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The influence of propolis on the rheological behaviour of pure honey

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Abstract

The present work refers to an investigation of the rheological behaviour of pure honey mixed with different percentages of propolis. Work curves, such as Frequency Sweep, Stress Sweep and Viscosity of samples were examined, allowing rheological evaluation of the mixtures. The experiments were accomplished in a HAAKE-RS50 Rotating Rheometer, with geometry Cone-Plate and Double Gap Cylinder sensor system. The viscosity of the pure honey is considerably reduced with the addition of extract of propolis. Furthermore, a pronounced viscoelastic behaviour is observed in the samples with extract of propolis.

Keywords: Rheology; Foods; Honey; Propolis

1. Introduction

Honey, a viscous and aromatic product appreciated since ancient Greek times, is prepared by bees, mainly from the nectar of flowers or honeydew (Dustmann, 1993). The characteristic texture, appearance, flavour and sweetness of honey, as well as its medicinal properties, have attracted consumers (Zumlai & Lulat, 1989). This aliment, produced by bees, is highly commercialized in its pure form and mixed with innumerable other plants or products made by bees. In the present work, we used samples of pure honey, extract of propolis and mixtures of pure honey with extract of propolis.

Propolis (sometimes also referred to as 'bee glue') is the generic name for the resinous substance collected by honeybees from various plant sources (Chemid, 1996). The word propolis is derived from the Greek *pro*, for or in defence, and *polis*, the city, that is, defence of the city or the hive (Ghisalberti, 1979).

The precise composition of raw propolis varies with the source. In general, it is composed of 50% resin and vegetable balsam, 30% wax, 10% essential and aromatic oils, 5% pollen and 5% various other substances, including organic debris (Cisarino, Pisati, & Fasani, 1987). Ailments curable by propolis include bad breath (halitosis), eczema, eye infections, throat infections, ulcers and urinary infections (Hill, 1977). Up to 10% of propolis mixed with honey is currently being sold.

The following ratios in the tests were used: 5, 10, 15, and 20% of extract of propolis added to pure honey (wild flora). Also, the tests were carried out with pure honey and with extract of propolis only. The rheological behaviour of the mixtures were studied. Two tests were undertaken: (1) Steady shear, yeilding the viscosity curves and, (2) Sinusoidal shear, yielding the frequency sweep and stress sweep curves.

2. Material and methods

2.1. Material

The samples were obtained from the Cooperativa Apícola do Rio de Janeiro (COAPI-Rio). Only honey of wild flora was utilized. The extract of propolis used has the following composition: each 1.5 kg of raw propolis is diluted in 1.8 litres of distilled water and 4.2 litres of ethyl alcohol.

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2.2. Preparation of sample

The extract of propolis was carefully added to honey, giving 5, 10, 15, and 20% of extract of propolis mixed with pure honey. The mixtures were based on volume properties and, in this case, the instrument used had an accuracy of 0.1 ml. For example, to prepare 50 ml of sample with 5% of extract of propolis, 47.5 ml of honey and 2.5 ml of extract of propolis were used.

For each test performed, five different samples of the same material were used to improve the statistical value of the measurement and the mean value was used to plot the graphs in this paper.

2.3. Moisture of sample

Another important parameter obtained was the moisture of each sample. To measure the moisture of the sample, a table refractometer M/PZD, ref. RL3 with a scale of 0–85% was used. After observing the the R.I. in the refractometer, the corresponding value of moisture is obtained using Table 1 (Lara, Nazário, Almeida, & Pregnolatto, 1976).

2.4. Setting the equipment

All measurements were realized in a HAAKE-RS50 Rheometer, working with a thermo controller model K20-DC5. Two types of sensor geometry were utilized: Cone-Plate and Double Gap Cylinder. The specifications of each sensor are shown in Tables 2 and 3. The first sensor was used for measurements with pure honey and different ratios of extract of propolis. As the extract of propolis had a low viscosity, it was necessary to use the second technique mentioned above. For each test performed in the cone-plate sensor system, 2.0 ml of sample was necessary and, for each test in the double gap cylinder, 6.3 ml of sample was necessary.

To start the test it was necessary that the rheometer set to its zero point. After this, the sample was carefully placed on a plate (when the cone-plate sensor system was used) or inside of the cup (when the double gap cylinder sensor system was used). It was necessary to ensure that the plate did not overflow with the sample.

A thermo controller, linked to the rheometer, carefully controlled the sample temperature. In the present work all the tests were performed at 25 °C.

2.5. Shear test

In the shear test, a stress was applied to the sample (controlled stress method—CS) or a strain (controlled strain method—CR) to give one value of deformation or stress. This test yielded the viscosity of the sample.

2.6. Oscillation test

Oscillation tests are known as dynamic tests. In this test a stress amplitude sweep or a frequency sweep is imposed in the test sample and a strain or stress, dependent on time, is obtained.

In such tests, the stress and strain are temporary oscillatory functions. These functions can be in phase ($\delta = 0°$), out of phase ($\delta = 90°$) or between 0 and 90°. In the first case, a maximum deformation occurs for a maximum stress imposed and it distinguishes an elastic

Table 1
Table of Chataway[a]

Refractive Index at 20 °C	Moisture (%)	Refractive Index at 20 °C	Moisture (%)
1.5041	13.0	1.4940	17.0
1.5035	13.2	1.4935	17.2
1.5030	13.4	1.4930	17.4
1.5025	13.6	1.4925	17.6
1.5020	13.8	1.4920	17.8
1.5015	14.0	1.4915	18.0
1.5010	14.2	1.4910	18.2
1.5005	14.4	1.4905	18.4
1.5000	14.6	1.4900	18.6
1.4995	14.8	1.4895	18.8
1.4990	15.0	1.4890	19.0
1.4985	15.2	1.4885	19.2
1.4980	15.4	1.4880	19.4
1.4975	15.6	1.4876	19.6
1.4970	15.8	1.4871	19.8
1.4965	16.0	1.4866	20.0
1.4960	16.2	1.4862	20.2
1.4955	16.4	1.4858	20.4
1.4950	16.6	1.4853	20.6
1.4945	16.8	1.4849	20.8

[a] Correction for different temperatures: to add or to subtract 0.00023 from the value found in table to each degree above or under 20 °C.

fluid. In the second case, a maximum stress is imposed and a minimum deformation is obtained, corresponding to a viscous fluid. In the third case, it is a viscoelastic fluid.

Oscillation tests give important results, such as the Complex Modulus (G^*) that represents the total resistance of the substance due to a deformation applied on it (Macosko, 1994); we can write this as:

$$G^* = \frac{\tau_0}{\gamma_0}, \tag{1}$$

Where τ_0 and γ_o are the amplitude of stress and the amplitude of deformation, respectively.

Another way that the complex modulus can be represented is to write it as a function of the elastic modulus or storage modulus (G'), and as a function of the viscous modulus or loss modulus (G''):

$$G^* = G' + \mathrm{i}G'', \tag{2}$$

In Eq. (2), G' represents the temporary energy of storage during the test, can be recovered afterwards. In the same equation, G'' is the energy necessary for the fluid flow, being converted into heat. Thus a fluid can be considered viscous ($G'=0$ and $G''=G^*$), elastic ($G'=G^*$ and $G''=0$) or viscoelastic ($G'\neq 0$ and $G''\neq 0$).

Table 2
Specifications for the Cone-Plate sensor system (model C60/2°)

Cone diameter	59.996 mm
Plate diameter	100 mm
Cone angle	1.993 Deg
Truncation	0.104 mm

3. Results and discussion

The results shown in the present work represent the median value of five different samples of the same material. A difference of less than 4% was obtained between the results for the different samples during the same test.

The moistures of the samples obtained using a refractometer (Table 1) were: 19.1% for pure honey (wild flora), 20.6% for sample with 5% of extract of propolis; 21.7% for sample with 10% of extract of propolis, 23.6% for sample with 15% of extract of propolis and more than 25.0% for sample with 20% of extract of propolis.

Fig. 1 shows the viscosity of pure honey, extract of propolis and the mixtures of pure honey with extract of

Table 3
Specifications for the Double Gap Cylinder sensor system (model DG 41)

Inner diameter 1	35.500 mm
Inner diameter 2	36.000 mm
Outer diameter 1	42.800 mm
Outer diameter 2	43.400 mm
Sample volume	6.3 cm^3

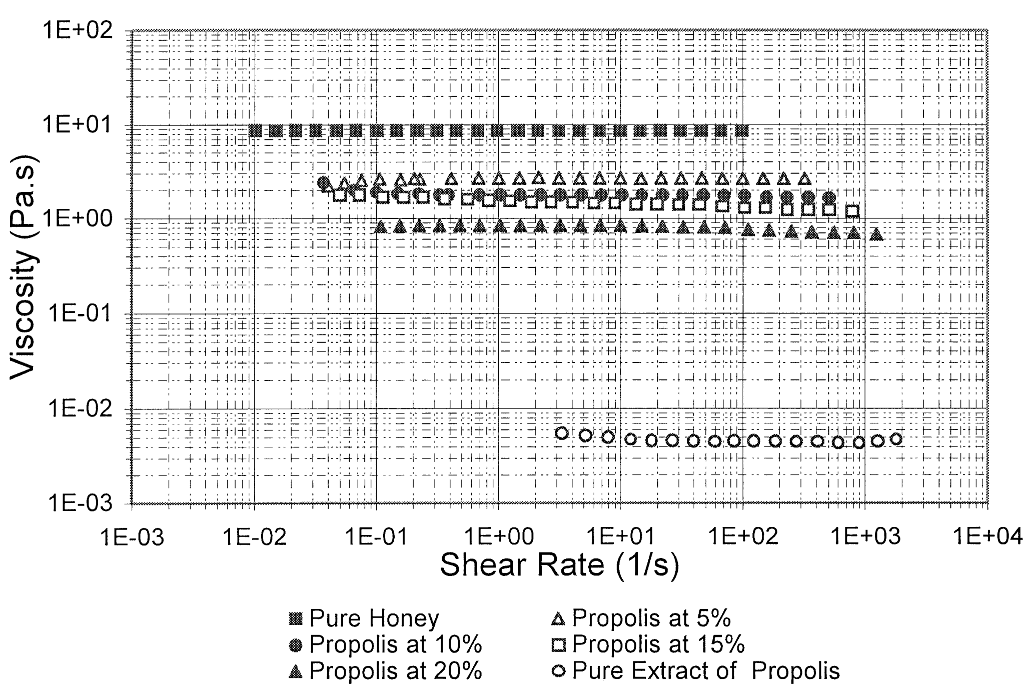

Fig. 1. Viscosity curves: obtained at a temperature of 25 °C.

propolis. These curves were obtained after performing a shear test, using a controlled stress method.

Fig. 1 shows significant differences among viscosities of samples after the differents shear rates applied. So, the value of viscosity shows how much extract of propolis there is in the honey. This test is therefore a good instrument for quality control.

Fig. 2 shows the stress sweep tests for pure honey, extract of propolis and other mixtures, performed at a frequency of 4.64 Hz and temperature of 25 °C. We can see that in this work range, all samples were within the linear viscoelastic limit, so that the tests could be performed in this range of stress without adulterating or breaking the structure of the sample. The constant value of the complex modulus (G^*), after different stresses applied, is an indication of this.

Figs. 3 and 4 show the frequency sweep tests performed at 25 °C and 1 Pa; that is, the tests were performed within the linear viscoelastic limit.

According to the experimental results showed in Fig. 3, we can conclude that, at low angular velocity, all samples showed a phase angle of 90° which makes clear

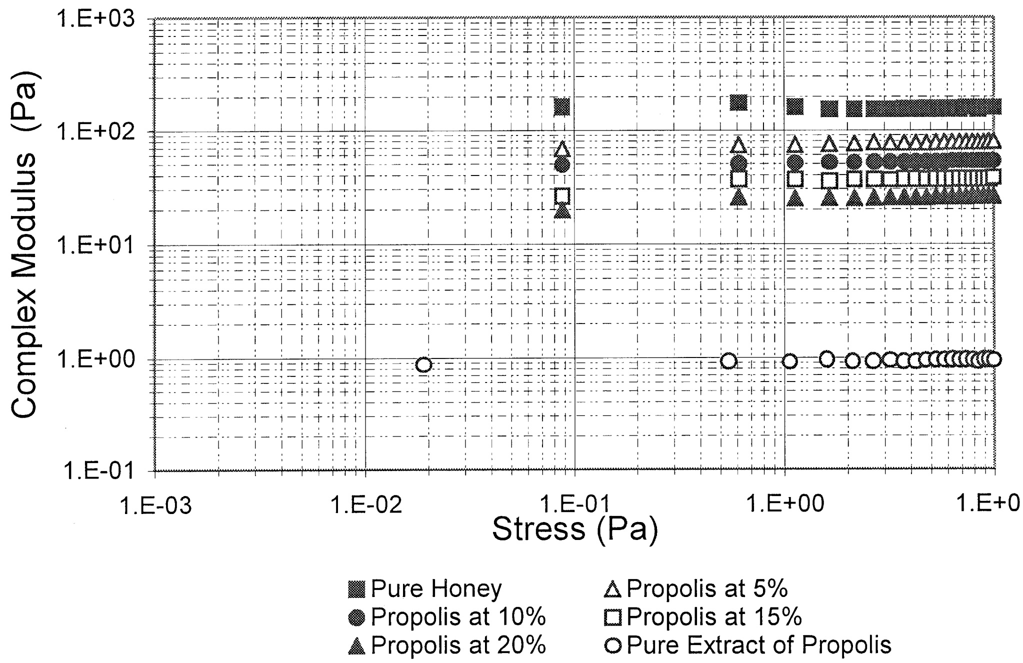

Fig. 2. Stress sweep tests: performed with a frequency of 4.64 Hz and temperature of 25 °C.

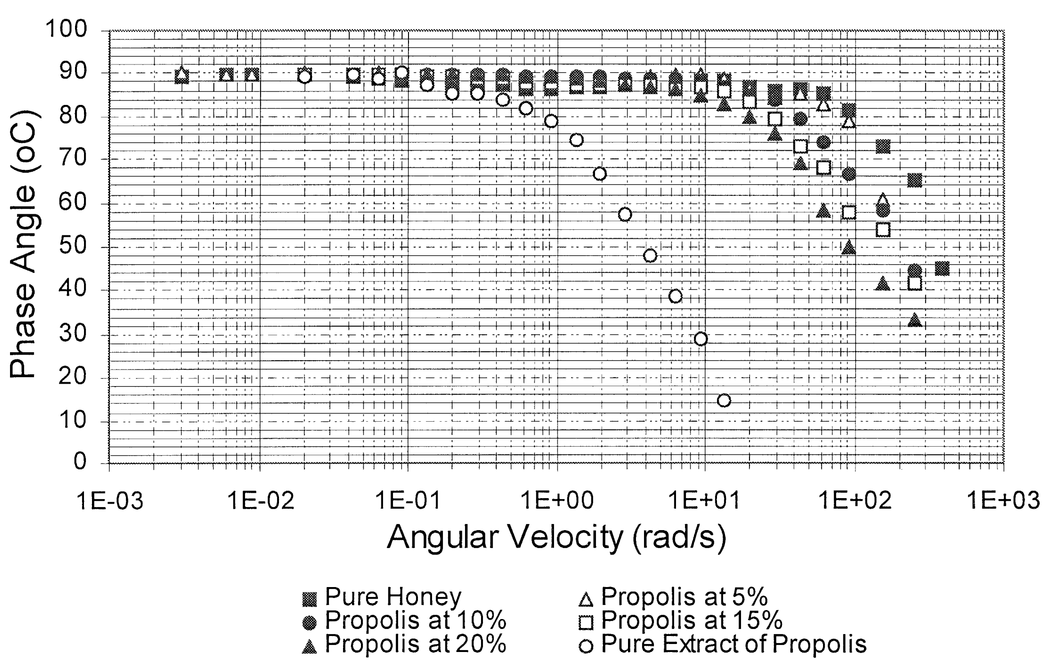

Fig. 3. Frequency sweep tests: performed with a stress of 1 Pa and temperature of 25 °C.

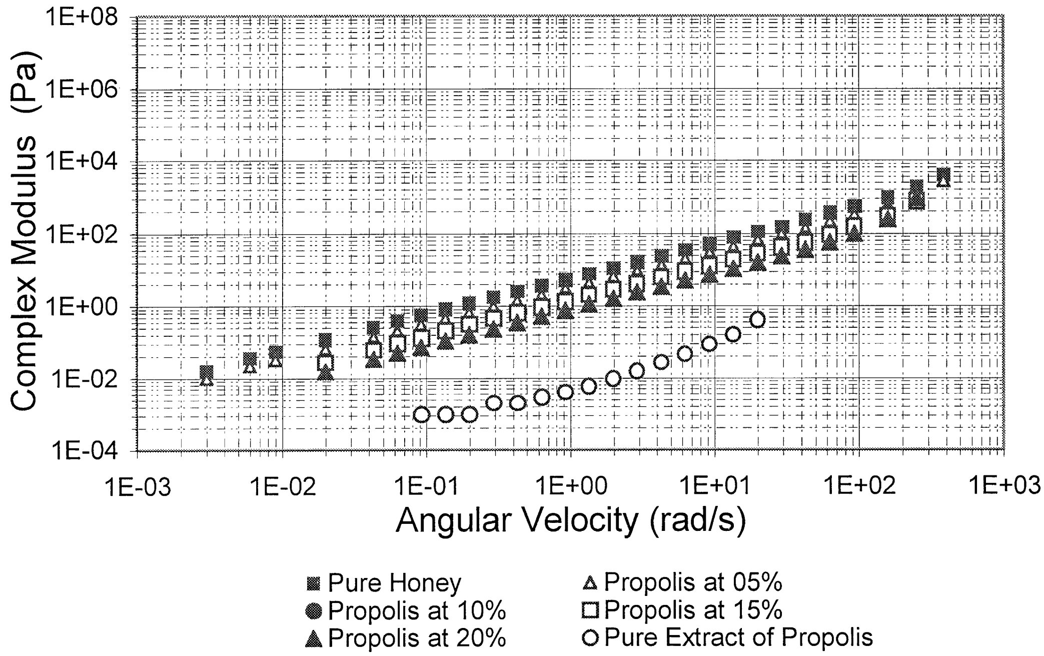

Fig. 4. Frequency sweep tests: performed with a stress of 1 Pa and temperature of 25 °C.

that the sample has the behaviour of a Newtonian fluid. As angular velocity increases, the phase angle decreases ($\delta < 90°$), indicating viscoelastic behaviour. This decrease is more accentuated when the extract of propolis is added to honey. At 100% of extract of propolis, the sample shows a more pronounced viscoelastic behaviour.

Fig. 4 shows the behaviour of the complex modulus for several samples in a Frequency sweep test. G^* increases as the angular velocity increases, indicating a more pronounced viscoelastic behaviour of the sample.

The frequency sweep test can determine the behaviour of the product for several velocities (frequencies), identifying the predominance of viscous or elastic effects able to influence the final product.

4. Conclusions

The rheological characterization of honey and propolis mixtures is very important for determining the quality of the product. From the viscosity, it is possible to determine the quantity of extract of propolis contained in a mixture of pure honey and extract of propolis. Furthermore, the addition of extract of propolis to the pure honey increases the viscoelastic behaviour of the sample. The moisture rises in the samples as extract of propolis is added. This fact embodies two points (1) the raw propolis has 8% of moisture, and (2) the ethyl alcohol, added in the extract of propolis, is very volatile, so a part of it is lost. This kind of analysis is very helpful for testing commercial products and in the development of new types.

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