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OPTICAL CHARACTERISTICS OF BIOPOLYMER FILMS FROM PECTIN AND GELATIN

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Biopolymer films from pectin with different degree of esterification and gelatin have been investigated. Data the effect of film thickness upon the spectral and refractometric film characteristics with different weight contents have been obtained. A comparative analysis of pectin films with a gelatin film has been carried out. The refractometric data are made for liquid phases with 1, 0.5 and 0.25 % at 633 and 790 nm, using He-Ne and semiconductor lasers. On the base of the measured refractive index the Sellmeier's relation is obtained.

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1. Introduction

Recently, there is an increase of investigations on food coverings obtained from biopolymer solutions. Applied upon food raw materials or products the biopolymer films can be looked upon as a part of their own that can be assimilated during consumption. This fact together with some other advantages has an ecological impact, as well. The edible films protect the product from oxidation, decrease the moisture- and gas-diffusion, create an additional mechanical protection, colour protection and gloss. The matrix created from biopolymer macromolecules in the film allows to include additives having an antimicrobial and antioxidative effect. The actuality of the problem concerning food coverings improvement is constantly increasing, which imposes to perform investigations upon the optical and physical characteristics of films from polysaccharides and proteins [1].

The purpose of this study is to investigate the optical characteristics of biopolymer solutions and their films from apple and citric pectin and gelatin by measuring their refraction indices (RI) and their transmission spectra. A theoretical connection has been established between the single-oscillation models of Sellmeier [2] and Didomeniko and Wemple [3], that allows to count the specific oscillation energy E_0 and the dispersion energy E_d for each sample only by means of IR measurement for two wavelengths.

2. Experimental

The refractive index of water solutions of apple and citric pectin, respectively with concentrations of 0.25%, 0.5% and 1% have been investigated. The results for RI of the biopolymers studied have been compared with the measured RI of gelatin water solution having the same concentrations. For each of the biopolymers studied films upon glass bases have been applied. During water evaporation at an ambient temperature, homogeneous layers of apple and citric pectin and gelatin have been obtained, respectively with concentrations of 0.25% and 1%.

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The measurement of RI of water solutions of investigation biopolymers and their films has been done with the laser refractometer description in [4, 5]

Because there is a close phenomenological connection between the RI value, the theory of Maxwell and the atomic structure of substances, we consider that it is interesting to count optical constants like specific, molecular refraction and optical polarity for the liquid phase of apple and citric pectin and gelatin at two wavelengths. For this purpose we use the dependencies given in [2]:

$$r = \frac{n^2 - 1}{n^2 + 2}\frac{1}{\rho}, \tag{1}$$

$$R = r.M = \frac{n^2 - 1}{n^2 + 2}\frac{M}{\rho}, \tag{2}$$

$$R = 2{,}52.10^{24}\alpha_p \tag{3}$$

where n is RI at a given wavelength, r is specific refraction, M is the molecular weight of the solution, and ρ is its density.

The refractive index of the studied one-percent biopolymer solutions have been measured at t = 18°C for λ_1 = 633nm and λ_2 = 790nm. Their density has been determined picnometrically at the same temperature. For that purpose, the picnometer with the studied and the standard liquid should be placed in a metal housing whose temperature is kept constant by means of a thermostat. The molecular weight of the studied apple and citric pectin and gelatin has been determined by measuring the intrinsic viscosity [η] of the biopolymers studied in$0.15\,\mu\ NaC\ell$ at $t = 18^{\circ}C$, kept constant by means of a thermostat [6].

As it is known, IR and the absorption coefficient are connected by means of the Kramers-Kroning relation. That is why, our study on the optical characteristics of the edible films from apple and citric pectin and gelatin presents also the spectral dependencies of the optical transmission $\tau(\lambda)$. The measurements have been carried out on a spectrophotometer Carry 5E, following the methodology, presented in [7, 8]. The sample studied is a film of the biopolymer discussed applied upon a glass substrate. Our study shows transmission spectra of edible films only in the infrared region because in the visible region they are all transparent and are of no significance.

In our study we have established a relation between the single-oscillating models of Sellmeier (4) and those of Didomeniko and Wemple (5):

$$n^2 = 1 + \frac{s\lambda^2}{\lambda^2 - \lambda_s^2} \tag{4}$$

$$n^2 = 1 + \frac{E_d E_0}{E_0^2 - \hbar^2\omega^2} \tag{5}$$

where $\hbar\omega$ is the photon energy, E_0 is the specific oscillating energy and E_d is the dispersion energy. The parameter E_d is a measure of the strength of intraconnection optical transfers and does not depend on the type of connection or the volume density of valent electrons. If we transform the expression (5), taking into account the relations:

$$E_0 = \hbar\omega_1, \omega = \frac{2\pi c}{\lambda}, \omega_1 = \frac{2\pi c}{\lambda_1}, \hbar = \frac{h}{2\pi}$$

and after simple transformations (5) one gets (6).

$$n^2 = 1 + \frac{E_d \lambda_1}{hc} \frac{\lambda^2}{\lambda^2 - \lambda_1^2} \tag{6}$$

When we make a comparison between (6) and (4) it is evident that there is a simple connection between the Sellmeier`s parameters s and λ_s and the oscillation energies E_0 and E_d.

$$\left| \begin{array}{l} E_0 = \hbar\omega_1 = \hbar \frac{2\pi c}{\lambda_1} = \frac{h}{2\pi} \frac{2\pi c}{\lambda_1} = \frac{hc}{\lambda_1} \\ s = \frac{E_d \lambda_1}{hc} \Rightarrow E_d = \frac{shc}{\lambda_1} \\ \lambda_1 = \lambda_s \end{array} \right. \tag{7}$$

$$\left| \begin{array}{l} E_d = \frac{hcs}{\lambda_s} \\ E_0 = \frac{hc}{\lambda_s} \end{array} \right.$$

We have calculated Sellmeier`s coefficients *S* and λ_s in our study by measuring RI of biopolymer solutions of pectin and gelatin for two wavelengths. For each one of them with the parameters *S* and λ_s from (7) system the energy E_0 and E_d valued have been obtained.

3. Results and discussion

The results given in Table 1 have been obtained when measuring RI of biopolymer solutions from apple, citric pectin and gelatin for λ_1 = 633 nm and λ_2 = 790 nm and of their films for λ_1 = 633 nm after the method of disappearing diffraction picture.

Table 1. RI data of biopolymer solutions investigated and the films obtained from them.

Type	Liquid Phase $n_1, \lambda_1 = 633$ nm	Liquid Phase $n_2, \lambda_2 = 790$ nm	Solid Phase $n, \lambda_1 = 633$ nm
0.25% apple pectin	1.3304	1.3255	1.5061
0.5% apple pectin	1.3310	1.3262	----------
1% apple pectin	1.3316	1.3281	1.5076
0.25% citric pectin	1.3305	1.3266	1.5011
0.5% citric pectin	1.3309	1.3273	----------
1% citric pectin	1.3319	1.3278	1.5070
0.25% gelatin	1.3305	1.3255	1.5069
0.5% gelatin	1.3310	1.3262	----------
1% gelatin	1.3317	1.3273	1.5118

For each one of the investigated biopolymers solutions, the coefficients of Sellmeier have been calculated and through them from (7) system numerical values for the oscillating energies E_0 and E_d have been obtained. The data are given in Table 2. As far as the studied biopolymers are concerned a polynom has been obtained from the first degree $n = f(C\%)$ and its correlation coefficient R has been calculated. The analytical expressions of the dependencies obtained have been given in Table 3.

For all one-percent solutions of the biopolymers studied non-optical constants-densities, intrinsic viscosity $[\eta]$ and molecular weight M have been measured which are necessary for calculating optical values, like specific, molecular refraction, polarity etc. for two wavelengths λ_1 and λ_2. The results have been written in Tables 4, 5 and 6.

Table 2. Sellmeier coefficients values, dispersion and oscillating energies of biopolymer solutions studied.

Type	s	λ_s ,nm	E_0 , eV	E_d ,eV
0.25% apple pectin	0.735	135.51	12.64	9.29
0.5% apple pectin	0.737	134.06	12.78	9.42
1% apple pectin	0.748	114.86	14.92	11.15
0.25% citric pectin	0.742	121.26	14.13	10.48
0.5% citric pectin	0.745	116.56	14.70	10.95
1% citric pectin	0.744	124.03	13.82	10.28
0.25% gelatin	0.734	136.82	12.52	9.19
0.5% gelatin	0.737	134.06	12.78	9.42
1% gelatin	0.742	128.39	13.35	9.90

Table 3. Regression dependencies of $n = f(C\%)$ for the liquid phase of the biopolymers studied.

Type	Correlation coefficient R for the dependence of RI on the concentration $n = f(C\%)$
Apple Pectin	0.98
Citric Pectin	1
Gelatin	0.99

Table 4. Specific density of the solutions studied.

Type	$\rho, kg.m^{-3}$
1% apple pectin	1002.7492
1% citric pectin	1002.8790
1% gelatin	999.40386

Table 5. Intrinsic viscosity and mean value molar weight of the biopolymers studied.

Type	$[\eta]$, $dl.g^{-1}$	molecular weight, $\overline{M}$	
		Owens [9]	Bert [10]
apple pectin	3.60	61000	79000
citric pectin	2.12	41000	38000
gelatin	0.828	100000	

Table 6. Specific and molecular refractions and optical polarity of the solutions studied.

Type	$r_1, cm^3.g^{-1}$	$r_2, cm^3.g^{-1}$	R_1, cm^3	R_2, cm^3	α_1, cm^3 10^{-24}	α_2, cm^3 10^{-24}
1% apple pectin	0.2043	0.2024	3.715	3.679	1.474	1.460
1% citric pectin	0.2039	0.2022	3.718	3.676	1.475	1.459
1% gelatin	0.2050	0.2026	3.729	3.684	1.480	1.462

From the data in Table 1 it can be seen that the studied biopolymer solutions possess very near RI while RI of the films obtained from the same biopolymers are considerably different. This fact shows that when creating a film from the biopolymer studied, additional connections appear that are non-existing in the solution.

By means of the coefficients of Sellmeier found from Table 2, RI of the nine biopolymer solutions for the length of the yellow sodium line ($\lambda = 589.3nm$) have been calculated and have been compared with those measured by Abbe refractometer at the same wavelength, at $t = 18^{\circ}C$. The coincidence between the experimental and theoretically calculated data for RI is a good one – for the apple pectin it is a few units into the fourth sign, and for gelatin and citric pectin it is $1 \div 2 \times 10^{-3}$. This fact allows by using the dispersion parameters *S* and λ_s to calculate RI of each one of the biopolymers studied in the visible region of the spectrum and to draw the dispersion dependence $n(\lambda)$ graphics.

Fig. 1 presents transmission spectra of one-percent films from citric pectin and gelatin, taken by means of Carry 5E spectrophotometer.

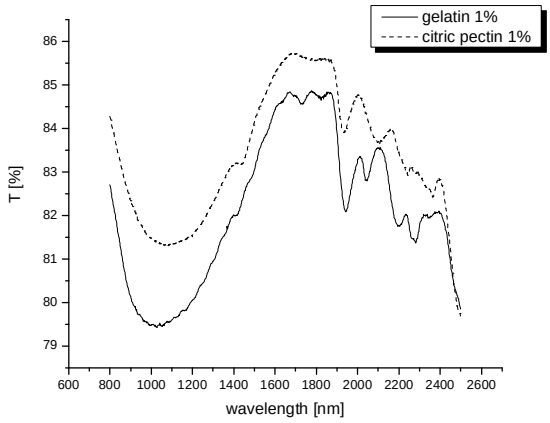

Fig. 1. Transmission spectra of 1% Gelatin and 1% Citric Pectin in the Infrared Region.

From Fig. 1 it can be seen that gelatin in the infrared region is less transparent than the citric pectin. Both biopolymers in the near infrared region have a clearly expressed absorption band, while in the region from 1600 to 1800 nm they are maximally transparent. From the transmission spectrum it can be seen that the citric pectin at 2100 nm possesses the maximum of absorption, and the gelatin – the maximum of transmission that is due to the different chemical groups contained in them.

Table 7. Comparative data for RI (calculated and measured).

Type	*n* calculated	*n* measured	Δn
0.25% apple pectin	1.3326	1.3331	5×10^{-4}
0.5% apple pectin	1.3331	1.3333	2×10^{-4}
1% apple pectin	1.3332	1.3338	6×10^{-4}
0.25% citric pectin	1.3322	1.3339	1.7×10^{-3}
0.5% citric pectin	1.3325	1.3341	1.7×10^{-3}
1% citric pectin	1.3337	1.3349	1.2×10^{-3}
0.25% gelatin	1.3329	1.3338	9×10^{-4}
0.5% gelatin	1.3331	1.3341	1×10^{-4}
1% gelatin	1.3336	1.3348	1.2×10^{-3}

4. Conclusions

Several conclusions can be drawn on the basis of the obtained experimental data:

1. The significant difference between RI of the studied biopolymer films as compared with their solutions witnesses for the creation of additional connections in the solid phase that are missing in the discussed material solution.

2. There is a significant difference between non-optical constants intrinsic viscosity and density of gelatin and both types of pectin. Gelatin has the smallest density and intrinsic viscosity, but have the greatest specific, molecular refraction and optical polarity. Gelatin solutions have a very close RI with those of apple pectin and almost equal to it RI increment.

3. From the transmission spectra $\tau(\lambda)$ it can be seen that citric pectin is more transparent in the infrared region than gelatin.

4. By determining the dispersion parameters of Sellmeier S and λ_s it is possible to determine RI for each wavelength from the visible region of the spectrum with a comparatively high accuracy. The determination of oscillating energy E_d value, only the sub-dispersion parameters S and λ_s allows for the quick investigation of edible films chemical properties.

5. From all conclusions made by now it follows that refractometric measurements allow some information to be obtained, concerning the structure of substances and analysis of the processes that flow at a micro-level. That is of great importance for improving physical parameters of the films that can be used as a packing material of foodstuffs.

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References

[1] J. J. Kester, O. R Fenna, Food Technology **47** (1986).
[2] B. Joffe, Refractometric Methods of Chemistry, Scientific and Technical Publishing House for Chemical Literature, Leningrad (1960).
[3] S. H. Wemple, M. Didomenico, Physical Review B **3**,1338 (1971).
[4] S. Sainov, N. Dushkina, Appl. Opt. **29**, 1406 (1990).
[5] S Sainov, Rev. Sci. Instrum. **62**, 3106 (1991).
[6] G. Moravetz, Macromolecules in a Solution, Publ.House Mir, Moscow (1967).
[7] I. Konstantinov, Tz. Babeva, S. Kitova, Appl. Opt. **37**, 4260-4267 (1998).
[8] Tz. Babeva, S. Kitova, I. Konstantinov, Appl. Opt. **40**, 2675-2681 (2001).
[9] U. S. Owens, R. M. McCready, A. D. Shepherd, A. I. C. Report, 340 (1952).
[10] G. Bert, H. Anger, D. Lexow, Die Nahrung **24**, 529 (1980).