Investigation of optical properties of thin polymer films

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Abstract. Several types of optical polymer materials produced by Eastman Chemical Company were studied. Thin films deposited on glass substrates from solutions were prepared and studied to reveal their refractometric, dispersive and transmission properties in the visible and infrared spectral regions. The refractive indices were measured by means of two modifications of a laser microrefractometer.

1. Introduction
Plastic materials are commonly used in the design and fabrication of optical elements and devices. They have several key advantages over optical glasses, including low cost and weight, high impact resistance and ability to integrate proper mechanical and optical parameters [1]. Polymer optical elements and systems appear in a wide spectrum of industrial, medical, scientific, military and consumer applications. Investigation of thin polymer films (TPFs) is also of great interest for production of optical sensors, displays, fibers and waveguides, etc. [2, 3]. However, the refractometric and dispersive properties of the films differ in comparison with bulk plastics, as established in our previous reports [4, 5]. These differences depend on the material studied, as well as on the film parameters.

In this paper, we report studies on the optical properties of several types of optical polymer materials produced by Eastman Chemical Company. TPFs were deposited on glass substrates from solutions. A laser microrefractometer (LMR), based on critical angle determination, was assembled to measure refractive indices at three wavelengths [6]. A modification of this LMR, as proposed in [7], was also assembled to obtain experimental data at four different laser wavelengths. In both cases, the measurements were conducted based on the principle of diffraction pattern disappearance. The refractometric and dispersive characteristics of the polymer materials were measured for various film thicknesses and types of plastic material. A comparison with the properties of bulk plastic samples is also provided.

2. Experimental
2.1. Sample preparation
Pellets of polyester, polyarylate, polyacrylate and cellulose were dissolved in chloroform, while two

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types of copolyesters were dissolved in 1,1,2,2-tetrachloroethane. Solutions of the first four materials were prepared with concentration of 10 wt%, while the concentration of the copolyesters' solutions was 1 wt%. TPFs with different thickness $d$ were obtained by casting a certain amount of the solution on a glass substrate. All of the plastics studied, except for the cellulose layers, were deposited on a heavy TF4 glass plate. A TK2I glass was used for the low refractive cellulose material. The samples were dried at a temperature of 20 °C for 48 hours and then heated up to 60 °C during 6 hours to evaporate the remaining solvent. The TPFs prepared were preserved in a desiccator. A digital micrometer (Mitutoyo Corporation) was used for measuring $d$ with an accuracy of ± 1 μm.

2.2. Transmission spectra

The transmittance of the TPFs was measured in the spectral range from 400 to 2500 nm using a Varian Carry 5E UV-VIS-NIR spectrophotometer. The materials studied transmit well in the visible (VIS) and near-infrared (NIR) regions of the spectrum (figure 1). Transmission spectra of polyarylate films with varying thickness $d$ are presented in figure 1-a. For $d = 20$ μm, transmittance exceeding 80% is observed up to 2260 nm. The thicker layers exhibit greater absorption, especially in the VIS range. The polyester film (figure 1-b) shows transmission of about 90% in the VIS and NIR regions up to 1700 nm. In both cases, the spectra presented show weak absorption bands between 1660 and 1700 nm due to the first overtone of the C–H group. A considerable transmission decrease is observed at wavelengths greater than 2200 nm where absorption by other C–H groups occurs.

![Figure 1](image.png)

**Figure 1.** Transmission spectra of: a) polyarylate films with different thicknesses; b) 20 μm thick polyester film.

2.3. Measuring the refractive indices of optical polymer films

Two modifications of a LMR, based on the same measuring principle, were used (figure 2). The experimental schemes in both cases differ in the illumination part. As shown in figure 2-a, a He-Ne laser, 1, and two laser diodes, 2, 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, 3, to form a common beam. In the case of the four-wavelength scheme of the LMR (figure 2-b), illumination is achieved by means of laser diodes, 4, with a power supply, 5, emitting at 406, 656, 910 and 1320 nm. The diodes are placed at four fixed positions and switching between the separate laser sources is realized mechanically. Each laser beam is carefully adjusted in the vertical and horizontal plane to ensure passing of the beam through the two diaphragms, 6, which are separated at a distance of 250 mm and have an equal diameter of 2 mm.

The laser beam in both cases illuminates the internal surface of the prism unit, 7, which is made of heavy flint optical glass TF4 (figure 2-c). Unit 7 is mounted on a rotary goniometric stage, 8, with resolution of 1 arcmin. The sample examined, 9, is placed between the prism and a chromium diffraction grating, 10, with a 40-μm period. The optical contact between the sample measured, the
prism and the grating is realized using methylene iodide. At angles less than the critical angle $\varphi_c$ of the sample film, the incident laser beam passes through the polymer layer and diffracts at the metal grating. The reflected diffraction pattern is observed on a screen, 11.

When the angle of incidence reaches the critical angle of the material, the diffraction orders disappear. An infrared beam-finder card, model IRC32R (Electrophysics), with peak emission at 655 nm and spectral range 800 to 1700 nm, was used to visualize the diffraction image in infrared light. The refractive index of the sample is calculated by the expression:

$$n = N \sin \left[ A \pm \arcsin \left( \frac{\sin \varphi_c}{N} \right) \right].$$  \hspace{1cm} (1)

The prism's vertex angle is $A = 64.76^\circ$, while $N$ is its refractive index at the illumination wavelength $\lambda$, which is calculated by fitting the $N(\lambda)$ data published in Lomo Glass Catalogue [8]. The uncertainty of the measurement results was estimated in [6] and a maximal deviation of $2\times10^{-4}$ was obtained for polymer solutions. In case of polymer films, the accuracy established is $2\times10^{-3}$ [5].

3. Results and discussion

The transmission spectra and the refractive indices measured of the TPFs examined reveal normal dispersion of the materials in the spectral region considered. We used the Cauchy-Schott's and Sellmeier's approximations [4, 5] to calculate the dispersion coefficients, curves and Abbe numbers.

The refractive indices measured of some of the examined films, as well as the calculated dispersion curves, are presented in figure 3. The polymer materials in figure 3-a are measured by means of the four-wavelength LMR, while figures 3-b,-c,-d present results obtained by the three-wavelength LMR.

Dispersion curves of different types of TPFs studied are illustrated in figure 3-a. It is obvious that the dispersion is greater in the VIS spectral region and smaller in the NIR light. The Abbe numbers $v_d$ for mean dispersion and $v_{1010}$ for partial dispersion are calculated by the expressions:

$$v_d = \frac{n_d - 1}{n_F - n_C} \quad \text{and} \quad v_{1010} = \frac{n_{1010} - 1}{n_{700} - n_{1320}},$$  \hspace{1cm} (2)

where $n_d$, $n_F$ and $n_C$ are the calculated indices at spectral lines 587.6, 486.1 and 656.3 nm. The partial dispersion in the NIR is estimated by the values obtained of the refractive indices $n_{700}$, $n_{1010}$, $n_{1320}$. Our results show that the polyester and polyacrylate films exhibit higher Abbe numbers in comparison with the cellulose samples and, therefore, possess lower dispersion. In case of the three-wavelength LMR results, the Abbe numbers $v_{633}$ of the films investigated were calculated in a similar manner using the refractive indices measured $n_{633}$, $n_{532}$, $n_{700}$.

Figures 3-b,-c,-d present the dispersion curves of selected polymer materials, namely polyarylate,
polyacrylate and copolyester B. The film thickness in microns, as well as the corresponding Abbe number $n_{633}$, are quoted in each chart. In the case of the polyarylate films (figure 3-b), the refractive indices values and the Abbe numbers decrease as the film thickness is increased, which could be explained by the increase in the polymer packing near the film surface due to surface tension forces. We established a similar dependence for the copolyester B and cellulose films.

We observed an opposite dependence for the polyacrylate and copolyester A films. The refractive indices and Abbe numbers of the polyacrylate samples decrease for smaller film thickness, while their dispersion grows (figure 3-c). These results show that the dispersion properties of the TPFs depend on the type of the material and its structure. The local refractive index measured is influenced by the film quality and uniformity and is related to the solution viscosity and film adhesion to the glass substrate.

A comparison between the refractive and dispersive properties of a TPF and the bulk material is illustrated in figure 3-d on the example of the copolyester B plastic. In this case, the film has significantly higher refractive indices compared to the bulk sample. However, the slopes of the dispersion curves and the Abbe numbers are similar. An opposite tendency was observed for the polyacrylate film and bulk material. We should note, however, that an average volume refractive index is measured in the case of bulk optical samples, while for the TPFs a local surface value is obtained. The latter depends on the film thickness at the place of laser beam incidence, as well as on the film properties.

**Conclusions**

The TPFs refractometric and transmission data measured reveal their normal dispersion in the spectral range from 400 nm to 1065 nm. Cauchy-Schott’s and Sellmeier’s approximations were used to calculate the dispersion coefficients, curves and Abbe numbers. All TPFs studied have greater dispersion in the visible spectrum and lower one in NIR. The refractive and dispersive properties
depend on the type of the material and on the film thickness. The results are also influenced by the polymer packing near the surface and by the quality and uniformity of the film, these being related to the solution viscosity and film adhesion to the glass substrate. The refractive and dispersive characteristics of the TPFs differ in comparison to the respective bulk polymer samples, where the average bulk refractive index is measured. In the case of TPFs, local values are obtained, which depend on the type of the material and the film properties.

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