Refractive characteristics of thin polymer films♣

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In this study, we have investigated five types of optical plastic thin films, deposited on glass substrates from solutions with different concentrations. The refractive indices of Polyarylate, Polycarbonate, Polyester, Copolyesters A and B, produced by Eastman Chemical Company, have been measured on the principle of critical angle determination by means of diffraction pattern disappearance. A He-Ne laser and two laser diodes, emitting at 632.8 nm, 532 nm and 790 nm respectively, were used as light sources, and refractive index data of the investigated polymer films at these wavelengths have been obtained. On the basis of the measurements, the dispersion coefficients of the Sellmeier`s and Cauchy`s approximations were calculated. Comparative dispersion curves of the examined materials are presented.

1. Introduction

The optical properties of polymer materials are of great importance in contemporary optical design. Thin polymer films appear in a wide spectrum of applications such as photonics, data storage, communications and sensor devices.

We have previously investigated several types of bulk plastic materials [1,2]. Refractive index data of the examined polymers at different wavelengths from 435 nm to 1052 nm have been obtained by means of the deviation angle method. Refractometric, ellipsometric and interferometric methods are typically used for determination of the refractive indices of thin solid materials. These methods require very high quality film preparation.

The purpose of this work is to study the refractive characteristics of thin polymer films. We apply a simple method, based on the critical angle measurement by means of the diffraction pattern disappearance, which has previously been used for measuring the refractive indices of thin organic films at two wavelengths [3,4]. In this report, a similar set-up of a three-wavelength laser microrefractometer is utilized, as in [5]. The refractive indices of various polymer samples with different film thicknesses are measured. The dispersion coefficients and

dispersion curves of the examined polymer materials are computed and compared.

2. Experimental

2.1 Sample preparation

Pellets of five plastic materials were dissolved as follows: Polycarbonate, Polyarylate and Polyester in chloroform and Copolyester A and Copolyester B in 1,1,2,2-Tetrachloroethane. Solutions with different concentrations were coated on glass substrates placed on a horizontal plane surface. A high refractive index TF4 glass [6] has been chosen as the substrate material for all polymers, except for the Polyester which was deposited on ordinary glass plates. The samples were dried at a temperature of 20 °C for 48 hours, and then were heated to 60 °C over 6 hours, to evaporate the rest of the solvent. The thin polymer films were preserved in a desiccator.

2.2 Instrumental

The transmission spectra of the examined thin polymer films were obtained using a UV-VIS-NIR Spectrophotometer Varian Carry 5E, in the spectral range 400 to 2500 nm. The film thicknesses were determined

with a digital micrometer produced by Mitutoyo Corporation, with a measurement accuracy of ± 1 μm.

The refractive indices of the thin polymer films were measured in the experimental set-up illustrated in Fig. 1. The examined sample, 7, was placed between the prism, 6, and the metal diffraction grating, 8. A He-Ne laser, 1, and two laser diodes, 2, 3, emitting at 632.8 nm, 532 nm and 790 nm respectively, were used as light sources. The three beams were collected by the two splitters, 4, to form a common beam illuminating the internal surface of the prism unit. At small angles of incidence, diffraction orders are observed in reflection on the screen, 9. When the angle of incidence reaches the critical angle of the material, the diffraction pattern disappears.
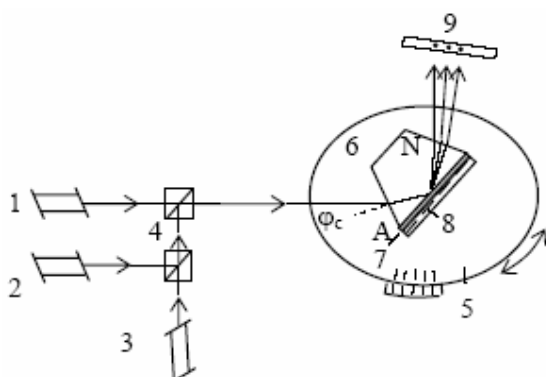

Fig. 1. Principle scheme of the experimental set-up:
1 – He-Ne laser; 2, 3 – laser diodes, 4 – beam splitters; 5 – goniometer; 6 – TF4 prism; 7 – thin polymer film; 8 – diffraction grating; 9 – screen.

As we carefully rotated the goniometric table, 5, the critical angle φ_c could be measured and the refractive index of the sample then could be calculated by the expression:

$$n = N \sin\left[A \pm \sin^{-1}\left(\frac{\sin \varphi_c}{N} \right) \right], \qquad (1)$$

where N and A are the refractive index and the vertex angle of the prism, respectively. We used a TF4 heavy glass prism with $A = 65°$ and values of $N_{532} = 1.7490$, $N_{632.8} = 1.7347$ and $N_{790} = 1.7230$, at the corresponding wavelengths that allowed us to measure samples with high refractive indices. The sign in the square brackets of Eq. (1) depends on the rotation direction.

A matching liquid should be applied to ensure the optical contact during the measurements. We used methylene iodide with a refractive index $n_{633} = 1.732$ for the high refractive polymers, and microscopic immersion oil with $n_d = 1.52$ for the Polyester. The measurements were carried out at a room temperature of 24 °C.

3. Results and discussion

The transmission spectra of the Polycarbonate (a) and Polyarylate (b) films with thicknesses of 35 and 140 μm respectively, are illustrated in Fig. 2. All obtained transmission spectra show that absorption bands of the examined materials are observed at wavelengths greater than 1500 nm. Therefore, the investigated thin polymer films are transparent in the considered spectral range from 500 to 800 nm, and their refractive properties can be analysed by the dispersion approximations, valid in the case of normal dispersion.
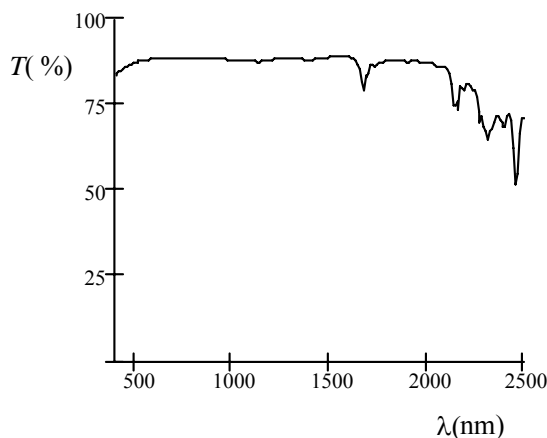
(a)
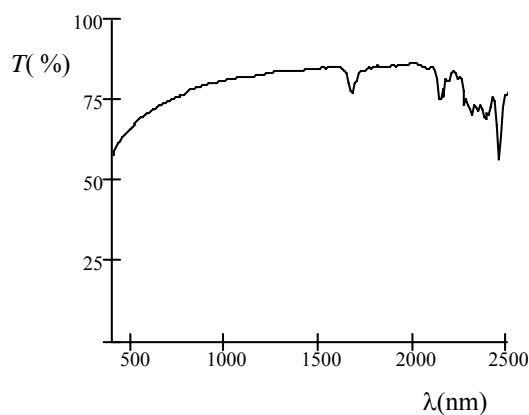
(b)

Fig. 2. Transmission spectra of: (a) Polycarbonate and (b) Polyarylate films.

The measured refractive indices of Polyester and Copolyester A films, at three wavelengths of 532, 632.8 and 790 nm, are presented in Table 1, where d is the film thickness. The estimated maximal standard deviation is ± 0.002. As we reported in [5] the measurement accuracy of the utilized three-wavelength laser microrefractometer is 2×10^{-4} for transparent liquids and solutions. In the case of these polymer films, the accuracy is less, mainly because of the additional noise introduced by multiple surface reflections. Some light scattering in the polymer medium also occurs.

The presented measurement results differ from the refractive index data obtained for bulk polymers [2]. They are usually of smaller value, as a consequence of the Lorentz–Lorenz relation. In addition, the deviation angle method determines the volume-average refractive index, while the critical angle method measures the local surface value of n [7].

Table 1. Refractive indices of thin polymer films measured with a three-wavelength laser microrefractometer.

Sample	d (μm)	Refractive index		
		532 (nm)	632.8 (nm)	790 (nm)
Polyester	10	1.508	1.500	1.492
	40	1.506	1.501	1.494
Copolyester A	3	1.538	1.525	1.510

On the basis of the measurements any value of the material refractive index can be calculated using the well known dispersion equations [8]. The Cauchy's and Sellmeier's formulae are typically used in the region of normal dispersion [9]. In [1], we have used the modified Cauchy's equation involving six dispersion coefficients which had been determined on the basis of our experimental results, obtained at a number of wavelengths. In the present investigation, we measured the refractive indices of the samples only at three wavelengths. Therefore, the two coefficients of the Sellmeier's and the three coefficients of the Cauchy's equations, respectively, can be calculated by the following expressions:

$$n^2(\lambda) = 1 + \frac{B\lambda^2}{\lambda^2 - C}, \qquad (2)$$

$$n^2(\lambda) = A_1 + A_2\lambda^2 + \frac{A_3}{\lambda^2}, \qquad (3)$$

where n is the refractive index at light wavelength λ (in micrometers), B and C are the Sellmeier constants related to the oscillator strength and the resonance wavelength, A_1, A_2 and A_3 are the Cauchy's coefficients depending on the material. The values of B and C in Eq. (2) and A_1, A_2, A_3 in Eq. (3) are calculated and presented in Table 2 and Table 3, respectively.

Table 2. Sellmeier's dispersion coefficients of thin polymer films.

Sample	d (μm)	Dispersion coefficients according to Eq. (2)	
		B	C
Polyester	10	1.191	0.019
	40	1.208	0.014
Copolyester A	3	1.220	0.031

Table 3. Cauchy's dispersion coefficients of thin polymer films.

Sample	d (μm)	Dispersion coefficients according to Eq. (3)		
		A_1	A_2	A_3
Polyester	10	2.200	-0.014	0.022
	40	2.246	-0.046	0.010
Copolyester A	3	2.283	-0.082	0.030

The calculated dispersion coefficients can be used to draw the dispersion curves of the materials in the examined spectral range from 500 to 800 nm. A plot of the refractive index of the 10 μm thick film of Polyester versus a wavelength obtained from the data in Table 2 and Table 3 is illustrated in Fig. 3. As can be seen, the dispersion curves coincide well within the range 550 to 770 nm. There is a slight deviation of the two curves at both ends of the spectral region. The dispersion coefficients obtained by the Cauchy's equation depend more strongly on the measurement accuracy. The Sellmeier's formula corresponds better to the dispersion properties of the materials, in the region of transparence.

There were some difficulties in the observation of the diffraction pattern at 790 nm for some of the samples, because of the reduced eye sensitivity at this wavelength and the intense light scattering of the polymer films as typical haze media. Because of this, the refractive indices of the rest of the polymer films were obtained at wavelengths of 532 and 632.8 nm. The measurement results for three Polyarylate films, two films of Copolyester B and one Polycarbonate film are presented in Table 4. The obtained refractive index data in this case are closer to our previous results, especially for thicker samples. A tendency for a decrease in the refractive index with increasing polymer film thickness is observed. The dispersion coefficients of the polymer materials in Table 4 can be determined too. However, the refractive index data obtained at only two wavelengths are not sufficient to calculate the dispersion curve with a satisfactory accuracy in a wide spectral range.
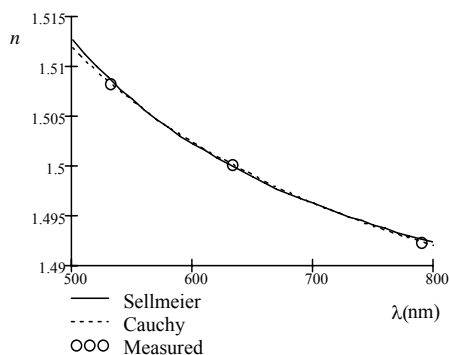
Fig. 3. Dispersion curves of the 10 μm thick Polyester film, according to Sellmeier and Cauchy.
Table 4. Refractive indices of thin polymer films measured at two wavelengths.

Sample	$d(\mu m)$	Refractive index	
		532(nm)	632.8(nm)
Polyarylate	15	1.656	1.642
	80	1.637	1.626
	140	1.616	1.603
Copolyester B	33	1.649	1.635
	42	1.595	1.562
Polycarbonate	35	1.599	1.595

4. Summary

The refractive indices of thin films, deposited from five types of polymer materials, have been measured in the region of their normal dispersion. A three-wavelength laser microrefractometer was utilized, which gave local values of the refractive index. The results for the Polyester and Copolyester A films were obtained at wavelengths of 532, 632.8 and 790 nm. The Sellmeier's and Cauchy's dispersion coefficients were determined, and the dispersion curves were computed and compared in the spectral region 500 to 800 nm. The thin films of the Polyarylate, Copolyester B and Polycarbonate were measured at the first two wavelengths mentioned above.

Further measurements of the refractive indices of thin polymer films with varying thickness and concentration could establish a correlation between their refractive properties and film parameters.

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