Application of optical polymers in plastic or hybrid glass-plastic optics

N. SULTANOVA^{a*}, S. KASAROVA^a, I. NIKOLOV^b

^aDepartment of Mathematics and Physics, University "Assen Zlatarov" - Bourgas, 1 Prof. Yakimov Str., 8010 Bourgas, Bulgaria.

^bDepartment of Optics and Spectroscopy, Faculty of Physics, Sofia University, 5 J. Bourchier Blvd., 1164 Sofia, Bulgaria.

We have examined various types of basic and commercial optical polymers. Bulk specimens as well as thin polymer films were investigated to determine their refractive and dispersive properties in the visible and NIR region. Several measuring techniques have been used to obtain extensive refractometric data. On the base of measured results dispersion coefficients, curves, Abbe numbers and thermo-optic coefficients are calculated. A comparison of studied polymers to catalogue glasses is presented to determine the possibility of their integration in hybrid glass-polymer components.

(Received September 25, 2012; accepted February 20, 2013)

Keywords: Optical polymers, Refractive index, Dispersion curves, Abbe numbers

1. Introduction

The optical properties of polymer materials are of great importance in contemporary optical design. They are an excellent alternative to glasses not only in consumer but in high quality optics, too [1,2]. Optical polymers (OPs) have several key advantages over glass including low price and weight, high impact resistance and ability to integrate proper mechanical and optical features. Great economies are possible through usage of polymers for reproducing aspheric and other complex geometric surfaces or elements with small dimensions, which are costly to produce in glass.

OPs, however, present several challenges to the designers including a limited range of refractive index values, thermal effects and stress birefringence. Recently, attention is drawn to hybrid glass-polymer optics which combines the advantages of glass and polymer materials and meets the requirements of high quality imaging in various environment conditions. Such systems integrate low manufacturing cost, broad thermal range functionality and better correction of aberrations. Glass components carry the optical power while the OPs, usually as a layer over the glass, are used for reproducing unique geometric surfaces to take advantage of the inherent quality and consistency of plastic moulding [3].

The purpose of this work is to study refractive and dispersive characteristics of OPs moulded as bulk samples as well as thin films deposited on glass substrate. Comparison to properties of some optical glass types is presented to illustrate compatibility of glass and plastic materials in vision systems.

2. Measured refractometric data of OPs

2.1. Bulk samples

In the visible (VIS) range of spectrum we have used the Carl Zeiss Jena Pulfrich-Refractometer PR2 with its Vtype SF3 glass prism (VoF3 prism). Measurements are based on the deviation angle method. Samples were produced as injection moulded plates or cubes with two fairly well polished, mutually perpendicular surfaces to obtain good refractometric data [4,5]. Proper immersion emulsions with a suitable refractive index were used to ensure the optical contact between the samples and the prism. Refractive indices were measured at five emission wavelengths of the spectral lamps of the PR2 instrument with an accuracy of 2×10^{-5} [6].

The V-type prism with its thermostatic housing is suitable to obtain refractometric data at varying temperatures. Some of the OPs were measured in the range between 10 and 50 °C using a MLW thermostat U4 with a water bath. Thus temperature influence on refraction was investigated. Measured refractive indices at d-line (587.6 nm) at several temperatures are presented in Table 1 for some of the basic OPs: polymethyl methacrylate (PMMA), polystyrene (PS), polycarbonate (PC), styrene acrylonitrile (SAN) and five polymer trade marks. Results at g-line (435.83 nm) at temperature of 20°C according the European standard are also included.

Refractive		PS	PC	SAN	CTE-	Bayer	PMMA	Zeonex	Optorez	S (low
index					Rich.			E48R	1330	styrene)
	10 °C	1.5930	1.5854	1.5677	1.5816	1.5865	1.4923	1.5321	1.5104	1.5176
	20 °C	1.5917	1.5849	1.5667	1.5802	1.5857	1.4914	1.5309	1.5094	1.5162
$n_{\rm d}$	30 °C	1.5904	1.5838	1.5655	1.5787	1.5849	1.4900	1.5295	1.4981	1.5146
(R)	40 °C	1.5891	1.5829	1.5645	1.5773	1.5837	1.4887	1.5282	1.4970	1.5129
	50 °C	1.5878	1.5819	1.5634	1.5760	1.5825	1.4874	1.5269	1.4958	1.5113
n _{g (R)}		1.6171	1.6117	1.5882	1.6023	1.6121	1.5025	1.5431	1.5219	1.5310
n _{632.8} (L)		1.5872	1.5802	1.5626	1.5760	1.5814	1.4890	1.5284	1.5075	1.5142
n _{833 (G)}		1.577	1.570	1.554	1.566	1.571	1.484	1.523	1.503	1.509
<i>n</i> ₁₀₅₂ (G)		1.572	1.565	1.550	1.562	1.566	1.481	1.520	1.498	1.506

Table 1. Refractive indices of OPs measured by the PR2 refractometer (R), goniometric set-up with IFs (G)and laser illumination (L)

Additional goniometric set-up with the VoF3 prism, a white lighting module (a 250 W halogen lamp and a condenser system) with interference filters (IFs) and a photo detector device was applied for measuring in the entire VIS and NIR region. The transmission maxima of IFs are as follows: 548, 589, 659, 703 nm for the VIS light, and 752, 804, 833, 879 and 1052 nm for the NIR region. A G5-LOMO goniometer with an accuracy of 1 arc second was used [4,5]. Comparison between the obtained results measured with the PR2 refractometer and the goniometric set-up in VIS light was possible. The metrological tests in [4] pointed out that our measurements of the OPs' indices guarantee accuracy better than ± 0.001 . A number of polymer specimens have been measured with this goniometric set-up and a He-Ne laser at 632.8 nm as a lighting module [7]. Some of the obtained results at temperature of 20°C are included in Table 1.

2.2. Thin polymer films

Thin polymer films (TPFs) appear in a wide spectrum of applications such as data storage, communications, sensor devices, etc. Therefore, refractive indices of TPFs have been studied separately. Pellets of different OPs were dissolved in proper solvents [8]. TPFs were obtained by casting a certain amount of the solution on a glass substrate. For measuring the film refractive index we have used a laser microrefractometer (LMR), based on the critical angle determination. Two modifications of LMR were assembled at three [8] or four illuminating laser wavelengths [9]. In both cases, measurements were completed on the principle of diffraction pattern disappearance. The established accuracy is 2×10^{-3} . Some of the obtained results are included in Table 2. The thickness of the polymer films is indicated.

A comparison of refractometric properties to bulk samples is accomplished. 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. Though bulk samples have been measured at 16 wavelengths in VIS and NIR region, calculation of refractive indices at emission wavelengths of the applied diode lasers was needed. For this purpose the Cauchy-Schott's approximation was used [4].

Table 2 illustrates that refractive properties of films differ compared to those of bulk materials. The PC film has been measured by the three-wavelength LMR. The obtained values are greater than those of the bulk sample. The cellulose and polyacrylate TPFs have been studied by the four-wavelength LMR. Additional measurements of the same films at emission wavelengths 532 and 632.8 nm of different diode lasers have been accomplished to obtain more extensive refractometric data. The results for the cellulose film are very close to the values of the bulk sample, though they are a little bit smaller. There is an exception for the calculated value of the bulk sample at 406 nm which is out of the measuring spectral region on the one hand, and on the other hand corresponds to the most dispersive part of OPs in the VIS spectrum. Similar dependence is noticed for the polyacrylate film where refractive index deviations of about 10⁻² are established at all wavelengths. Our study on TPFs prepared from different OPs (not included in Table 2) do not allow us to generalize a common tendency in refraction of TPFs, compared to bulk samples. However, we should underline the fact that microrefractometric results present local values of refractive indices while in case of bulk polymer specimens, volume values are measured.

A dependence of refractive index value on film thickness has been also established. For some of the materials, e.g. the polyarylate film, as the film thickness is increased, a decrease of refractive indices values is observed [8]. This could be explained by the increase of polymer packing near the film surface, due to the surface tension forces. An opposite tendency is noticed, however, for the polyacrylate films. Obviously, refractometric properties of TPFs strongly depend on the type of the material and its structure as well as on the film uniformity. Local refractive index values are also influenced by the polymer solution viscosity and film adhesion to the glass substrate.

Ontical	n olympon	Wavelength [nm]							
Optical	polymer	406	532	632.8	656	790	910	1320	
DC	Bulk		1.591	1.581		1.574			
rC	35 µm film		1.599	1.595		1.591			
Callulana	Bulk	1.483	1.474	1.469	1.468	-	1.462	1.459	
Cellulose	9 µm film	1.493	1.473	1.467	1.466	_	1.460	1.457	
Dalasa amalata	Bulk	1.514	1.497	1.492	1.492	-	1.487	1.484	
Polyacrylate	6 μm film	1.501	1.490	1.485	1.484	_	1.478	1.476	

Table 2. Comparison between refractive indices of bulk samples and thin polymer films

3. Dispersive and additional refractive characteristics

Possible applications of OPs in plastic or hybrid glassplastic optics should be regarded on the base of their optical characteristics and compatibility to properties of glass. Dispersion behaviour of optical materials is usually evaluated by their principal dispersion $n_{\rm F} - n_{\rm C}$ and Abbe numbers $v_{\rm d}$ or $v_{\rm e}$ [10]. A more accurate description of optical properties is achievable with the aid of the relative partial dispersions $P_{\rm x,y}$ at selected wavelengths x and y, which is necessary in the design of precise optics. The thermo-optic coefficients are also important and should be taken into consideration to assure thermal stability of the designed elements.

In Table 3 refractive and dispersive characteristics of OPs and catalogue glasses are presented. Abbe numbers v_d and an additional analogous parameter v_{879} for the NIR region are determined on the base of measured refractive indices. Relative partial dispersions $P_{d,C}$, $P_{s,t}$ and v_{879} are calculated by the expressions:

$$P_{\rm d,C} = \frac{n_{\rm d} - n_{\rm C}}{n_{\rm F} - n_{\rm C}}, \ P_{\rm s,t} = \frac{n_{\rm s} - n_{\rm t}}{n_{703} - n_{1052}}, \ \nu_{879} = \frac{n_{879} - 1}{n_{703} - n_{1052}},$$

where s- and t- line correspond to 852.1 and 1014 nm, respectively. Glass data in VIS region is collected from SCHOTT catalogue [10] while v_{879} and $P_{s,t}$ values are evaluated through the Sellmeier's dispersion coefficients.

Presented data of OPs and glasses confirms greater dispersion of plastics in VIS region. As for example, the PMMA polymer, which is with similar refraction to the N-BK10 glass, has greater principal dispersion and respectively lower value of v_d . The same relation is observed for the pair of PS and N-BAF4. Values of v_{879} , however, show that some of the considered OPs have lower dispersion in the NIR region. Among all materials in Table 3 the least dispersive in NIR spectrum are the PMMA and Zeonex plastics. Relative partial dispersions are important for chromatic corrections. In the design of multiple component optical systems $P_{x,y}$ should be closely matched while Abbe numbers should differ substantially. As for example, in the VIS region the PMMA polymer could be combined with the PS material in a plastic doublet, or with the SF57 glass in a hybrid achromatic pair. For night vision application the Bayer plastic could be incorporated with N-BK10 since the $P_{s,t}$ values are very close. The PMMA or Zeonex material and PS plastic also form a suitable pair.

Thermal properties of OPs are rather different compared to glass. Measured n_d values at varying temperatures are included in Table 1. Our results show a decrease of refractive indices with increasing temperature for all of the studied polymer materials. The determined thermo-optic coefficients at the e-line of some of the OPs are presented in Table 3 and comparison to included glass types is possible. The negative values of the temperature gradient dn/dT of OPs contrast to the positive coefficients of the presented glasses. It seems that integration of plastic and glass materials in a hybrid component may result in its thermal stability.

As it can be seen from Table 3, the values of dn/dT of polymer materials are with about two orders of magnitude larger than those for glasses. Therefore, a TPF can be laid on the glass component for stable thermal behaviour of the hybrid. In addition, if the polymer layer is with aspheric surface, better correction of the aberrations is possible. An advantage of hybrid optics is that elements can be designed with high imaging quality and at the same time can be less sensitive to thermal changes.

Measured transmission spectra of all investigated OPs in VIS and NIR region up to about 1600 nm show transmittance better than 85% [8]. Therefore, dispersion coefficients of studied OPs have been calculated by means of Cauchy–Schott's and Sellmeier's approximations [4]. Calculation of dispersion curves was possible. We have used our program OptiColor based on the Cauchy-Schott's equation [5].

Characteristics		0	Ps		Optical glasses				
Characteristics	PMMA	Zeonex	PS	Bayer	N-BK10	N-KF9	N-BAF4	SF57	
n _d	1.4914	1.5309	1.5917	1.5857	1.4978	1.5235	1.6057	1.8467	
$n_{\rm F}$ – $n_{\rm C}$	0.0083	0.0094	0.0194	0.0195	0.00743	0.01016	0.01385	0.03560	
ν_d	59.2	56.5	30.5	30.0	66.95	51.54	43.72	23.78	
v_{879}	96.7	100.5	56.4	54.3	83.21	73.76	65.22	41.57	
$P_{\rm d,C}$	0.289	0.287	0.283	0.277	0.3093	0.3012	0.2972	0.2855	
P _{s,t}	0.340	0.339	0.350	0.400	0.4069	0.3913	0.3877	0.3691	
$\frac{\Delta n_{\rm e}/\Delta T \times 10^{-6}/\rm K}{(20 \div 40^{\circ}\rm C)}$	-130	-126	-131	-120	3.4	1.8	3.3	2.2	

Table 3. Comparison between OPs and glasses

Fig. 1 presents dispersive charts of some OPs and glasses. Lower refractive materials are included in Fig. 1a and with higher refractive index – in Fig. 1b. In both cases presented glasses are less dispersive in VIS light. In the NIR region, the PMMA, Zeonex and N-BK10 (Fig.1a) show similar dispersion. Figure 1b confirms that usually higher refractive materials have higher dispersion. The slopes of the charts in the VIS spectrum vary significantly and decrease in the NIR region.



Fig. 1. Dispersion curves of lower (a) and higher (b) refractive materials.

4. Conclusions

Possible applications of OPs are defined mainly by their optical properties in terms of refractive indices, transmission, dispersion and thermo-optic coefficients. In this report on the base of measured refractometric data characterization of optical properties of bulk polymer specimens and TPFs is accomplished. Obtained results show that refraction and dispersion of TPFs may differ substantially. Our analysis confirms that optical properties of OPs are sufficiently good for precise imaging applications. Comparison to glasses is carried out to confirm their usage and compatibility in hybrid optics. Incorporation of polymer and glass materials may result in thermally stable and well-corrected optical systems.

Calculated refractometric, dispersive and thermo-optic characteristics of polymer materials could be used in the design of optical elements and devices.

References

- J. Menendez, F. Erismann, M. Gauvin, Opt. Photon. News 10, 28 (1999).
- [2] P. Tolley, Photon. Spectra **10**, 76 (2003).
- [3] V. Doushkina, Photon. Spectra 4, 54 (2010).
- [4] N. Sultanova, I. Nikolov, C. Ivanov, Opt. Quant. Electron. 35, 21 (2003).
- [5] S. Kasarova, N. Sultanova, C. Ivanov, I. Nikolov, Opt. Mater. 29, 1481 (2007).
- [6] The Manual of PR2, Carl Zeiss JENA Jena D-77830, Germany, (1976).
- [7] I. Nikolov, N. Sultanova, S. Kasarova, Proc. SPIE 5830, 511 (2005).
- [8] S. Kasarova, N. Sultanova, T. Petrova, V. Dragostinova, I. Nikolov, J. Optoelectron. Adv. Mater. 11, 1440 (2009).
- [9] S. Kasarova, N. Sultanova, T. Petrova, V. Dragostinova, I. Nikolov, Proc. SPIE **7501**, 75010P, (2009).
- [10] SCHOTT Glass Technologies, http://www.us.schott.com

*Corresponding author: ninasultanova@yahoo.com; sultanova@btu.bg