Optical plastic refractive measurements in the visible and the near-infrared regions

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Some new refractometric results are obtained in the visible and the near-infrared spectral regions. The main optical plastics are analyzed: poly(methyl methacrylate), polystyrene, polycarbonate, and styrene acrylonitrile. New materials, such as methyl methacrylate styrene copolmer, CTE-Richardson, Zeonex, Optorez, and Bayer are examined. The refractive indices are measured for wavelengths from 435.8 to 1052 nm with a new device. Abbe constants and dispersion coefficients are calculated. The measured and computed data is intended for designers and technologists. © 2000 Optical Society of America

OCIS codes: 160.0160, 220.0220, 120.3930, 160.5470, 220.4830, 160.2750.

1. Introduction

The index of refraction of transparent organic materials can be determined as described in Ref. 1. The refractometric methods are shown in Ref. 2. The principal optical plastics (OP's) characterized in this paper are poly(methyl methacrylate) (PMMA), polystyrene (PS), polycarbonate (PC), methyl methacrylate styrene copolymer, styrene acrylonitrile (SAN), and methylpentene. The optical properties of plastics are quite good for different design configurations.[3] The most important spectral areas for optical systems are the visible (VIS) and the near-infrared (NIR) regions.[4] Using new optical materials, one can improve the performance and balance the production costs.[5–9] Success in the application of OP's depends on knowledge of their optical transmission, refraction, homogeneity, and birefringence. The measurement principles and procedures for OP's properties determination are quite different. The well-known test instrument is the Abbe refractometer.[1] The value of the index of refraction for the sodium *D*-line can be read directly from the instrument. The Abbe refractometer is convenient for measurement of small OP specimens, with an accuracy of ±0.01. The Zeiss Pulfrich-Refractometer (PR 2) works only in the VIS region.[2] The indices of refraction can be measured with the aid of a V-type SF3 glass prism on the PR 2 instrument. The Vo F5 refractometric prism requires OP samples having two polished optical surfaces. The second surface of the specimen must be perpendicular to the basic contact surface. A saturated aqueous solution of zinc chloride for PMMA and a solution of potassium-mercuric-iodide for PS and PC are recommended in Ref. 1. Some useful data for the optical designers collected from the OP material manufacturers is presented in Ref. 10. Many lenses are patented with OP components.[11–15] The main OP's such as PMMA, PS, PC, and SAN are included into the Zemax Glass Catalog.[16]

In this paper some new refractometric results are discussed. Indices of refraction and dispersion coefficients of ten optical materials are examined. A more effective device for optical plastic measurements in the VIS and the NIR regions is realized. The obtained data is used for NIR optical system design.

2. Refractometric Calculations

The main problem of OP's design and production is the small number of optical materials available.[3,5–9] The optical properties of plastics are not so well studied in comparison with those of glasses.[9,10] The OP's refractive index n_λ can be calculated with one of the well-known dispersive formulas for a given wavelength λ.[5] Cauchy's equation is correct for the range of wavelengths from 365.0 to 1013.9 nm. It can be expressed as

$$n_\lambda{}^2 = A_1 + A_2\lambda^2 + A_3/\lambda^2 + A_4/\lambda^4 + A_5/\lambda^6 + A_6/\lambda^8, \quad (1)$$

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Received 18 August 1999; revised manuscript received 13 December 1999.

0003-6935/00/132067-04$15.00/0

Table 1. Optical Plastic Refractive Indices Computed for Numerous Selected Laser Wavelengths

Plastic	Wavelengths										
	442	488	514.5	543	568.2	594	632.8	647.1	694.3	890	1060
PMMA	1.4995	1.4956	1.4945	1.4932	1.4919	1.4906	1.4888	1.4881	1.4864	1.4833	1.4812
PS	1.6135	1.6037	1.5995	1.5957	1.5928	1.5901	1.5867	1.5855	1.5824	1.5752	1.5717
PC	1.6083	1.5976	1.5929	1.5888	1.5856	1.5830	1.5796	1.5784	1.5754	1.5679	1.5644
SAN	1.5849	1.5765	1.5731	1.5700	1.5674	1.5651	1.5621	1.5610	1.5583	1.5524	1.5495
CTE	1.6014	1.5938	1.5894	1.5857	1.5832	1.5809	1.5775	1.5763	1.5728	1.5651	1.5621
NAS	1.5924	1.5837	1.5797	1.5758	1.5735	1.5715	1.5693	1.5678	1.5654	1.5575	1.5549
S	1.5281	1.5229	1.5210	1.5191	1.5175	1.5157	1.5136	1.5128	1.5107	1.5063	1.5039
Optorez	1.5190	1.5147	1.5133	1.5118	1.5104	1.5089	1.5069	1.5961	1.5042	1.5004	1.4983
Zeonex	1.5402	1.5260	1.5348	1.5334	1.5320	1.5305	1.5285	1.5278	1.5259	1.5224	1.5203
Bayer	1.6134	1.6013	1.5981	1.5951	1.5903	1.5858	1.5823	1.5814	1.5784	1.5685	1.5662

where A_1, A_2, A_3, A_4, A_5, and A_6 are the calculated dispersion coefficients. Sellmeier's formula better describes the dispersion curve in the entire wavelength range from the UV through the VIS to the IR area.[4] For anomalous dispersion, it can be presented as

$$n_\lambda^2 - 1 = B_1\lambda^2/(\lambda^2 - C_1) + B_2\lambda^2/(\lambda^2 - C_2) + B_3\lambda^2/(\lambda^2 - C_3), \quad (2)$$

where B_1, B_2, B_3, and C_1, C_2, C_3 are the new dispersion coefficients. Ohara Optical Glass and Hoya Glass Works apply the Laurent and Sellmeier 2 formulas for the same range of wavelengths from 365.0 to 2325.4 nm.[13,15] Sometimes Eq. (1) is called the Kettler or the Schott formula. Dr. Max Herzberger offered an experimental formula for the VIS spectral region.[5] It is accurate for water and IR optical materials such as NaCl and ZnS. Equations (1) and (2) are applied for the design of optical systems with program libraries.[8,11,15,16] It is possible to measure six OP indices from $n_{\lambda 1}$ to $n_{\lambda 6}$ for standard wavelengths such as $\lambda_1 = 546.07$, $\lambda_2 = 587.56$, $\lambda_3 = 656.27$, $\lambda_4 = 706.52$, $\lambda_5 = 852.11$, and $\lambda_6 = 1013.98$ nm. A program was created that computes the dispersion coefficients from A_1 to A_6 with a set of six equations of type (1).[11] The main plastics such as PMMA, PS, PC, and SAN are determined with n_D/V_D of 1.491/61.4, 1.590/31.1, 1.586/34.5, and 1.569/37.8, respectively, for the sodium D-line 589.29 nm.[10] The calculated refractive indices for some selected laser wavelengths are presented in Table 1.

3. Index Measurements

The PR 2 instrument operates with three spectral lamps: a mercury source with a green e-line (546.07 nm) and a blue g-line (435.83 nm), a helium source for a yellow d-line (587.56 nm) and a red r-line (706.52 nm), and a hydrogen source for a blue F-line (486.13 nm) and a red C-line (656.27 nm).[2] The PR 2 standard measuring prism requires a thick cubic specimen with satisfactorily polished surfaces to observe the sharpness of the dividing line between the light and the dark field as seen in the eyepiece of the instrument. One needs to have rather large OP samples to be able to make a measurement on the PR 2 device. The end of the OP's specimen must be processed with a fair polish to obtain total internal reflection from the PR 2 prism. The OP samples have coefficients of thermal expansion approximately ten times higher than that of glass.[3,9] The ordinary PR 2 prism is not convenient for OP index measurements with an accuracy up to ± 0.001. To avoid the difficulties, we had to apply the Vo F5 prism having a refractive index of 1.740102 for the d-line. The Vo F5 prism we used provides good reproducibility during measurement with the PR 2 instrument, and it is very convenient for operations with a precision goniometer of 1 arc sec. Silicon oil was found with a refractive index of 1.5601 for the D-line. It is applicable as a contacting liquid for OP measurements. The K-Hg-J solution has an index of refraction of 1.7301 for the e-line, and it is used for high-refractive-index OP samples.

The experimental results are from a precision G5 (LOMO, Russia) goniometer of 1 arc sec with the Vo F5 prism as shown in Fig. 1. The OP plates are injection molded with a thickness from 2.54 to 5.1 mm. The OP sample is positioned in the Vo F5 prism and covered. The measuring prism is made as a glass block assembled into a massive metal body with a thermometer housing. The prism cap is made of stainless steel and has a mirrored internal surface so that it decreases the OP sample temperature fluctuations. Care must be taken to ensure that the matching liquid does not evaporate. The collimated beam falls perpendicularly to the entrance surface of the Vo F5 prism. Temperature regulation to 0.2 °C is achieved to ensure stability. The PR 2 refractometer has no ability to detect NIR spectral signals. A new photodetector device was assembled

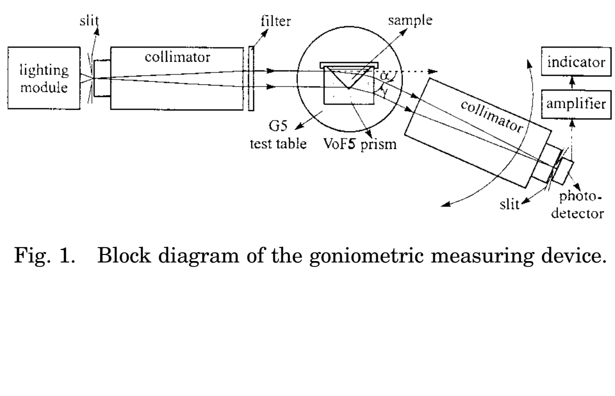

Fig. 1. Block diagram of the goniometric measuring device.

Table 2. Optical Plastic Refractive Indices Measured for Wavelengths in the VIS and the NIR Regions

Plastic	Wavelengths											
	r:436	r:486	r:546	r:588	e:633	r:656	g:703	g:752	g:804	g:833	g:879	g:1052
PMMA	1.503	1.497	1.493	1.491	1.489	1.489	1.486	1.485	1.484	1.484	1.483	1.481
PS	1.617	1.606	1.596	1.592	1.587	1.586	1.582	1.579	1.578	1.577	1.576	1.572
PC	1.612	1.599	1.590	1.585	1.580	1.579	1.575	1.572	1.570	1.570	1.568	1.565
SAN	1.588	1.578	1.571	1.567	1.562	1.562	1.558	1.556	1.554	1.554	1.553	1.550
CTE	1.602	1.593	1.584	1.580	1.575	1.575	1.571	1.569	1.567	1.566	1.565	1.562
NAS	1.593	1.584	1.575	1.571	1.567	1.567	1.564	1.561	1.559	1.558	1.557	1.554
S	1.531	1.525	1.519	1.516	1.514	1.514	1.512	1.510	1.509	1.509	1.508	1.506
Optorez	1.522	1.516	1.512	1.509	1.508	1.507	1.505	1.504	1.503	1.503	1.502	1.498
Zeonex	1.543	1.538	1.533	1.531	1.530	1.528	1.526	1.524	1.523	1.523	1.522	1.520
Bayer	1.612	1.600	1.591	1.586	1.580	1.580	1.577	1.574	1.572	1.571	1.570	1.566

r-PR 2 refractometric spectral wavelength; g - G5 goniometric filter wavelength; e - ellipsometric laser wavelength.

with the aid of a plane silicon diode, an operational amplifier, and an indicating module. The collimator forms a white-light beam to the fixed filter. The Vo F5 prism with the OP sample is positioned on the G5 test table. The prism block is illuminated monochromatically. A set of metal interference filters made by Zeiss is used. The filters were measured with the aid of a Varian Carry 5 VIS–NIR Spectrophotometer to confirm their wavelength. The spectral half-width of the filters is approximately 7 nm. The illuminator is a precise multimirror stabilized BAB lamp having a peak either at 732 (Q20MR16 USA 52 source) or at 812 nm (Q20MR16C USA 13), and uses Kodak Wratten Filters 88A or 87. The illuminator can also operate with a 250-W halogen lamp applied over the entire VIS and NIR regions with filters from 450 to 1052 nm. The measuring angle α is determined by the right-hand collimator with the attached photodetector.

The angle of deviation γ is measured on the G5 goniometer setup as shown in Fig. 1. It is formed by the OP sample located in the V-shaped prism. The OP's index of refraction n_λ is calculated as follows:

$$n_\lambda^{\,2} = N_\lambda^{\,2} - \cos\gamma(N_\lambda^{\,2} - \cos\gamma^2)^{1/2}, \qquad \gamma = 90° - \alpha, \quad (3)$$

where N_λ is the refractive index of the Vo F5 prism, γ is the calculated angle of the deviated beam, and α is the measured angle on the G5 setup. The index N_λ of the SF3 glass is determined from the tables published in Refs. 2 and 4 for standard spectral wavelengths. It is computed for the NIR region with our dispersion coefficients calculated on the basis of the Vo F5 prism data. The OP's indices are calculated with Eq. (3). The obtained indices are summarized in Table 2 for the selected filter set.

It is possible to compare the data shown in Tables 1 and 2. The error and accuracy could be evaluated, and the computed indices with the aid of Eq. (1) are usable. The determined indices for numerous laser wavelengths are close to some measured values. A comparison of the refractive indices and Abbe constants is listed in Table 3. It is obvious that the refractometric data shown in Table 3 is rather different. Some of our indices are quite close to the information in Refs. 9 and 16. Three to five samples are measured, and the final index is averaged for every selected OP material. The refractometric Vo F5 glass prism is measured with an error of 1×10^{-6}.[2] The refractive index of the SF3 glass is given by the manufacturer (Schott) with an accuracy of 1×10^{-3}

Table 3. Optical Plastic Refractometric Data for a Comparative Analysis: Index and Abbe Constant, n_λ, V_λ

Plastic:	Published Refractometric Data					Measured G 5 Data	
	Ref. 3(n_D/V_D)	Ref. 9(n_D/V_D)	Ref. 10(n_D/V_D)	Ref. 14(n_e/V_e)	Zemax (n_d/V_d)	(n_D/V_D)	(n_{804}/V_{804})
PMMA	1.491/57.0	1.492/57.8	1.491/61.4	1.4935/57.34	1.4917/55.31	1.491/59.2	1.484/108
PS	1.590/31.0	1.591/30.8	1.590/31.1	1.5950/30.70	1.5905/30.87	1.591/30.5	1.578/61.4
PC	1.580/30.0	1.586/29.9	1.586/34.5		1.5855/29.91	1.584/29.1	1.570/58.8
SAN		1.569/35.7	1.569/37.8		1.5674/34.81	1.566/35.4	1.554/74.9
CTE						1.579/32.0	1.567/64.4
NAS	1.562/35.0	1.533/42.4	1.533/35.0			1.570/33.3	1.559/55.3
S						1.516/44.9	1.508/102
Optorez						1.509/52.0	1.502/129
Zeonex						1.531/56.5	1.523/114
Bayer						1.584/30.8	1.572/54.5
TPX			1.467/51.9				
ADC		1.498/53.6	1.504/56.0				
COC			1.530/58.0				

for different wavelengths, independent of the individual melt.[4] The PR 2 instrument and the G5 goniometer setup assembled with the Vo F5 prism have been calibrated with a standard sodium spectral lamp and the Refractive Index Standard 7.17 made from Sovirel BCD C 23-57 Optical Glass (n_D = 1.62270 at 20 °C). The calibration instrumental error of the G5 setup is ±0.0005. The metrologic tests showed that the OP indices shown in Table 2 were measured with an accuracy of ±0.001.

4. Summary and Conclusions

Ten types of American, Japanese, and German OP materials were measured on the laser ellipsometer at a wavelength of 632.8 nm. The obtained indices of refraction were used for matching liquid determinations. It was found that the standard methods and devices cannot guarantee the required accuracy for the OP's refractometric measurements. With Cauchy's and Sellmeier's dispersive formulas [Eqs. (1) and (2)], a theoretical examination was made for OP's index computer modeling. An experimental verification was carried out by application of the PR 2 instrument and G5 goniometer in the VIS region from 404.7 to 706.5 nm. Our polarimetric investigations of the OP's materials indicated some significant internal stresses that affect the index. A new sensitive photodetector device that ensures correct localization of the measured spectral peaks was made. The OP's indices are obtained for some new materials, namely, NAS-21 Novacor, CTE-Richardson, Zeonex, Optorez, and Bayer. The new measured and computed refractometric data would be useful for optical designers and production technologists. The calculated dispersion coefficients were compared with the data from optical design programs for the principal OP's, namely, PMMA, PS, PC, and SAN. The Optorez and the S samples have close dispersion data, Zeonex and COC are equal, and Bayer is a PC-type plastic material (see Table 3).

The authors thank Lucy Wended and David Wended from Logic Int. for their advice and help in this research and development study and Agnessa Paneva from the University of Sofia for the ellipsometric measurements.

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