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# Physical characteristics of wax-containing pectin aqueous solutions♣

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The rheological and optical characteristics of pectin aqueous solutions containing plant and beeswax are considered. The results obtained can be used in the production of pectin- and wax-based emulsion coatings to prolong the shelf-life of food products. The applicability of the models of Oswald-de Waele, Casson, Herschel-Buckley, and Newton to describe the rheological behaviour of pectin emulsion solutions is examined. A spectroturbodimetric method is proposed to assess the stability of the solutions.

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*Keywords*: Bee and plant waxes, Rheology, Refractive index, Spectroturbodimetric method

## 1. Introduction

The use of edible films as an alternative to synthetic packing is based on the film forming property of polysaccharides and proteins. The main disadvantage of similar edible films is the hydrophilic capacity of their macromolecules, which renders them inefficient as a barrier film against water and water vapours. In order to increase the water impermeability of edible films, butyric acids, waxes and other hydrophobic components are employed.

Pectin is an ionic polysaccharide from higher plants, consisting mainly of D-galacturonic acid, and neutral sugars, such as L-arabinose, L-rhamuose and D-galactose. They are organized in chain-like combinations, wherein the D- galacturonic acid residues are covalently $\alpha(1 \rightarrow 4)$ linked to form a linear backbone.

Natural waxes such as bees and plant waxes are generally recognized as safe and approved by the Food & Drug Admistration for use in fruit and vegetables coating, beverages, confections, gravies, bread and other food [1].

The main components of beeswaxes are palmilate, palmitoleate and hydroxypalmilate. Beeswax has a high melting point range of $(62 \div 64)^{\circ}C$. If it is heated above $85^0C$, discoloration occurs. The glass transition point of beeswax is $204.4^0C$. It contains a high proportion of wax esters $(35\% \div 80\%)$. These consist of $C_{40}$ to $C_{46}$ molecular species, based on 16:0 and 18:0 fatty acids, some with xydroxyl groups in the $\omega - 2$ and $\omega - 3$ positions. In addition, some esters with up to 64 carbons may be present, together with trimesters, hydroxypolyesters and free acids [2].

Plant surface waxes contain n-alkanes, alkyl esters, fatty acids, fatty alcohols, fatty aldehydes and organic substances. The amount of each lipid class, and the nature and proportions of the various molecular species within each class vary greatly according to the plant species and the site of wax deposition ( leaf, flower, fruit, etc.)[3].

This study is aimed at investigating some physical properties of emulsion pectin solutions containing beeswax or plant wax, which are used as a basis for producing edible films.

## 2.Materials and methods

### 2.1. Samples

Citrus pectin, with a degree of esterification of 65.2%, a molecular mass of 186 kD and a polyurodnine content of 78%, was used, obtained through classical extraction [4] in a water solution of 0.5 M HCl at a temperature of $85^0C$, hydromodule 1:20 and a period of time 45 minutes. The physical characteristics were determined in accordance with [5-6].

The beeswax was purchased from the market, the sunflower wax was obtained as a waste product from the manufacture of sunflower oil, and the plant waxes were obtained from *Prunus cerasifera* and *Prunus domestica*, by the method of Morzova and Salakova [7].

The emulsion solutions were prepared by adding the necessary quantity of melted wax to a 1% pectin aqueous solution, heated to $80^0C$. The mixture was homogenized through a Polytron, Kinematica CH-6010, Kriens-Lu, Switzerland, for 30 minutes.

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### 2.2 Analytical methods

The thermocalorific-physical characteristics of the waxes were determined through Differential Scanning Calorimetry (DSC). A model DSC SETARAM 141 was used.

The rheological characteristics of the emulsion pectin solutions were determined using a Rheoviscometer Rheotest-2, Germany. The refractive indices of the investigated solutions were determined by means of an Abbe refractometer (Carl Zeiss, Germany), The optic spectra in the visible range $400\text{nm} < \lambda < 720\text{nm}$ were recorded on a spectrophotometer, Lovibond PFX 880 (Tintometer Limited, UK)

The average size $\bar{r}$ and the number of diffracting particles $N$ per unit volume of the emulsion solutions were determined by the turbometric method of the opacity spectrum [8].

## 3. Results and discussion

The calorific-physical characteristics of the waxes, obtained through DSC, are presented in Table 1. The data are necessary because an important factor in preparing a wax in water emulsion is the temperature of emulsification. For instance, beeswax melts at $64.05\,^{\circ}\mathrm{C}$ (Table 1), therefore the emulsion temperature should be several degrees above the melting point and reduce the viscosity of the dispersed phase, and thus enable efficient passage through the homogenizeris value. The temperature of homogenization should be moderate, to avoid boiling of the continuous phase.

*Table 1 Thermophysical characteristics for six waxes, from heating and cooling programs.*

| Type of wax | Onset temperature for heating $^{\circ}\mathrm{C}$ | Onset temperature for cooling $^{\circ}\mathrm{C}$ | Average onset temperature, $^{\circ}\mathrm{C}$ |
|---|---|---|---|
| Beeswax | 64.62 | 63,48 | 64,05 |
| Sunflower wax | 56.17 | 64,53 | 60.35 |
| *Prunus cerasifera* hard wax | 53.17 | 60,10 | 56.64 |
| *Prunus cerasifera* soft wax | 36.91 | 48,11 | 42.51 |
| *Prunus domestica*-hard wax | 59.44 | 57,41 | 58.43 |
| *Prunus domestica*-soft wax | 58.27 | 53,57 | 55.92 |

The experimental data for the investigated pectin solutions, containing different types of waxes, as obtained by means of a Rheoviscometer Rheotest-2 at a $1.5 \le \gamma \le 1312\,\mathrm{s}^{-1}$ shear rate were subjected to regression analysis, in order to check the applicability of the rheological models of Newton $\tau = \eta\gamma$, the power law model for non- Newton flow behaviour of Oswald-de Waele $\tau = K\gamma^{n}$, the generalized power law model of Herschel-Buckley $\tau = \tau_y + K''\gamma^{n}$, and the Casson model $\tau^{1/2} = \tilde{\tau}_y^{1/2} + +K'\gamma^{1/2}$, where $\tau$ is the shear stress and $\gamma$ the shear rate.

Tables 2, 3, 4 present the numerical values for the rheological parameters of $K, n, \tau_y, K'', \tilde{\tau}_y, K'$ from the models of Oswald-de Waele, Herschel- Buckley and Casson, whereas the model of Newton having exhibited the lowest factor of the correlative dependence $R^2$ and the dependence on the tangential stress $\tau = f(\gamma)$ was eliminated. This fact confirms the conclusion of other researchers, that pectin solutions exhibit a non-Newton flow behaviour [4]. The parameter of $K$ in the equation of Oswald-de Waele is the consistency factor and n is the flow behaviour index, varying from 0.1 to 1.0. The dimensions of K are $\mathrm{Pa.s}^{n}$. When n increases, K decreases and vice versa. This is proven by our results, as well as the fact that as the temperature increases, K and n decrease in all investigated solutions, with the exception of the solution containing sunflower wax. The magnitude of the yield stress will determine the thickness of the coating on a vertical surface. This behaviour of pectin solutions is substantiated better by the factor of the correlative dependence $R^2$ in the model of Herschel-Buckley. The lowest values for $\tau_y$ were obtained when beeswax was added, and the highest ones when sunflower wax was added.

*Table 2. Parameters for Oswald-de Waele, Herschel-Buckley and Casson models at* $t = 20^{0}\,\mathrm{C}$

| Type of wax | Beeswax | *Prunus domestica-* hard wax | *Prunus cerasifera* hard wax | Sunflower wax |
|---|---|---|---|---|
| K | 0.831 | 0.905 | 0.786 | 2.806 |
| n | 0.724 | 0.700 | 0.723 | 0.475 |
| $R^2$ | 0.990 | 0.982 | 0.980 | 0.965 |
| $K''$ | 0.281 | 0.182 | 0.161 | 0.383 |
| $\tau_y$ | 8.235 | 10.426 | 10.579 | 11.936 |
| n | 0.872 | 0.92 | 0.941 | 0.744 |
| $R^2$ | 0.999 | 0.998 | 0.997 | 0.989 |
| $k'$ | 0.286 | 0.269 | 0.275 | 0.179 |
| $\tilde{\tau}_y$ | 4.297 | 4.792 | 4.382 | 9.704 |
| $R^2$ | 0.998 | 0.997 | 0.995 | 0.991 |

*Table 3 Parameters for Oswald- de Waele, Herschel-Buckley and Casson models at* $t = 30^0\,C$

| Type of wax | Beeswax | *Prunus domestic-ca-* hard wax | *Prunus cerasi-fera* hard wax | Sunflower wax |
|---|---|---|---|---|
| K | 0.751 | 0.738 | 0.624 | 0.751 |
| n | 0.697 | 0.691 | 0.714 | 0.697 |
| $R^2$ | 0.984 | 0.981 | 0.974 | 0.984 |
| $K''$ | 0.177 | 0.169 | 0.095 | 0.177 |
| $\tau_y$ | 8.057 | 7.684 | 8.957 | 8.057 |
| n | 0.894 | 0.892 | 0.972 | 0.894 |
| $R^2$ | 0.999 | 0.995 | 0.997 | 0.998 |
| $k'$ | 0.242 | 0.234 | 0.235 | 0.242 |
| $\tilde{\tau}_y$ | 3.979 | 3.851 | 3.53 | 3.9792 |
| $R^2$ | 0.997 | 0.995 | 0.992 | 0.997 |

*Table 4 Parameters for the Oswald-de Waele, Herschel-Buckley and Casson models at* $t = 40^0\,C$

| Type of wax | Beeswax | *Prunus domestca* hard wax | *Prunus cerasi-fera* hard wax | Sunflo-wer wax |
|---|---|---|---|---|
| K | 0.654 | 0.685 | 0.717 | 0.599 |
| n | 0.684 | 0.665 | 0.664 | 0.697 |
| $R^2$ | 0.981 | 0.978 | 0.997 | 0.981 |
| $K''$ | 0.158 | 0.145 | 0.143 | 0.155 |
| $\tau_y$ | 6.331 | 6.451 | 6.986 | 6.441 |
| n | 0.878 | 0.877 | 0.884 | 0.881 |
| $R^2$ | 0.993 | 0.993 | 0.997 | 0.993 |
| $k'$ | 0.214 | 0.202 | 0.205 | 0.214 |
| $\tilde{\tau}_y$ | 3.348 | 3.481 | 3.701 | 3.350 |
| $R^2$ | 0.994 | 0.993 | 0.996 | 0.994 |

Temperature dependences of $\tau_y, K', K''$ for all investigated solutions are present. The temperature influence on the dynamic viscosity is expressed by the Arrhenius equation $\eta = \eta_\infty \exp\left(\frac{E_a}{R.T}\right)$, in which $\eta_\infty$ is a parameter, $E_a$ is the flow activation energy, R is the gas constant and T is the absolute temperature. In Table 5, data on $E_a$ from regression analysis of the Arrhenius equation at a shear rate of $\gamma = 121.5\,s^{-1}$ are presented. The highest values for $E_a$ are for solutions containing hard plant waxes. These values are close to those obtained in [9] on the activation energy of pectin emulsions whose rheological behaviour is explained by the theory of Eyring, according to which the activation energy is the energy needed for a molecule to overcome the potential barrier in moving to a nearby "hole". The theory assumes a homogeneous liquid of identical non-deformable molecules of very small size compared to particles which we have in our solutions $(\bar{r} = 1\,\mu m)$.

Dolz et al. [9] also use the rheological method of Herschel-Buckley as the most adequate for pectin solutions.

*Table 5. Activation energy for the Arrhenius model at a share rate of* $\gamma = 121.5\,s^{-1}$

| Type of wax | Beeswax | *Prunus domesti-ca* hard wax | *Prunus cerasi-fera* hard wax | Sunflo-wer wax |
|---|---|---|---|---|
| $E_a$, kJ/mol | 16.039 | 17.031 | 17.277 | 15.261 |
| $R^2$ | 0.961 | 0.997 | 0.999 | 0.999 |

The stability of the emulsion solutions is an important characteristic determining their efficiency in obtaining edible films. The physical parameters, determining the tendency towards phase stratification, are the size and number of dispersion particles in the solution. To determine them, we used the spectroturbodimetric method of opacity [8].In Table 6, the presented data are the optical data on the increment of the refractive index $\frac{d\mu}{dC}$, the relative refractive index of the dispersion phase m, the wave exponent $n = \frac{\partial \lg D}{\partial \lg \lambda}$, obtained from the wave function of opacity $D = f(\lambda)$ by which the average size $\bar{r}$ and $N$ of the particles in 0.1% pectin solutions containing various waxes in accordance with formulae obtained from [8], are determined.

*Table 6 Data on the average number and size of the particles in a unit volume of 0.1% pectin solutions containing various waxes.*

| type | $\frac{d\mu}{dC}$ | $m = \mu/\mu_0$ | $n = \frac{\partial g\tau}{\partial g\lambda}$ | $\bar{r}$, μm | N, $cm^{-3}$ $\times 10^{-7}$ |
|---|---|---|---|---|---|
| bees wax | 0,15 | 1,11 | 0.622 | 1.04 | 2.28 |
| sunflower wax | 0,13 | 1,10 | 1.082 | 0.96 | 3.83 |
| *Prunus cerasifera-hard* | 0,14 | 1,11 | 0.506 | 1.06 | 3.95 |
| *Prunus domestica-hard* | 0,12 | 1,09 | 1.102 | 1.04 | 2.21 |

The presented data show that $\bar{r}$ is around $1\ \mu m$, and the number N in $1\ cm^{-3}$ is the lowest $\left(2.207.10^{7}\ cm^{-3}\right)$ in pectin solution containing *Prunus domestica (hard wax)* for which $\frac{d\mu}{dC}$ and m also have the lowest values. The lowest values of the wave exponent with beeswax and *Prunus cerasifera* hard wax can be related to the lower polydispersion of their particles, as compared to the other investigated systems. In the future work, we shall present data on the changes in $\bar{r}$ and N, caused by the aging of solutions and the influence of the added waxes on the rate of these changes.

## 4. Conclusions

1. All investigated waxes (with the exception of *Prunus domestica* soft wax), can be used to obtain edible films.

2.The investigated pectin aqueous solutions containing wax exhibit a behaviour of non-Newtonian liquids, which is best described by means of the model of Herschel-Buckley.

3.The activation flow energy at a shear rate of $\gamma = 121.5\ s^{-1}$ is in the interval $(15,3 < E_a < 17,3)$ kJ.mol$^{-1}$ for the different pectin solutions. $\left(2.2\times10^{7} < N < 3.9\times10^{7}\right)cm^{-3}$.

4. The average size $\bar{r}$ of the light-diffracting centres in the solutions is around $1\ \mu m$, and their average number N is in the interval of $\left(2.2\times10^{7} < N < 3.9\times10^{7}\right)cm^{-3}$

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