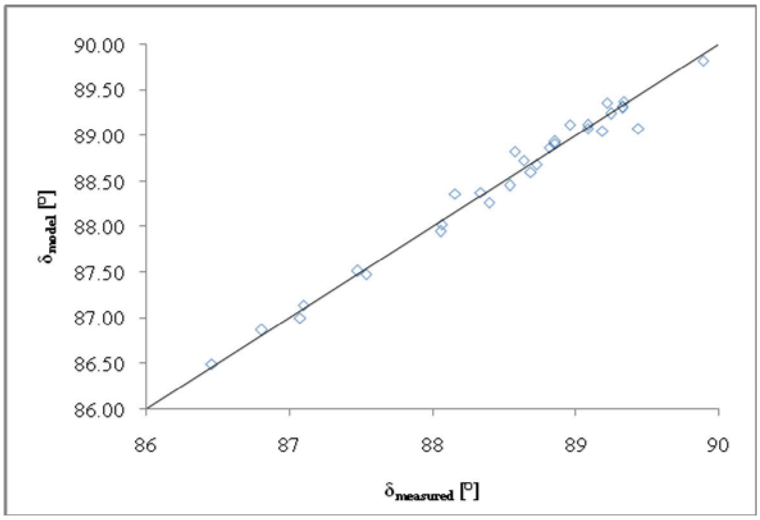

Fig. 2. Measured vs. predicted of phase angle of honey using polynomial equations

In figure 2 are plotted the predicted values versus measured values of the phase angle. It can be seen that the pairs of values are closed to the line with the equation x = y, this fact confirms the validity of the model based on chemical composition and temperature modelling of the phase angle of honey.

Parameter optimization

The optimization of the parameters simultaneously is very important for product quality. The desirability function approach is used to optimize the multiple characteristics concurrently. In the desirability function approach, first each characteristic, y_i, is converted into an individual desirability function, d_i, that varies over the range (eq. 3.)

$$0 \leq d_i \leq 1 \qquad (3)$$

If the characteristic y_i i is at its target, then d_i = 1. If the characteristic is outside an acceptable region, then d_i = 0. Finally, the design variables can be chosen to maximize the overall desirability (eq. 4)

$$D = (d_1 x d_2 x \dots x d_n)^{1/n} \qquad (4)$$

where n is the number of characteristics. When the target (T) for the characteristic y is a maximum value and the lower limit is denoted by L,

$$d_i = \begin{cases} 0 & y < L \\ \left(\frac{y-L}{T-L}\right)^r & L \leq y \leq T \\ 1 & y > T \end{cases} \qquad (5)$$

when the target (T) for the characteristic y is a minimum value and the upper limit is denoted by U (Mo,'05).

$$d_i = \begin{cases} 0 & y < T \\ \left(\frac{U-y}{U-T}\right)^r & T \leq y \leq U \\ 1 & y > U \end{cases} \qquad (6)$$

where r = 1.

The phase angle value would be maxim at 42.85% fructose, 30.27% glucose, 1.13% sucrose, 7.66% sugars, 16.39% moisture, 1.69% non-sugar substances and 32.1 °C respectively.

4. Conclusions

According to the phase angle, honey is a viscous viscoelastical material, having a viscous part much greater than the elastic part (δ > 45°). It can be observed that at 30 °C, 35 °C, 40 °C and 45 °C, the phase angle evolution is not influenced by the frequency applied; the phase angle is changing a little with the frequency. At 50 °C, the phase angle is strongly influenced by the frequency, is decreasing its value proportionally with frequency. The phase angle value would be maxim at 42.85% fructose, 30.27% glucose, 1.13% sucrose, 7.66% sugars, 16.39% moisture, 1.69% non-sugar substances and 32.1 °C respectively

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