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Thermophysical and optical characteristics of bee and plant waxes♣

K R. NIKOLOVA*, I. PANCHEV, D. KOVACHEVA[a], S. PASHOVA[b]
Department of Physics, University of Food Technologies, 4002 Plovdiv, 26 Maritza Blvd., Bulgaria
[a]*Institute of General and Inorganic Chemistry, Bulgarian academy of Sciences, 1113, Sofia, Bulgaria*
[b]*Department of Commodity Science, University of Economics, 9002 Varna, Kniaz Boris I blvd. 77, Bulgaria*

Sunflower and beeswaxes, as well as waxes obtained from *Prunus cerasifera* and *Prunus domestica* are considered. Data on the chemical composition and physical characteristics of the waxes were obtained by Differential Scanning Calorimetry (DSC), infrared spectroscopy (IR spectroscopy) and X-ray structural analysis. DSC allows one to determine the melting and crystallization points, as well as the enthalpy for each of the separate processes, while IR spectroscopy and X-ray structural analysis gave information on the structure and the degree of crystallinity of each of the wax materials. DSC findings showed that *Prunus domestica* and beeswaxes had the highest enthalpy when heated, viz. 205.76 J/g and 206.94 J/g, respectively, while sunflower wax showed the lowest enthalpy (24.14 J/g). Using X-ray diffraction analysis, it was found that beeswax had the highest degree of crystallinity, while the amorphous structure was predominant in the soft plant waxes. The prevailing component in the hard waxes was M-paraffin, while in the soft waxes it was glycerol fluorate. The experimental results obtained can be used in determining the purity of waxes, in view of their use in the surface coatings of food products.

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Keywords: Bee and plant waxes, Differential scanning calorimetry, IR spectroscopy, X- ray structural analysis

1. Introduction

Waxes are being used in the development of new products in various fields such as cosmetics, pharmaceuticals, engineering and industry [1]. They are used as adhesives, as painting media, sealing components, and in cosmetics. Recently, they have been applied as ingredients of the protective coating over food [2].

Beeswax consists of hydrocarbons, alcohols, free acids, and esters [3], plus concentrated highly-molecular butyric acids and alcohols like the cetyle, ceryle, carnaubic ones and others [4].

The aim of the present work is the thermo-physical and optical characteristics of the beewax and the sunflower plant waxes, as well as the ones extracted from *Prunus cerasifera* and *Prunus domestica,* by the means of IR spectroscopy, Differential Scanning Calorimetry (DSC) and X- ray analysis.

2. Materials and methods

2.1. Samples

The present work studies some beeswax, bought by the trade network, some sunflower wax, extracted as a waste product after the industrial production of the sunflower oil and plant waxes, extracted by the cuticle of *Prunus cerasifera* and *Prunus domestica*, following the Morzova and Salukova method. [5]

This method consists of the separation of the cuticle from the pellicle (in an acetate buffer with a pH of 4, at temperature of 37^0C in a thermostat), washing and drying of the cuticle, extraction of the wax into Soxhlet apparatus with petroleum ether and diethyl ether, separation of the hardened from melted wax, hydrolysis of the cutin complex by the means of a methanol solution with potassium hydroxide, extraction of the cutin using diethyl ether, and drying of the separate waxes and cutin until permanent aggregation is reached.

2.2 Analytical methods

The optical and thermo-physical characteristics, obtained by the means of the Differential Scanning Calorimetry, X-ray structural analysis and IR-spectroscopy, are being studied in the materials indicated above. The data received are necessary for the use of the waxes as components of protective coatings. DSC allows the determination of the melting point and thermal characterization point of the waxes, while IR spectroscopy can provide molecular structural information on them.

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The thermal properties of the present waxes were examined by the DSC method. A model DSC SETARAM 141 instrument was used. The test was made in the standard way:

- Heating from room temperature to 130 $^\circ C$, with a heating rate of 5^0C/min.
- Holding for 3 min at 130 $^\circ C$.
- Cooling to –30 $^\circ C$, with a cooling rate of 5^0C/min.
- Isotherm al treatment for 3 min at –30 $^\circ C$.
- Heating to room temperature, with a heating rate of 5^0C/min.
- 9.8 mg of each of the waxes was used.

X- Ray powder diffraction spectra were collected at room temperature on a Bruker D8 Advance instrument with CuKα radiation and a SolX detector within the 2θ range from 10 to 80^o, with a constant step 0.04^o 2θ at counting time 1 sec./step. Data evaluation was made with the use of a Software package EVA.

3. Results and discussion

Fig. 1 presents the peaks of the thermograms obtained from *Prunus domestica* soft wax during heating and cooling at 5^0C/min each. A typical parameter is the onset temperature, which indicates the start of the melting or hardening processes. It is defined as the intersection of the tangent of the first leg of the main peak with the base line [6].

The results for the onset temperatures, the temperatures of the peak maxima and the enthalpies obtained from six investigated waxes are shown in Table 1 from the heating program, and in Table 2 from the cooling program.

Hard wax from *Prunus Domestica* has avalue of the enthalpy upon heating (205.2 J/g) that is close to that of the beeswax (206.9 J/g). The sunflower wax and the other studied plant waxes have their lowest values of enthalpy upon heating and highest values upon cooling. According to their thermo-physical parameters (the onset temperature, the temperature at the peak maximum and the enthalpy), the hard waxes from *Prunus cerasifera* and *Prunus domestica* studied by us can be used as components of the protective coating of fruit and vegetables. Such a conclusion cannot be drawn, however, for the soft waxes, extracted by the cuticle of the same plants, because the onset temperature for the soft wax heating from *Prunus cerasifera* is 36.91 $^\circ C$. This is lower than 40 $^\circ C$, which is a prerequisite condition for the use of wax as a protective coating. According to the scientific data [7], paraffin wax has a similar melting temperature $(t = 39.5^\circ C)$. Such waxes have low molecular weights and usually contain C numbers as low as C16, which contribute to the low melting point [8].

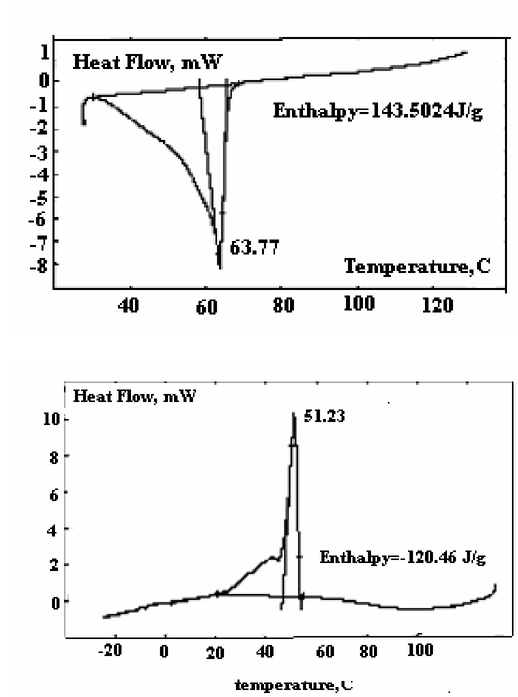

Fig. 1. Thermograms of Prunus domestica soft wax: (a) from the heating program, (b) from the cooling program

According to [9], DSC can be used for the evaluation of the purity of the waxes studied. If in the thermogram more than two peak points are distinguished clearly at the endothermic or exothermic processes, then there are other admixtures in the wax. This is the reason why not only the thermograms in Fig. 1 are presented, but also the thermograms from *Prunus cerasifera* hard wax in Fig.2. This (see Fig. 2) has two peak points for the exothermic process, clearly separated from each other.

Table 1 Thermophysical characteristics for six waxes, from the heating program

Type of wax	Onset tempe-rature $^\circ C$	Maximum tempera-ture $^\circ C$	Enthalpy, J/g
Beeswax	64.62	69.72	206.9
Sunflower wax	-23.33; 56.17	-12.39; 67.56	24.1
Prunus cerasifera hard	53.17	67.66	221.1
Prunus cerasifera soft	36.91	57.34	45.2
Prunus domestica-hard	59.44	69.33	205.2
Prunus domestica-soft	58.27	63.77	143.5

The same effect can be seen for the exothermic and endothermic processes of the sunflower wax (see table 1 and table 2). The previous fact proves the presence of other components in the substances studied. The data in tables 1 and 2 show that the other waxes studied do not appear to have such admixtures in their contents. The beeswax melts at $64.4^\circ C$, and this melting point is a constant one for the ripening of the wax [9]. The value derived by us ($64.6^\circ C$) is very close to this, which is evidence for the experiment precision.

Table 2 Thermophysical characteristics for six waxes, from the cooling program

Type of wax	Onset tempe-rature $^\circ C$	Maxi-mum tempe-rature $^\circ C$	Enthalpy, J/g
Beeswax	63,48	51,59; 61,53	-159,2
Sunflower wax	-10,96; 64,53	-16,53; 62,38	-2,3 -23,1
Prunus cerasifera-hard	60,10	44,74; 56,51	-200,4
Prunus cerasifera soft	48,11	42,77	-42,7
Prunus domestica hard	57,41	53,66;	-196
Prunus domestica-soft	53,57	51,23	-120,5

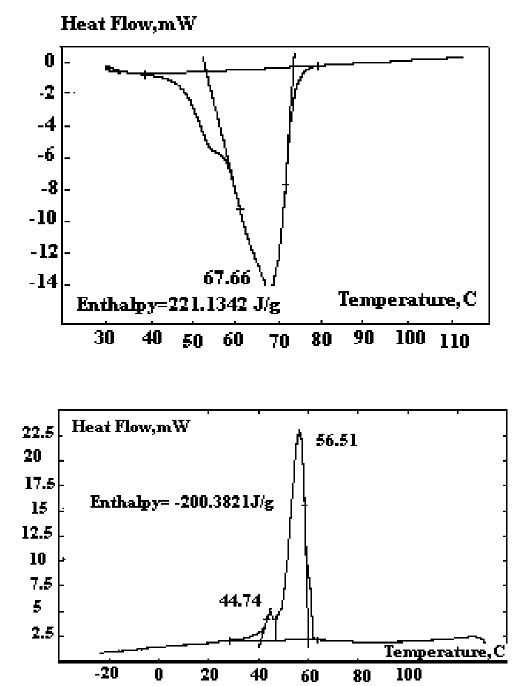

Fig. 2. Thermograms of Prunus cerasifera hard wax: (a) from the heating program, (b) from the cooling program

By the means of IR spectroscopy, it is possible to examine the difference between the mineral waxes and those containing lipids and butyric acids. The waxes studied by us belong to the second type, and their spectra seem much more complicated compared to those of the mineral waxes. From the frequencies of the absorption, it is possible to determine whether various functional groups are present or absent [10]. In Fig. 3, the IR spectra of the hard and soft waxes from *Prunus cerasifera* and *Prunus domestica* are presented, compared to those for beeswax. Except for the C-H groups, examined at about 1470 cm^{-1}, all other studied waxes reach a clear peak point at about 720 cm^{-1}, corresponding to $-CH_2$ groups. The basic difference between the waxes and minerals presented by us is the presence of a peak point at about (1700- 1740) cm^{-1}, which corresponds to a carbonyl $C=O$ stretching vibration from free carboxylic acid and from esters. In the soft wax from *Prunus cerasifera*, the presence of the $-CH_3$ group at about 1460 cm^{-1} can be seen. In the spectra, there can even be seen peak points at about 1200 cm^{-1}, 2920 cm^{-1} and 3400 cm^{-1}. The identification of which these will be done in a following study, by means of gas chromatography.

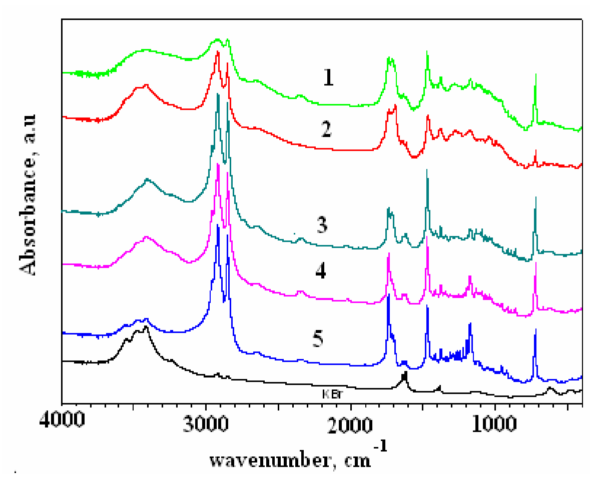

Fig. 3 Infra-Red spectra of the plant waxes and beeswax: 1- soft wax of Prunus domestica; 2- soft wax of Prunus cerasifera; 3- 1-hard wax of Prunus cerasifera; 4- hard wax of Prunus domestica; 5- beeswax

From a study of the waxes identified above, by means of the X-ray structure analysis, it was ascertained that the dominating component in the hard waxes is glycerol flourate. The obtained X-ray photographs are presented in Fig. 4.

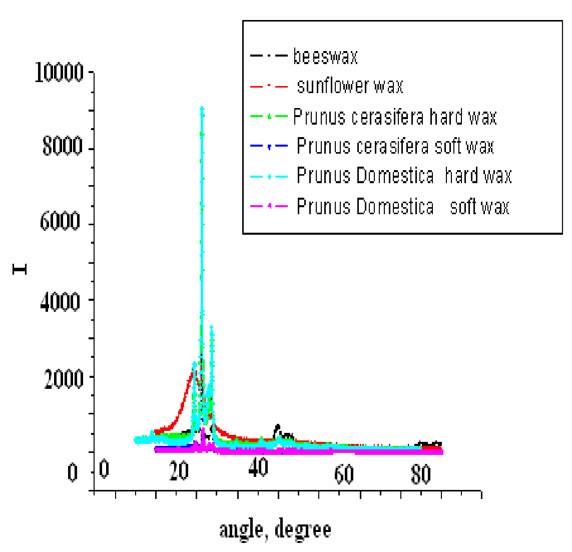

Fig. 4. Results from X-ray structural analysis

4. Conclusions

From our results, we can draw the following conclusions:

1. All plant waxes and beeswaxes can be used as components of protective coatings, excluding the soft wax from *Prunus cerasifera,* whose temperature of melting is 36.91^0C i.e. it is lower than 40^0C.

2. Beeswax had the highest degree of crystallinity, while the amorphous structure was predominant in the soft plant waxes. The prevailing component in the hard waxes was M-paraffin, while in the soft waxes it was glycerol fluorate.

3. Unlike the mineral waxes, containing C-H and -CH_2 groups, we determined the presence of a peak point at about (1700- 1740) cm^{-1}, which corresponds to a carbonyl $C=O$ stretching vibration from free carboxylic acid and from esters.

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References

[1] Ns. Al-Waili, Complementary Therapies in Medicine **11**, 226 (2003).
[2] V. Thirupath, S. Sasikala, Z. Kennedy, Science Technology Entrepreneur **8**, 605 (2006).
[3] N. Garnier, C. Gren-Olive, C. Ronaldo, M. Regert, Analytical Chemistry **74**, 4868 (2002).
[4] B. Tyutyunnikov, Chemistry of Fats, Food Industry, Moscow (1974).
[5] N. Morzova, E. Salkova, Defining Plant Waxes, Publishing House, Moscow (1975).
[6] G. Widmann, R. Riesen, Thermoanalyse, Huethig Verlag, Heidelberg (1984).
[7] J. S. Mills, R. White, The Organic Chemistry of Museum Objects, Butterworth (1987).
[8] I. Masschelein-Kleiner, Ancient Binding Media, Varnishes and Adhesives, Rome (1995).
[9] U. Knuutinen, A. Norrman, 15th WCNDT, Roma, (2000).
[10] H. Dudley, I. Fleming, Spectroscopic Methods in Organic Chemistry, Clarendon Press, London (1989).

*Corresponding author: kr.nikolova@abv.bg