POLYMER MATERIALS FOR NIR AND LASER APPLICATIONS

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Abstract: *Polymer materials are nowadays used not only in the design of consumer but also of precise optical systems and devices. Because of molding technological process great economies are possible in the production of optical elements with complex geometric surfaces. Polymer materials exhibit also valuable optical as well as physical and mechanical properties.*

ПОЛИМЕРНИ МАТЕРИАЛИ ЗА ИЧ И ЛАЗЕРНИ ПРИЛОЖЕНИЯ

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Ключови думи: *Оптични полимери, показатели на пречупване, проектиране на оптични системи*

Резюме: *В съвременните оптични конструкции полимерните материали заемат важно място. Те се ползват не само в масовата оптика, но и за прецизни елементи със сложна геометрична форма с високо качество на образа. Причина за това са както ниската себестойност на полимерните изделия в резултат на високата производителност на технологиите, така и ценните оптични и физикомеханични свойства на полимерните материали.*

Introduction

In this report characterization of optical and some important material parameters of polymers in the design of imaging devices is accomplished. Principal polymer materials (PMs) as well as many trade-marks of optical plastics and some development materials are investigated. Different measuring techniques are applied to obtain precise refractometric data of bulk samples and thin polymer films (TPFs) in the visible and near-infrared spectrum up to 1320 nm [1-4]. Dispersive curves in the region of normal dispersion of PMs are presented in visible (VIS) and near-infrared (NIR) regions. Influence of temperature on refraction is considered. Refractive indices (RIs) of studied PMs have been calculated at twenty laser emission wavelengths from 405 nm to 1064 nm [3]. Examples of optical design of dispersive optimized all-plastic systems intended for laser (CD/DVD) and night vision instruments are presented. Some new applications of PMs in nano-photonic moduli, laser and NIR communication networks, medical technologies, etc. are indicated.

Optical memories on CDs are the mass polymer products made from polycarbonate (PC). Plastic read/write micro-lens heads can focus laser beams into spots from 400 nm up to 100 nm. Optical PMs are used from consumer products to optoelectronic stations intended for remote imaging diagnostics of Earth's surface reflectivity. Components made of PMs operate in the optical systems of video spectrometers and helmet displays. During last decades PMs are implanted into the organic optoelectronics and nano-technological structures [4, 5].

Refractometry of optical PMs secures the measuring accuracy for estimation of their dispersive characteristics [1-8]. Optical plastics are applied in the UV (280-380 nm), VIS (380-760 nm), IR-A (760-1400 nm), and IR-B (1400-2500 nm) spectral regions. The optimal sphero-chromatic correction of the HD digital camera objectives is limited by measured dispersive data of PMs. The production accuracy of the existing optical technology is from 1/10 to 1/20 of the wavelength, that is about 54-27 nm, during the precise lens surface micro- and nano-metrology [5-8].

Refractometry of optical polymers

Refractometry covers the analysis and measurements of the refractive and dispersive characteristics of different materials such as glasses, polymers, crystals, composites, solutions, transparent film structures, nano-layers, etc. [1-6]. Nano-photonics (NP) is defined as nanoscale optical science and technology [5]. NP field offers challenging opportunities for the research and development of novel nano-structural optical materials such as polymers and plastic composites [6]. Nano-metrology secures nanoscale measurements and nano-topographic inspection of the optical surfaces, integrated arrays and photonic devices [5, 8]. Polymer layers with metallic nano-clasters ranging from 1 nm up to 100 nm exhibit size-tunable electrical and optical properties that may be applied in the tomorrow's computer architectures. Some new applications of optical polymers in NIR and laser photonics devices are indicated.

We have studied optical properties of various types of plastics, including principal and some new development polymers. The principal OPs are polymethyl methacrylate (PMMA), polystyrene (PS), polycarbonate (PC), methyl methacrylate styrene copolymer (NAS), and styrene acrylonitrile (SAN). Different trade-marks of OPs as NAS-21 Novacor, CTE-Richardson, Zeonex, Optorez, Bayer, etc. and polymers produced by the American Eastman Chemical Company (ECC) are also examined.

Depending on the specifics of the application, PMs are used as bulk bodies or thin layers deposited over different substrates. Our refractometric measurements show different values of RIs in both cases for one and the same material [4]. We have used refractometric and goniometric methods to obtain extensive refractometric data of bulk samples in VIS and NIR spectral regions. In both cases the deviation angle method is used [8]. The classical Zeiss Pulfrich refractometer (PR2) with its V-type SF3 glass prism (VoF3) is used to measure RIs of bulk OPs at five emission wavelengths λ of the spectral lamps of the device in the VIS region, namely, at green e-line 546.07 nm and blue g-line 435.83 nm (mercury lamp), yellow d-line 587.56 nm (helium source), and blue F-line 486.13 nm and red C-line 656.27 nm (hydrogen lamp).

Additional goniometric set-up with the VoF3 prism, a white lighting module (a 250 W halogen lamp and a condenser system) with interference filters with spectral bandwidths of about 7-9 nm was assembled for measuring in the entire VIS and NIR regions up to 1060 nm (Fig. 1). A G5-LOMO goniometer with an accuracy of one arc second was used with the VoF3 unit, positioned on the G5 test table. The collimated beam falls perpendicularly to the entrance surface of the prism. The angle of deviation γ is formed by the sample located into the V-shaped block. The right-hand collimator with the attached photo detector determines the measuring angle α. The photo detector device is assembled with the aid of a plane silicon diode, operating amplifier and indicator. Polymer specimens were produced as injection moulded plates or cubes having two fairly well polished, mutually perpendicular surfaces. An immersion emulsion with a proper RI is required to ensure the optical contact during the measurements [2]. The thermostatic housing of the VoF3 prism allowed us to maintain temperature of 20 ºC with stability of 0.2 °C.

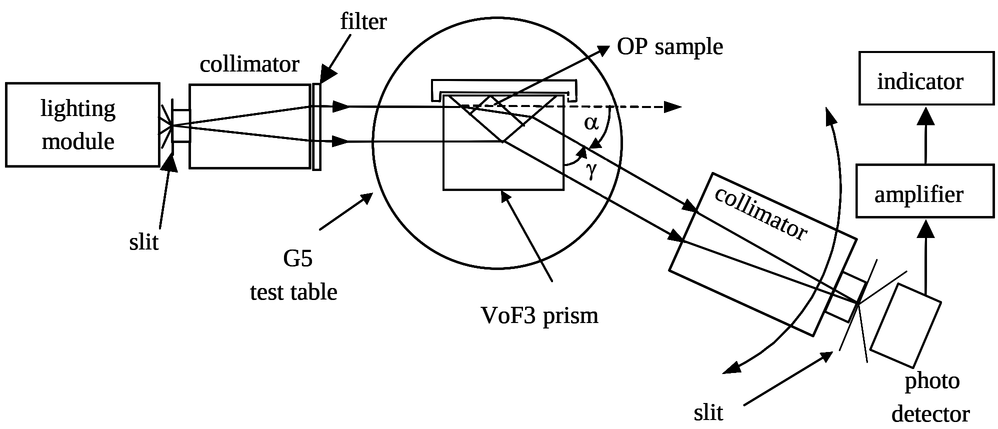


Fig. 1. Our goniometric setup for the VIS and NIR refractive measurements

In case of refractometric and goniometric measurements, the refractive index n_λ of the examined polymer is calculated as follows:

(1) $$n_\lambda^2 = N_\lambda^2 - \cos\gamma\left(N_\lambda^2 - \cos^2\gamma\right)^{1/2}, \quad \gamma = 90^{\circ} - \alpha ,$$

where N_λ is the RI of the VoF3 prism at the illumination wavelength. This is determined by means of a modified Caushy's dispersion formula (3) and catalogue data for the SF3 glass. Refractometric and goniometric results coincide within the limits of ± 1×10^{-3} for all studied PMs in the VIS region [2]. Measurements of RIs with a conventional 1 mW He-Ne laser and the goniometric set-up have been carried out [9].

Two modifications of a laser microrefractometer (LMR) were assembled to obtain RIs of TPFs. In both cases the measuring principle is based on the critical angle determination by means of the diffraction pattern disappearance [10]. Measured sample is placed between a prism made of a heavy flint glass and a chromium diffraction grating.The optical schemes of the two LMRs differ only in the illumination block [4]. Diode lasers emitting at 406, 532, 656, 790, 910 and 1320 nm, as well as a He-Ne laser (632.8 nm) have been used. It should be underlined that obtained results in case of TPFs yield surface values of RIs while refractometric and goniometric measurements present average index values of bulk polymer samples.

Analysis of RI metrology of all applied measuring techniques is accomplished in [11]. The instrumental error of the PR2 instrument is $\pm2\times10^{-5}$ but the maximal combined standard uncertainty is $\pm5.4\times10^{-5}$ because of the slight birefringence in the polymers. Laser measurements of bulk samples, carried out by means of the goniometric set-up, reveal maximal combined uncertainty of 3.65×10^{-4}. In case of microrefractometric measurements of TPFs, the accuracy is less, mainly because of the extra noise introduced by the multiple surface reflections in the film and the substrate. Some light scattering in the polymer medium also occurs. The standard deviation was estimated to be $\pm2\times10^{-3}$.

Results for bulk specimens are presented in Table 1 and for TPFs in Table 2. Wavelengths of the PR2 instrument are indicated as (r) while (g) represent the maxima of the interference filters of the goniometric set-up and (l) denotes laser goniometric measurements (Table 1). Obtained RIs decrease monotonically in the entire VIS and considered NIR region and indicate normal dispersion of PMs. Transmittances of the TPFs were measured in the spectral range from 400 to 2500 nm using a UV-VIS-NIR spectrophotometer Varian Carry 5E. Studied materials transmit well in the VIS and NIR regions of the spectrum [4]. Transmission spectra confirm also normal dispersion up to 1600 nm. There are some weak absorption bands between 1660 and 1700 nm which are due to the first overtone of the –CH group. Considerable transmission decrease is observed at wavelengths greater than 2200 nm where absorption of other C–H groups occurs.

Table 1. Measured RIs of bulk PMs and their Abbe numbers in VIS and NIR spectra

PM	Refractive index							Abbe numbers	
	435.8 nm, (r)	486.1 nm, (r)	587.6 nm, (r)	632.8 nm, (l)	703 nm, (g)	833 nm, (g)	1052 nm, (g)	ν_d	ν_{879}
PMMA	1.502	1.497	1.491	1.489	1.486	1.484	1.481	59.2	96.7
PS	1.617	1.606	1.592	1.587	1.582	1.577	1.572	29.1	56.4
PC	1.612	1.599	1.585	1.580	1.575	1.570	1.565	30.5	54.6
SAN	1.588	1.578	1.567	1.562	1.558	1.554	1.550	35.4	66.6
CTE Richardson®	1.602	1.593	1.580	1.576	1.571	1.566	1.562	32.8	62.8
NAS-21®	1.593	1.584	1.571	1.568	1.564	1.558	1.554	35.5	55.7
S (low styrene) ®	1.532	1.526	1.518	1.514	1.512	1.509	1.506	44.9	79.3
Optorez 1330®	1.522	1.516	1.509	1.507	1.505	1.503	1.498	52.0	71.7
Zeonex E48R®	1.543	1.538	1.531	1.528	1.526	1.523	1.520	56.5	100.5
Bayer®	1.612	1.600	1.586	1.581	1.577	1.571	1.566	30.0	54.3
Cellulose[a]	1.480	1.477	1.471	1.469	1.466	1.463	1.461	54.1	92.6
Polyacrylate[a]	1.507	1.500	1.494	1.492	1.491	1.489	1.486	63.3	97.6
Styrene[a]	1.534	1.527	1.519	1.516	1.513	1.510	1.507	42.9	84.8
Polycarbonate[a]	1.597	1.587	1.572	1.568	1.565	1.560	1.555	28.9	55.9
Polystyrene[a]	1.615	1.604	1.592	1.587	1.582	1.576	1.572	32.0	57.4
Acrylic[a]	1.502	1.498	1.492	1.490	1.488	1.485	1.483	57.8	97.0

[a]control samples of ECC polymers

On the base of the obtained results Abbe numbers are calculated and included in Tables 1 and 2. In VIS region ν_d is determined by measured RIs at the Fraunhofer spectral lines. Additional parameters ν_{879} and ν_{1010}, fitted to the respective NIR measuring spectral range for bulk PMs and TPFs, are provided. Abbe numbers are calculated as follows:

$$(2) \qquad \nu_d = \frac{n_d - 1}{n_F - n_C}; \quad \nu_{879} = \frac{n_{879} - 1}{n_{703} - n_{1052}}; \quad \nu_{1010} = \frac{n_{1010} - 1}{n_{700} - n_{1320}} .$$

Comparison among Abbe numbers of studied bulk PMs up to ν_d of about 35 (Table 1) indicate the most dispersive polymers in VIS spectrum. In NIR region all materials show lower dispersion. Acrylic polymers, Cellulose and Zeonex with their high ν_{879} are the most suitable plastics for night vision applications. They are even lower dispersive materials in NIR area than most optical glasses with similar refraction [8]. Results for TPFs show some differences compared to bulk samples for one and the same material and therefore polymer emulsions should be studied separately.

Table 2. Measured RIs of TPFs and their Abbe numbers in VIS and NIR spectra

PM	*d* [μm]	Refractive index						Abbe numbers	
		406 nm	532 nm	632.8 nm	656 nm	910 nm	1320 nm	ν_d	ν_{1010}
Polyester	40	1.513	1.502	1.496	1.495	1.489	1.486	53.8	62.6
Polyacrylate	6	1.501	1.490	1.485	1.484	1.478	1.476	55.2	72.4
Cellulose	9	1.493	1.473	1.467	1.466	1.460	1.457	40.9	61.2

We have applied a modified Caushy's formula involving six dispersion coefficients which assures calculation accuracy better than ± 0.0001 [3]:

$$(3) \qquad n_\lambda^2 = A_1 + A_2\lambda^2 + A_3/\lambda^2 + A_4/\lambda^4 + A_5/\lambda^6 + A_6/\lambda^8 .$$

The coefficients A_1,…, A_6 are determined with the aid of a system consisting of six linear equations [2] on the base of measured RIs. Dispersion coefficients, curves, random RIs and Abbe numbers are calculated by our program OptiColor based on approximation (3). Dispersion charts of some of the studied PMs are presented in Fig. 2. Flatness of curves in NIR spectrum illustrates the appropriate usage of polymers in night vision applications.

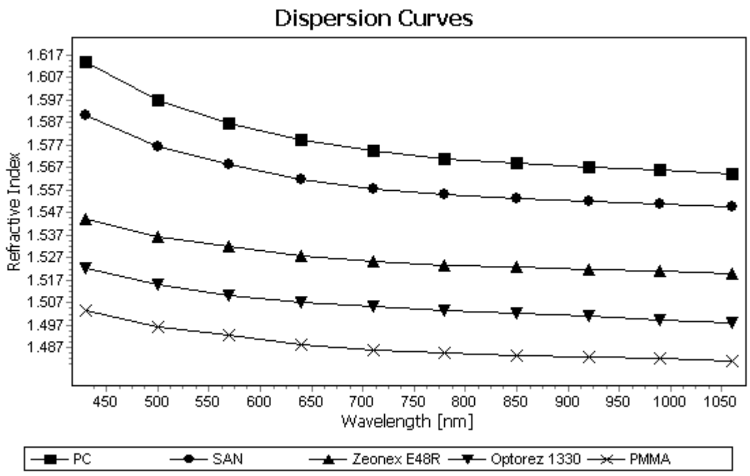


Fig. 2. Dispersion of some of studied PMs in the measuring spectral range

RIs of ten PMs at twenty laser emission wavelengths from 405 nm (GaN) to 1064 nm (Nd:YAG) are calculated by means of OptiColor program and results are presented in Table 3. The refractometric data could be useful in the design and production technology of laser optical systems. Using some new optical materials, it is possible to improve the performance and balance the production expenses.

Table 3. Refractive indices of PMs at laser emission wavelengths in the entire VIS and NIR spectra

Lasing medium	WLs (nm)	PMMA	PS	PC	CTE	SAN	NAS-21	S low styrene	Optorez 1330	Zeonex E48R	Bayer
Ga N	405	1.516	1.633	1.630	1.616	1.607	1.593	1.540	1.526	1.554	1.627
Krypton	416	1.509	1.626	1.621	1.609	1.598	1.595	1.536	1.525	1.549	1.621
N2+	428	1.504	1.620	1.615	1.605	1.591	1.594	1.533	1.523	1.545	1.615
HeCd	442	1.501	1.615	1.609	1.601	1.586	1.592	1.531	1.521	1.542	1.610
Argon	488	1.497	1.605	1.599	1.592	1.578	1.583	1.526	1.516	1.538	1.599
Argon	514.5	1.496	1.601	1.595	1.589	1.575	1.579	1.524	1.514	1.536	1.595
Nd: YAG	532	1.495	1.599	1.592	1.587	1.573	1.577	1.522	1.513	1.534	1.592
He-Ne	543.3	1.494	1.597	1.590	1.585	1.572	1.575	1.521	1.512	1.534	1.591
Krypton	568.2	1.492	1.594	1.587	1.582	1.569	1.573	1.519	1.511	1.532	1.588
Cu	578.2	1.492	1.593	1.586	1.581	1.568	1.572	1.518	1.510	1.531	1.587
He-Ne	593.9	1.491	1.591	1.584	1.580	1.566	1.571	1.517	1.509	1.531	1.585
He-Ne	632.8	1.489	1.587	1.580	1.576	1.562	1.568	1.515	1.508	1.528	1.581
Krypton	647.1	1.488	1.586	1.579	1.575	1.561	1.567	1.514	1.507	1.528	1.580
Krypton	676.4	1.487	1.584	1.577	1.573	1.559	1.566	1.513	1.506	1.527	1.578
Ruby	694.3	1.487	1.583	1.575	1.572	1.558	1.565	1.512	1.506	1.526	1.577
Krypton	752.5	1.485	1.580	1.572	1.569	1.556	1.562	1.511	1.504	1.524	1.574
GaAs	840	1.484	1.576	1.569	1.566	1.554	1.558	1.509	1.502	1.523	1.571
Nd: YAG	940	1.483	1.574	1.567	1.564	1.552	1.555	1.508	1.501	1.522	1.568
InGaAs	980	1.482	1.573	1.566	1.563	1.551	1.555	1.507	1.500	1.521	1.568
Nd: YAG	1064	1.481	1.572	1.564	1.561	1.549	1.554	1.506	1.498	1.520	1.566

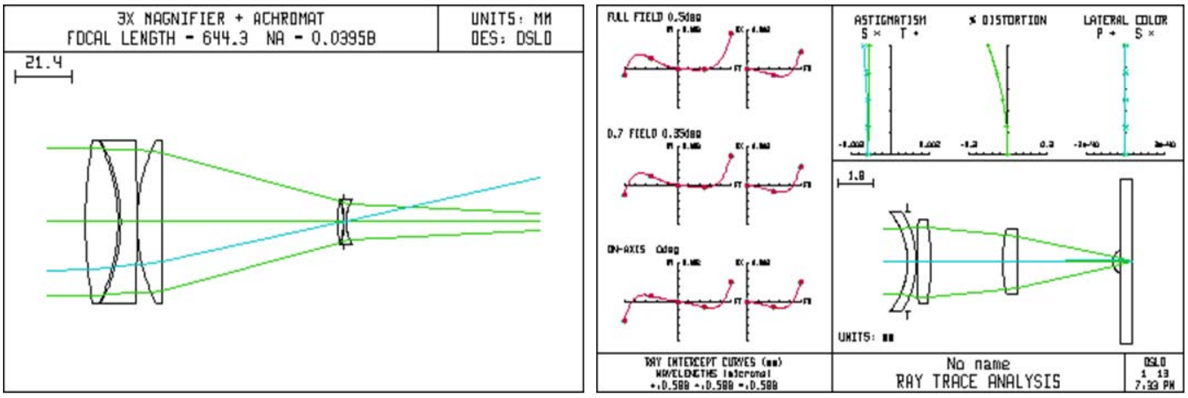
Design of all-plastics optical systems

Today's plastics allow for higher transmittance from the ultraviolet to the infrared region. Mechanical and thermal properties of PMs are very important for their applications too. Spectral range *SR* for several PMs, densities ρ, Young's elastic moduli, maximal service temperature T_{max} as well as some thermal characteristics as linear thermal expansion coefficients α_T and temperature RI gradient $\Delta n_d/\Delta T$ are presented in Table 4. Young's tensile moduli E_{us}, obtained by means of our ultrasound investigations, ρ and $\Delta n_d/\Delta T$ are measured results while rest of the values are based on literature data [8]. It is worth mentioning that E_{us} is a dynamic modulus, given in optical catalogues, and E presents the elastic modulus during static testing of the specimen. The negative thermo-optic coefficients of PMs contrast to the positive values of glasses and are with order or two higher. The thermo induced aberrations of plastic optics should be carefully considered by designers [8]. Examples for all-plastic optical design are illustrated in Fig. 3.

Table 4. Some general material characteristics of studied PMs

PMs	*SR* nm	$\rho\times10^3$ kg/m^3	E_{us} GPa	E GPa	T_{max} °C	α_T $\times10^{-5}$/°C	$\Delta n_d/\Delta T$ $\times10^{-4}$
PMMA	360÷1600	1.187	4.17÷5.57	2.24÷3.8	86	5÷9	–1.30
PS	380÷1600	1.040	3.69	2.28÷4.1	80	6÷8	–1.31
PC	380÷1600	1.195	2.78÷3.37	2÷2.44	130	6.6÷7	–1.00
SAN	360÷1600	1.160	4.30	3.3	79÷88	6.5÷6.7	–1.10
Optorez 1330	410÷?	1.202	6.10	–	100	7	–1.20
Zeonex E48R	360÷1200	1.007	3.66	2.50	123	6	–1.26
Bayer	380÷1600	1.204	2.98÷3.53	2.40	130	6.5	–1.20

Different optical systems designed from PMs are widely used in optoelectronics [8]. A magnifier applied to the channels of NIR goggles is presented in Fig. 3(a): the system is assembled from a three-lens objective (PMMA, PS, PMMA) and a two-lens eyepiece (PMMA, PS). The triplet is with back focal length 644.3 mm, numerical aperture 0.0396 and 3x magnification. The optical system is compact with low weight and therefore suitable to enhance magnification of night-vision devices. A monochromatic micro-lens having a 4.00 mm focal length and a numerical aperture of 0.40 is shown in Fig. 3(b): the four-component system, made from PMMA, has a focused spot under 0.00045 mm over the PC disk track. Geometric aberrations are calculated by means of OSLO design software and ray intercept curves are presented at wavelength of 588 nm at different field heights within the image. The all-plastic CD and DVD lenses are computed for a fixed laser emission wavelength selected from the VIS (405-752 nm) and NIR (840-980 nm) spectral ranges.



a) b)

Fig. 3. Design of all-plastic optical systems: (a) a 3x magnifier for NIR goggles; (b) a CD micro-lens

Conclusions

Polymer materials are widely used in science and technology for night vision and laser systems, auto building, and military industry, optoelectronics, optical communications, etc. [1-4]. Some new applications of PMs are the hybrid and nano-composite structures assembled in aerospace stations, defensive systems, information networks et al. [5-8]. PMs exhibit a number of valuable optical, physical and mechanical properties [8]. We have obtained precise refractometric data of bulk samples and thin films in the VIS and NIR spectral areas up to 1320 nm. RIs of ten PMs at twenty laser wavelengths from 405 nm to 1064 nm have been computed [8, 9].

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