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Polymer materials in optical design

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Due to the low weight and cost polymer optical elements and systems appear in a wide spectrum of industrial, medical, scientific, military and consumer applications. Optical properties as transmission, refraction and dispersion of various types of polymers are studied. Extensive refractometric data obtained by different measuring methods is presented. Dispersion in the visible and near-infrared regions is examined. Some important material, mechanical and thermal characteristics have been also determined. Presented results are useful in the design of all-plastic or hybrid glass-plastic optics.

Key words: optical polymers, refractive indices, dispersion, elastic modulus, thermo-optic coefficients

INTRODUCTION

Polymer materials are presently used in the design and fabrication of consumer as well as precise optical elements and devices. In photonic applications, plastics offer key advantages over glasses as low cost and weight, high impact resistance, ability to integrate proper mechanical and optical features, flexibility, etc. Optical plastics are clear polymers that provide excellent light transmission in the visible (VIS) and near-infrared (NIR) regions. Polymer manufacturing includes lenses for video and still cameras, compact disk drives, light-emitting diodes, printers and bar-code readers, biomedical optics and ophthalmic lenses, light-guides, optical films, high-density optical storage media, diffractive optics, flat panel displays, metallised reflectors, optical fibers, couplers, power splitters, modulators, switches and connectors for optical communication networks [1, 2]. Great economies are possible through usage of moulded polymers for reproducing aspheric and other complex geometric surfaces, which are costly to produce in glass as well as in the production of miniature optical elements, necessary in the medical vision instruments, as laparoscopes, arthroscopes, cystoscopes, endoscopes, etc [3].

The principal optical polymers (OPs) are polymethyl methacrylate (PMMA), polystyrene (PS), polycarbonate (PC), methyl methacrylate styrene copolymer (NAS), styrene acrylonitrile (SAN), and methylpentene (TPX) [4]. Chemical companies produce various trade-marks of OPs as NAS–21 Novacor, CTE–Richardson, Zeonex (cyclo olefin polymers of Zeon Corporation), Optorez (alicyclic methacrylate copolymers of Hitachi Chemicals), Bayer, etc. and develop new types of polymer materials.

Application of polymer materials in optical design is determined not only by their optical but also by their mechanical, thermal and some physical characteristics. Because of some major drawbacks of OPs as temperature sensitivity, lower scratch resistance, higher water absorption and some other peculiarities in comparison to glasses, nowadays hybrid plastic and glass components are preferable. Incorporation of these materials may result in high quality optics taking the advantage of lower weight of plastics and thermal and chemical stability of glasses.

The aim of this paper is characterization of optical as well as some additional properties of OPs, important in the lens design. We have studied principal polymers, some trade-marks and materials produced by Eastman Chemical Company, USA (ECC). Transmittance, refraction and dispersion are investigated in the visible and near-infrared spectra. Extensive refractometric data of bulk polymers as well as thin films has been obtained by different measuring techniques. Normal dispersion of polymer materials is studied on base of Cauchy-Schott and Sellmeier's approximations. Important dispersive characteristics as principal, partial and first order dispersions, Abbe numbers, dispersion curves, etc. in the VIS and NIR regions have been obtained. Thermal instability of OPs is determined by their refractive

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index dependence with temperature and dimensional changes which we analyse on base of measured refractometric data. We derive the thermo-optic coefficients as well as thermal expansion coefficients of OPs in the range between 10°C and 50°C. Elastic moduli have been investigated by ultrasonic measurements of polymers. Comparison to glasses of the obtained results is presented.

OPTICAL CHARACTERISTICS

Application of a given material in optical and photonic design requires precise data of its optical characteristics. Refraction, absorption, scattering of light are of great importance for transparent media. The first two are determined by average values of the material characteristics in volume samples, while scattering is due to local fluctuations of optical uniformity within the medium [5].

Transmission of optical polymers

Transmittance of the materials depends on their structure and sample thickness d. Most OPs are optically transparent in the VIS and NIR spectra, and consequently optical losses of polymer waveguides are low in the three telecommunication windows around 850, 1310 and 1550 nm. Tipically, they are totally opaque in the ultraviolet and infrared regions beyond 2100 nm, though there are weak absorption bands at about 900 nm, 1150 nm, 1350 nm and 1675 nm [1,6].

We used a UV-VIS-NIR spectrophotometer Varian Carry 5E and transmittances of thin polymer films of ECC materials were measured in the spectral range from 400 nm to 2500 nm. In Fig.1 transmission spectra of a polycarbonate film with $d = 35$ μm and a copolyester film with $d = 33$ μm are presented. Both polymer layers transmit well in the VIS and NIR regions up to 1700 nm. Presented spectra have weak absorption bands between 1660 and 1700 nm, due to the first overtone of the –CH group. A considerable transmission decrease is observed at wavelengths greater than 2200 nm where absorption of other C–H groups occurs. Similar results have been obtained for all other studied polymer films. Absorption bands can be shifted to the longer wavelength regions outside the telecommunication–spectral windows by replacing the lighter hydrogen atom in the C–H bonds with heavier ones such as deuterium and halogens [1]. Recently, low–loss fluorinated polymer materials in the NIR region have been synthesized and applied for producing of various functional optical devices [2].

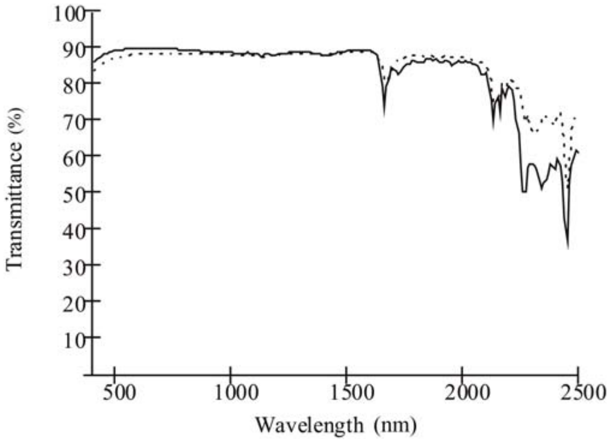

Fig. 1. Transmission spectra of a polycarbonate and a copolyester film with close thickness.

Refractive index measurement of OPs

We have investigated more than 20 types of OPs made in USA, Japan and Germany. Different methods and techniques were applied to measure refractive index values of bulk specimens [7] and thin polymer films [8,9].

Measurements of bulk polymer samples. A classical Pulfrich–Refractometer PR2 with its V–shaped SF3 glass prism (VoF3) has been used to determine refractive indices of volume polymer samples in the VIS spectrum. Measurements are based on the deviation angle method. Polymer plates with thickness varying from 2.5 mm to 5.5 mm and cubic specimens with two polished, mutually perpendicular faces have been prepared according to the requirements of the measuring method and the applied VoF3 prism [7]. Proper immersion emulsions with a suitable refractive index were used to ensure the optical contact between the plastic samples and the prism. Measuring temperature of 20°C was maintained and thermostatic regulation was possible with stability of 0.1°C. Refractive indices were measured at the emission wavelengths of the spectral lamps of the PR2 instrument in the VIS region: green e–line 546.07 nm and blue g–line 435.83 nm of the mercury source, yellow d–line 587.56 nm of the helium source, and blue F–line 486.13 nm as well as red C–line 656.27 nm of the hydrogen lamp. Measurement accuracy of the Pulfrich–Refractometer is 2×10^{-5} [10]. The V–type prism with its thermostatic housing is suitable to obtain precise refractometric data at varying temperature. Some of the polymers were measured in the range between 10 and 50°C using a MLW thermostat U4 with a water bath, made in Germany. Thus, influence of temperature on refraction and dispersion of OPs was investigated.

Additional goniometric set-up with the same prism, a white lighting module (a 250 W halogen lamp and a condenser system) with interference filters (IFs) and a photo detector device has been assembled to obtain refractometric data in the entire VIS and NIR regions up to 1052 nm [7]. The amplitude transmittances of the IFs have been measured with the aid of a Varian Carry 5E VIS–NIR spectrophotometer and the wavelengths of maximal transmission have been determined as 548, 589, 597, 659, 703 and 752 nm for the VIS region, and 804, 833, 879 and 1052 nm for the NIR spectrum. A G5–LOMO goniometer with an accuracy of one arc second was used to measure the deviation angle. Comparison between the obtained results by the PR2 refractometer and the goniometric set–up in VIS light was possible. A number of polymer specimens have been measured with this goniometric set-up and a He–Ne laser emitting at 632.8 nm as a lighting module [11]. A detailed metrological analysis of the applied measuring techniques pointed out that our measurements of the refractive indices of bulk polymer samples guarantee accuracy better than ±0.001 [12].

Measurements of thin films. Among studied OPs, films were possible to be obtained only for the ECC materials, which have been delivered in the form of pellets. Measured samples with varying thickness were prepared by casting of some amount of the polymer solutions on glass substrates. The pellets of polycarbonate, polyester, polyaryate, polyacrylate, and cellulose materials were dissolved in chloroform and the two types of copolyesters A and B – in 1,1,2,2–tetrachloroethane. Solutions of the first five materials were prepared with concentration of 10 wt% while the concentration of the copolyester solutions was 1 wt%. Higher refractive polymers were deposited on heavy TF4 glass plates. TK21 glass plates were used for the low refractive materials. The substrates were with surface areas of about 5 cm^2 or 8 cm^2. The obtained films were dried at temperature of 20^{o}C for 48 hours and then were heated up to 60^{o}C during 6 hours to evaporate the rest of the solvent. Film thickness d was measured by a digital micrometer (Mitutoyo Corporation) with an accuracy of ±1 μm.

We have used the total internal reflection method to measure refractive indices of thin polymer films by means of laboratory assembled laser microrefractometers (LMR) with three [8] or four wavelength illumination [9]. Measuring principle is based on the critical angle determination by means of the diffraction pattern disappearance [13]. The experimental schemes in both cases differ in the illumination part. Measuring wavelengths in case of the three–wavelength LMR are 532, 632.8 and 790 nm, while for the four–wavelength LMR, they are 406, 656, 910 and 1320 nm. The examined samples are placed between a TF4 glass prism and a chromium diffraction grating with a 40 μm period. The optical contact between the measured film, prism and the grating is realised using methylene iodide with a measured refractive index value $n_{633} = 1.732$ for high index polymers and microscopic immersion oil with $n_d = 1.52$, in case of low refractive OPs. The prism unit with the sample is mounted on a rotary goniometric stage with resolution of 1 arcmin. At small angles of incidence, diffraction orders are observed in reflection on a screen. At the critical angle of the examined material, total internal reflection occurs at the interface prism – film, and the diffraction pattern disappears. The incident angle φ_c is then measured on the goniometric scale. An infrared beam–finder card, model IRC32R (Electrophysics), with peak emission at 655 nm and spectral range $800 \div 1700$ nm, was used to visualise the diffraction image in the infrared light.

The experimental uncertainty of the laser microrefractometric method depends mainly on the accuracy of evaluation of the angle of incidence when total internal reflection of studied polymers occurs. Extra noise, introduced by the multiple surface reflections in the film and the glass substrate, and light scattering in the polymer medium also influence on the reading value of the angle φ_c. The estimated standard uncertainty of the results was found to be ±0.002, taking into account the maximal standard deviation of the mean refractive index, calculated on base of several measurements of each polymer film [12].

Refractive index results. Some of the obtained refractive indices of bulk polymer samples and thin films at selected wavelengths in VIS and NIR spectral regions are included in Table 1. Presented results for the volume specimens were obtained by the PR2 instrument and the goniometric set–up at measuring temperature of 20^{o}C. In case of polymer films, the first four samples were measured at room temperature of 23^{o}C by the three–wavelength LMR and the rest three – by both modifications of the LMR to obtain additional dispersion data.

Table 1. Measured refractive indices of bulk polymers and thin films

Polymer		**Bulk OPs**						
		n_g	n_F	n_d	n_{633}	n_{804}	n_{879}	n_{1052}
PMMA		1.5025	1.4973	1.4914	1.4890	1.4843	1.4835	1.4813
PS		1.6171	1.6056	1.5917	1.5872	1.5775	1.5756	1.5718
PC		1.6117	1.5994	1.5849	1.5802	1.5703	1.5683	1.5645
SAN		1.5882	1.5783	1.5667	1.5626	1.5543	1.5526	1.5496
Zeonex E48R		1.5431	1.5376	1.5309	1.5284	1.5234	1.5224	1.5204
Optorez 1330		1.5219	1.5163	1.5094	1.5075	1.5031	1.5021	1.4984
Cellulose		1.4804	1.4765	1.4706	1.4687	1.4639	1.4627	1.4608
Polyacrylate		1.5065	1.4995	1.4941	1.4924	1.4888	1.4880	1.4855
EBM copolyester		1.5861	1.5747	1.5613	1.5580	1.5493	1.5465	1.5449
		Thin polymer films						
		n_{406}	n_{532}	n_{633}	n_{656}	n_{790}	n_{910}	n_{1320}
Polyarylate	$d = 15\ \mu$m	–	1.656	1.642	–	1.639	–	–
Copolyester A	$d = 6\ \mu$m	–	1.537	1.525	–	1.514	–	–
Copolyester B	$d = 33\ \mu$m	–	1.647	1.632	–	1.619	–	–
Polycarbonate	$d = 35\ \mu$m	–	1.599	1.595	–	1.591	–	–
Polyacrylate	$d = 6\ \mu$m	1.501	1.490	1.485	1.484	–	1.478	1.476
Polyester A	$d = 40\ \mu$m	1.513	1.502	1.496	1.495	–	1.489	1.486
Cellulose	$d = 9\ \mu$m	1.493	1.473	1.467	1.466	–	1.460	1.457

Presented results of n_d of the examined OPs vary in an interval from 1.4706 for the cellulose material up to 1.5917 for the PS polymer. The comparison to optical glasses [14,15] reveals a much more restricted range of refractive index values of the polymer materials. Recently, MITSUI Chemicals offers special high refractive index optical polymers with $n_e = 1.74$, which are especially suitable for ophthalmic lenses [16].

Comparison between refraction of bulk samples and thin polymer films, prepared from one and the same material, is possible at 632.8 nm. As it is seen from Table 1, refraction of bulk PC material is lower than that of the ECC polycarbonate film. Opposite relation is observed for the ECC polyacrylate volume specimen and the thin polymer layer. Refractive indices of the cellulose bulk specimen and film are similar and values differ in the third decimal place. The established differences due to the fact that in case of bulk samples average volume refractive index is measured, while for thin polymer films, a local value of the index is registered. The latter is influenced by the polymer packing and nonuniformity near the film free surface at the place of the laser beam incidence [12]. For some of the thin polymer films refractive index dependence on the thickness of the polymer layer has been established [17]. In case of the polyarylate material, refractive index increases with the thickness diminishing of the film. This could be explained with the increased polymer packing near the surface. However, such dependence was not observed for all of the polymers. Obviously, refraction of thin films is influenced by the specific material structure. Similar results have been obtained by other authors, too [18]. Refractive index values depend also on the film quality and uniformity as well as on the adhesion and viscosity of the solutions and their hardening time [5].

Dispersive characteristics of OPs

Presented transmittance spectra in Fig. 1 as well as measured refractive indices of OPs (Table 1) confirm their normal dispersion in the regarded VIS and NIR spectral regions. There are several approximating dispersive equations in literature as Herzberger's, Hartmann's, Cauchy's and Sellmeier's formulae [7]. Only the last one, however, has physical ground. Usually, three terms in the Sellmeier's approximation are used to ensure sufficient precision over the wavelength range from the ultraviolet to the infrared area [14,19]. We have applied the Cauchy–Schott dispersion equation [7,20] which can be derived from the Sellmeier's formula. It is valid for transparent media in their region of normal dispersion. In case of bulk polymer samples and thin films, measured by both LMRs, we

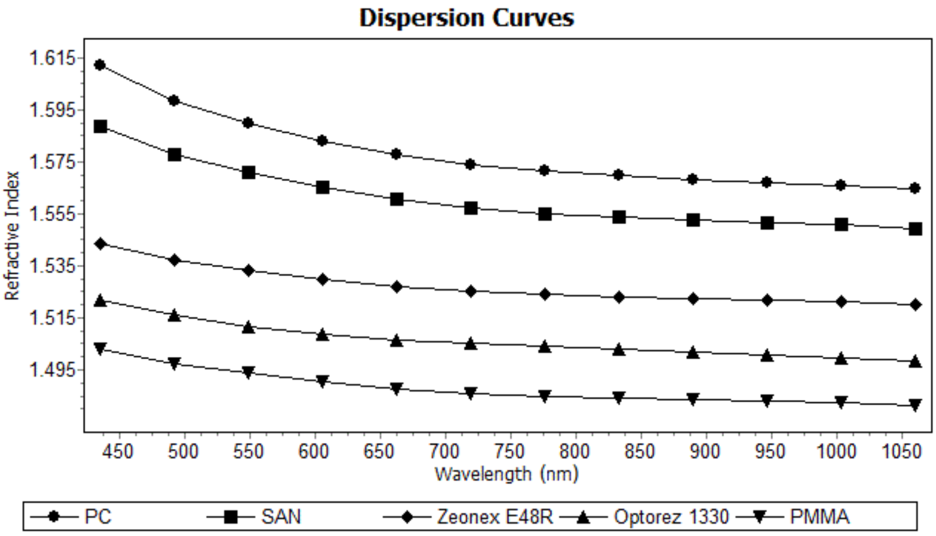

Fig. 2. Dispersion curves of bulk OPs.

have used six dispersion coefficients in the Cauchy–Schott approximation, as follows:

$$n^2 = A_1 + A_2\lambda^2 + \frac{A_3}{\lambda^2} + \frac{A_4}{\lambda^4} + \frac{A_5}{\lambda^6} + \frac{A_6}{\lambda^8}, \qquad (1)$$

where the wavelength λ is expressed in microns. Our analysis of Eq. (1) shows that the accuracy of the calculated refractive indices of optical glasses is better than $\pm 1 \times 10^{-4}$ in the entire VIS range and NIR spectrum up to 1060 nm and decreases to about $\pm 5 \times 10^{-4}$ at 1500 nm [12].

We have realised the program OptiColor on the base of Eq. (1) that allows us to obtain the dispersion coefficients from A_1 to A_6 using a system consisting of six linear equations. Other options of the program are calculation of dispersion curves, random refractive indices at selected wavelengths and Abbe numbers of the examined materials.

In Fig. 2 dispersion charts of some of the studied bulk polymers are presented while dispersion of thin films is illustrated in Fig. 3. Refraction of the polyacrylate, polyester A and cellulose films are measured by both modifications of LMR.

Presentation of several dispersion curves in one diagram makes possible the comparison between the values of refractive indices and dispersion behaviour of OPs. As it is seen in Fig. 2, the higher refractive PC and SAN materials show greater dispersion in the VIS region. For thin films in Fig. 3, this tendency is not observed. The least refractive cellulose film reveals highest dispersion in comparison to the polyester and polyacrylate films. In this case, however, broader wavelength interval is considered. In the NIR region, all studied OPs have lower dispersion which makes them useful materials for communication applications.

Dispersion curves of the polymer films, measured by the three-wavelength LMR, were calculated by the Cauchy-Schott Eq. (1) with three coefficients and Sellmeier's approximation with two terms in the series [8]. Similar calculation accuracy of the dispersion curves in both cases was established. Because of the restricted wavelength measuring range between 500 and 800 nm, the detailed analysis of the dispersion behavior of OPs is not efficient. Our investigations on thin polymer films with varying thickness show that their dispersive characteristics in the regarded spectral range are similar for one and the same material, though they differ in refraction [12, 17].

Dispersion behaviour of optical materials is usually evaluated by their principal dispersion $n_F - n_C$ and Abbe numbers ν_d or ν_e. A more accurate description of optical properties is achievable with the aid of the relative partial dispersions $\mathrm{P}_{x,y}$ at selected wavelengths x and y, which is necessary in the design of high quality optics. We have introduced additional analogous parameters to characterize dispersive properties of OPs for the NIR measuring spectrum. Partial dispersions $\Delta n_{\mathrm{NIR}} = n_{804} - n_{1052}$ and Abbe numbers ν_{879}, defined as:

$$\nu_{879} = \frac{n_{879} - 1}{n_{804} - n_{1052}}, \qquad (2)$$

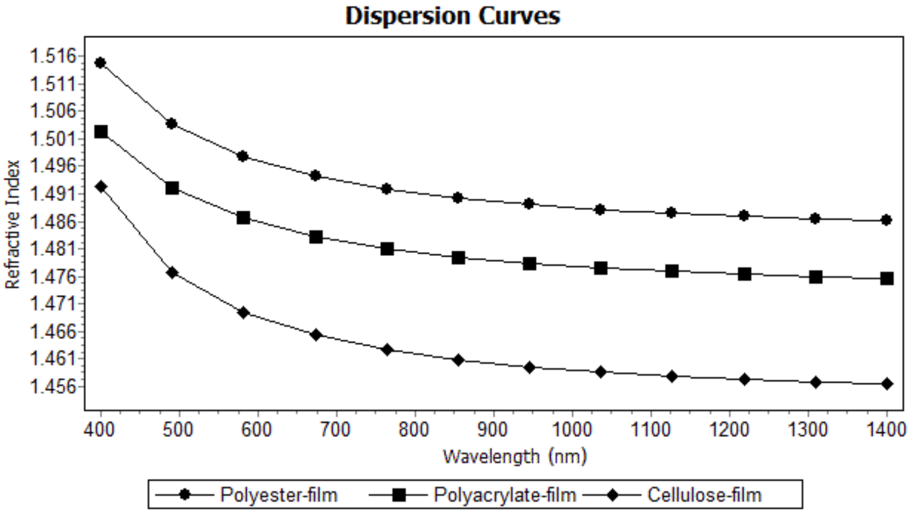

Fig. 3. Dispersion curves of thin polymer films.

are calculated for volume specimens. Estimation of ν_{879} is accomplished by substituting measured refractive indices at the wavelengths of maximal transmission of the applied NIR interference filters with the goniometric set-up. Principal and partial dispersions in VIS and NIR regions, as well as Abbe numbers ν_d and ν_{879} of some of the studied bulk polymers are included in Table 2.

Wavelength dependence of $dn/d\lambda$ assures more detailed examination of the dispersive properties of studied materials in various parts of the spectrum. In the region of normal dispersion obtained graphs of $|dn/d\lambda|$ versus λ should be smooth and monotonously decreasing for correctly measured refractive indices [12]. In Table 2 values of n_{850} and dispersion of first order $|dn/d\lambda|$ at d-line in VIS region and 850 nm for the data communication band are also included. Refraction and dispersion at 1310 and 1550 nm are not calculated, since these wavelengths do not lie in the measuring spectral interval of the bulk polymer samples. Polymers are set in order of decreasing values of ν_d which corresponds to growing principal $n_F - n_C$ and partial $n_g - n_F$ dispersions in the VIS region. Results show that greatest contribution to the principal dispersions is due to refractive index variations in the blue part of the spectrum. Partial dispersions in the measuring NIR area of the bulk OPs are with smaller values in respect to $n_F - n_C$ and $n_g - n_F$ and the rough estimation shows that Δn_{NIR} is of about one third from the principal dispersion for most of the polymers, included in Table 2. Comparison to Schott glass types with similar refractive index values (Table 3) shows that OPs are higher dispersive materials in the VIS light, especially in the blue part of the spectrum.

In the NIR region all of the presented materials (Tables 2 and 3) reveal lower dispersion, compared to VIS area. Abbe numbers ν_{879} of most OPs are

Table 2. Dispersive characteristics of bulk polymers

Characteristics	PMMA	Zeonex E48R	Optorez 1330	SAN	PS	PC
$n_F - n_C$	0.0083	0.0094	0.0098	0.0160	0.0194	0.0201
ν_d	59.2	56.5	52.0	35.4	30.5	29.1
$n_g - n_F$	0.0052	0.0055	0.0056	0.0099	0.0115	0.0123
$\lvert dn/d\lambda\rvert_d \times 10^{-5}$, nm^{-1}	5.75	6.06	4.74	10.13	11.04	11.59
Δn_{NIR}	0.0030	0.0030	0.0048	0.0047	0.0057	0.0058
ν_{879}	161.2	174.1	105.4	117.6	101.0	98.0
$\lvert dn/d\lambda\rvert_{850} \times 10^{-5}$, nm^{-1}	1.04	1.16	1.89	1.89	2.69	2.62
n_{850}	1.4837	1.5228	1.5023	1.5533	1.5762	1.5690

Table 3. Dispersive characteristics of Schott glasses

Characteristics	**N-BK10**	**N-BK7**	**N-PSK3**	**N-BAK2**	**LF5**	**F5**
n_d	1.49782	1.51680	1.55232	1.53996	1.58144	1.60342
$n_F - n_C$	0.00744	0.00805	0.00870	0.00904	0.01423	0.01587
ν_d	66.95	64.17	63.46	59.71	40.85	38.03
$n_g - n_F$	0.00394	0.00430	0.00467	0.00492	0.00818	0.00920
$\lvert dn/d\lambda \rvert_d \times 10^{-5}$, nm^{-1}	3.87	4.18	4.51	4.67	7.25	8.06
Δn_{NIR}	0.00375	0.00390	0.00412	0.00399	0.00539	0.00588
ν_{879}	131.0	130.5	132.1	133.3	105.6	100.4
$\lvert dn/d\lambda \rvert_{850} \times 10^{-5}$, nm^{-1}	1.69	1.77	1.88	1.85	2.58	2.82

with higher values in comparison to glass types with similar refraction. For example, the value of ν_{879} of PMMA (Table 2) is considerably greater than the respective Abbe number of the N-BK10 glass (Table 3), though their refractive indices are very close. The Zeonex E48R polymer is with similar refraction to the N-BK7 glass but it is considerably less dispersive material in the NIR region. In case of high refractive optical materials as flint types glass F5 or LF5 and PS or PC polymers, dispersion in NIR area is similar, regarding the ν_{879} and Δn_{NIR} values. However, among all of the examined materials the acrylic polymers and cyclo olefin trade-mark Zeonex E48R show lowest dispersion in this part of the spectrum. Obviously, these plastics seem to be the most suitable optical materials for night vision optics.

Comparison among values of first order dispersion $|dn/d\lambda|$ in the NIR region shows similarity for polymers and glasses. For all of the presented materials, $|dn/d\lambda|_{850} < 3 \times 10^{-5}$ nm^{-1}. In comparison to VIS area first order dispersion of OPs decrease about five times for most of the polymers. In case of presented glasses in Table 3, reduction of dispersion is less. However, results for the PMMA and Zeonex E48R materials confirm again their lowest dispersion in NIR spectrum.

ADDITIONAL CHARACTERISTICS OF POLYMERS IN OPTICAL DESIGN

Material, mechanical, thermal and environmental characteristics of polymers play an important role in the optical design, too. The use of plastic elements is preferable for the reduction of weight, due to the essentially smaller densities of the polymers. Generally, density ρ of the optical grade plastics is about 1 g/cm^3 and varies in the limits between $0.83 \div 1.4$ g/cm^3 [5, 12, 21]. In Table 4, values of ρ of some of the examined OPs at temperature of 20°C are included. Densities have been measured by the Archimedean immersion method and an uncertainty of the results is $\pm 1 \times 10^{-3}$ g/cm^3.

In addition to the optical requirements, plastics should be selected on the basis of their mechanical properties and environmental compatibility. Some of the considered mechanical characteristics of OPs in the design are elastic moduli, impact resistance I, in terms of the widely used Izod test, and Poisson's ratio μ. In Table 4 parameters I, μ and water absorption A_{H_2O} per 24 hours of the examined OPs, steeped in water, at temperature of 23°C in percents by weight, are given in accordance to literature data [22–25]. Ultrasonic measurements have been used to investigate elastic moduli of OPs. Influence of temperature on refraction and dimensional instability of polymers is evaluated on base of calculated thermo-optic coefficients $\Delta n_d/\Delta T$ and linear thermal expansion coefficients α.

In many applications polymer elements are subjected to various kinds of external forces that may cause them to deform or break. In such cases, polymer materials should have a sufficient degree of toughness and flexibility. Young's modulus E, also known as the tensile modulus, is a measure of the stiffness of an isotropic material. Poisson's ratio μ is another important material characteristic used in elastic analysis. Generally, "stiffer" materials will have lower Poisson's ratios than "softer" materials. There are other elastic moduli, such as bulk modulus and the shear modulus which are related to the values of E and μ.

Static and dynamic methods are usually applied for determination of the elastic moduli of solids. Experimental conditions such as magnitude of the external load as well as loading rate significantly affect the measuring accuracy of the results, obtained by static stress-strain measurements. The dynamic methods

Table 4. Some material characteristics of OPs

Optical Polymer	$\rho \times 10^3$ kg/m^3	E GPa	G GPa	μ	I J/m	$\Delta n_d/\Delta T$ $\times 10^{-4}, K^{-1}$	α $\times 10^{-5}, K^{-1}$	A_{H_2O}, %
PMMA	1.187	$4.17 \div 5.57$	$1.49 \div 2.06$	$0.35 \div 0.4$	$16 \div 32$	-1.30	7.5	0.3
PS	1.040	3.69	1.37	0.35	$19 \div 24$	-1.31	6	<0.1
PC	1.195	$2.78 \div 3.37$	$0.99 \div 1.23$	$0.37 \div 0.4$	$600 \div 850$	-1.00	4.7	0.2
SAN	1.160	4.30	1.57	0.37	$11 \div 21$	-1.10	5.3	0.28
Optorez 1330	1.202	4.76	2.29	0.37	-	-1.20	6.6	1
Zeonex E48R	1.007	3.66	1.34	0.37	21	-1.26	6.6	< 0.01
Bayer	1.204	2.98-3.53	1.07-1.30	0.36-0.39	850	-1.20	5.6	0.12

with a sinusoidal load are also applicable and are with a relatively high accuracy. According to the applied frequency range, the dynamic methods are classified as: acoustic (the frequency is below 10^4 Hz) and ultrasonic (the frequency is between 10^4 and 10^8 Hz). The dynamic methods are widely applied to study the elastic properties and determine the elastic moduli of glasses and glass-forming liquids. As it is known, velocity c_l of longitudinal acoustic waves depends on Young's modulus and Poisson's ratio, according to the relation:

$$c_l = \sqrt{\frac{E(1-\mu)}{\rho(1+\mu)(1-2\mu)}}\,. \tag{3}$$

Velocity of shear (transverse) wave c_t is related to shear modulus G by:

$$c_t = \sqrt{\frac{G}{\rho}}\,. \tag{4}$$

Equations (3) and (4) are valid for propagation of elastic waves in solid objects which transverse dimensions are much greater than the sound wavelength. Shear modulus G and bulk modulus K can be also calculated by the expressions:

$$G = \frac{E}{2(1+\mu)} \text{ and } K = \frac{E}{3(1-2\mu)}. \tag{5}$$

We have measured velocity of the longitudinal ultrasonic waves of bulk polymer samples. A digital ultrasonic precision thickness gauge CL-104, produced by Krautkramer-Branson, has been applied. The operating principle is based on the measurement of the travel time of the propagated and reflected ultrasonic pulse on the back wall of the specimen. The ultrasonic gauge has an option to determine the velocity in the material, if thickness of the investigated sample is entered manually via keyboard. A single element contact transducer CLF 4 with a delay line at operating frequency of 15 MHz and measuring range from 0.18 to 25 mm was used. It is suitable for measuring of thin samples where separation of the excitation pulse recovery from backwall echoes is necessary. Thicknesses of the samples were determined by a Kinex-G633 micrometer with an instrumental error of ±0.01 mm. Obtained values of c_l and ρ at 20°C were used to calculate the dynamic elastic moduli by Eqs. 3 and 5. Results for E and G moduli of some polymers are included in Table 4. Our comparison to the literature data of static elastic moduli of OPs reveals much higher values in case of dynamic measurements [12]. This is attributed to the high frequency of the ultrasonic waves. Since measurements from ultrasonic and from dynamic experiments depend on the frequency, the modulus of elasticity estimated by ultrasonic testing is compared with the storage modulus estimated by dynamic experiments [26]. Presented data of OPs gives the possibility for comparison to mechanical characteristics of optical glass types. Obtained values of E of OPs are about 20 to 30 times smaller in respect to Young's moduli of glasses which would result in easier deflection of plastic elements by external loading or intrinsic mass. However, glasses are fragile and with much lower impact resistance [14]. Obviously, unique priority of polymers over glass is safety which determines their only choice in medical applications.

Optical and mechanical properties of polymers may change as a function of temperature. Thermal stability of OPs is very important for their practical applications in systems and devices which operate in variable or extreme environmental conditions. Heating of polymers can cause undesirable transformations in their structure. Increase of maximal service temperature of optical systems can be achieved via introduction of suitable substituents in polymers [1] or usage of hybrid glass-polymer optics [27]. On the other hand, large thermo-optic coefficients of polymers allow for their application in active photonic devices as switchers, attenuators, modulators, amplifiers, controllers, etc. Thermo-optic coefficients of studied OPs have been calculated on base of our refractometric measurements at various temperatures between 10 and 50$^{\mathrm{o}}$C. Some of the obtained results at d-line are included in Table 4. Values of $|\Delta n/\Delta T|$ of polymer materials are with about two orders of magnitude larger than those for optical glass [14, 15]. Some variations of the thermo-optic coefficients with temperature and wavelengths are observed [27]. Differentiation of the Lorentz-Lorenz equation with respect to temperature arrives at the following expression:

$$\frac{dn}{dT} = \frac{(n^2-1)(n^2+2)}{6n}(\Phi - 3\alpha), \tag{6}$$

where Φ is the temperature coefficient of the molecular polarisability and α is the linear thermal expansion coefficient which is the fractional change in length per degree of temperature. Since for polymers the volume expansion coefficient β ($\beta \cong 3\alpha$) is always one or two orders of magnitude larger than Φ [28], polymers have negative thermo-optic coefficients. On base of our results on the temperature gradients of refractive indices, approximate values of α of studied OPs can be calculated by simplifying Eq. (6):

$$\alpha \approx \frac{2n}{(n^2-1)(n^2+2)}\frac{dn}{dT}. \tag{7}$$

Obtained linear thermal expansion coefficients are included in Table 4. Plastic optical materials typically show 10 times higher α values than those of metals and 20 times higher than those of glasses [14]. Thermal expansion alters the geometric parameters of optical systems as focal lengths, radii of curvature of surfaces, lens thicknesses, air spaces, diameters, etc. Consequently, thermally-induced optical aberrations of polymer elements appear. At low temperatures, metal rings and housing elements subject to compression the assembled lenses and optical components, wherein internal stresses and birefringence arise and degrade the optical image. Among presented OPs in Table 4, the PC polymer shows greatest thermal stability as well as highest impact resistance. For this reason, safety glasses and systems requiring durability often are made from polycarbonate, though it is a relatively soft plastic.

Moisture absorption can change a component's optical geometry, increases refractive index slightly and causes optical nonhomogeneities. The PMMA polymer is the most moisture-sensitive material in Table 4. The Zeonex plastic has lowest water absorption value of less than 0.01% (compare to PC – 0.2% and PMMA – 0.3%). Moisture absorption affects not only the dimensions and densities but also the refractive index of plastic optical materials. Moist atmosphere with relative humidity above 85%, high temperatures over 40$^{\mathrm{o}}$C and acidity of the medium damage the polished surfaces of the optical elements, forming stains and deposits. Ultraviolet and ionizing radiations degrade optical properties of OPs, too.

SUMMARY AND CONCLUSIONS

In this report optical, some mechanical, thermal and environmental characteristics of polymer materials are presented which are useful in the design of optical elements and systems. Transmission, refraction and dispersion of bulk polymers as well as thin films are studied. Obtained spectra (Fig. 1) show that OPs transmit well in the VIS and NIR regions up to 2100 nm. Refractive index measurements at nineteen wavelengths of various bulk polymer samples and at seven wavelengths of thin polymer films are carried out. Results (Table 1) show that volume plastics and thin layers have some differences in refraction and should be studied separately. Software program OptiColor is realised on base of the Cauchy-Schott approximation to calculate dispersion curves, refractive indices and Abbe numbers in the VIS and NIR regions (Fig. 2 and Fig. 3, Table 2). Principal, partial dispersions and first order dispersions $|dn/d\lambda|$ at d-line and data communication wavelength 850 nm are determined. Comparison of studied polymer materials to some optical glasses with similar refraction (Table 3) shows that OPs are more dispersive in the VIS range. In the NIR spectrum, dispersion of all materials is lower but there are some polymers which are more efficient for application in night vision instruments and data communication systems than glasses. Results show that OPs complement available classes of optical media with lower refractive but higher dispersive materials and broaden their combinations in achromatic hybrid pairs.

Some physical, mechanical and thermal characteristics of OPs are presented, too. On base of measured density and ultrasonic velocity dynamic elastic moduli E and G are determined. Their values are lower than for glasses but in combination with the high impact resistance, OPs are preferable materials in elements where flexibility and safety in usage are required. Thermal instability of OPs results primary in variation of refractive index and dimensional changes of optical elements, due to thermal expansion, playing a secondary role. Results on thermo-optic coefficients, linear thermal expansion coefficients, tensile and shear moduli, etc. are presented (Table 4). Measured and computed optical and material characteristics of OPs confirm their compatibility to glasses and may be useful in the design of all-plastic or hybrid glass-plastic optics.

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ПОЛИМЕРНИ МАТЕРИАЛИ ЗА ОПТИЧЕН ДИЗАЙН

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(Резюме)

Безспорните предимства на полимерните материали като по-малка плътност, устойчивост на удар, ниска себестойност на оптичните изделия, безопасността им при работа и др. наложиха използването им не само в битовата, но и в прецизна оптика. Приложението им е свързано с определяне на техните оптични характеристики, както и на механичните и топлинните им свойства, устойчивост към ултравиолетови и йонизиращи лъчения, химична резистивност и др.

В предложения доклад са представени резултатите от изследване рефракцията и дисперсията на различни оптични полимерни материали във видимия и близък инфрачервен спектър. Използвани са подходящи методи за измерване показателите на пречупване на обемни и тънкослойни полимерни образци в различни спектрални интервали [1-3]. Определени са основни дисперсионни характеристики като числа на Аббе, средни дисперсии, относителни и относителни частни дисперсии за видимата област и са въведени аналогични за измервателния инфрачервен диапазон. Изследвано е влиянието на температурата върху рефрактометричните и дисперсионни свойства на полимерите.

Рефрактометричните данни на полимерите не са достатъчни за правилния избор на материала за конкретната оптична система. Необходимо е физикомеханично охарактеризиране на материалите като твърдост, якост, износоустойчивост, съпротивление на драскане и др. В настоящата работа са представени резултати за еластичните модули на изследваните полимери, получени от ултразвукови измервания. Получените стойности дават възможност за сравнителна характеристика на полимерите с оптичните стъкла. Голямата чувствителност на полимерите към температурата може да бъде преодоляна чрез комбинирането на полимерни материали с подходящи оптични стъкла за получаване на атермални и ахроматни оптични елементи [4].

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