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OPTICAL AND MATERIAL CHARACTERIZATION OF POLYMER MATERIALS AND SAMPLES

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Abstract: *Application of polymers is determined by their optical and material characteristics. Different types of optical polymers have been investigated to reveal their refractometric, transmissive and dispersive properties in the visible and near-infrared spectral regions. Ultrasonic measurements have been accomplished for material characterization of plastics. Influence of operating temperature is also considered.*

Metrologic measurements are required to control the quality of polymer elements including micro- and nanometrology. Illustrations of our results are presented. Some new applications in aerospace technology as hybrid and nanocomposite polymer structures are pointed out.

ОПТИКОФИЗИЧНО ХАРАКТЕРИЗИРАНЕ НА ПОЛИМЕРНИ МАТЕРИАЛИ И ОБРАЗЦИ

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Ключови думи: *Оптични полимери, материални характеристики, оптични характеристики, микро- и нанометрология*

Резюме: *Приложението на полимерите се определя от техните оптични и материални характеристики. Изследвани са различни видове оптични полимери, като са определени техните рефрактометрични, трансмисионни и дисперсионни характеристики във видимата и близка ИЧ спектрална област. Проведени са ултразвукови измервания за установяване на материалните параметри на полимерите. Разгледано е също така влиянието на работната температура.*

За контрол на качеството на полимерните елементи са проведени микро- и нанометрологични измервания. Илюстрирани са някои от получените резултати. Посочени са нови приложения в аерокосмическите технологии като хибридни и нанокомпозитни полимерни структури.

Introduction

Polymer materials are nowadays used not only in the design of consumer but also of precise optical systems and devices. Because of the moulding 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.

Unique properties of optical polymers (OPs) as low cost and weight, high impact and shatter resistance, excellent light transmission and configuration flexibility determine their usage in optical aerospace tools and instruments. Typical applications include frontal module displays of helmets and suits, ophthalmic lenses and goggles, phototropic helmets to protect the eyes of pilots from bright laser beams, near-infrared (NIR) optical systems for remote observation of objects and hyper-spectral imaging devices for photometry of earth surface and cosmic bodies.

A large number of optical polymers including principal as polymethyl methacrylate (PMMA), polystyrene (PS), polycarbonate (PC), methyl methacrylate styrene copolymer (NAS), styrene acrylonitrile (SAN), some trade-marks of OPs as NAS-21 Novacor, CTE-Richardson, Zeonex E48R, Bayer, and development materials of Eastman Chemical Company (ECC) have been investigated. Extensive refractometric data of bulk polymers as well as thin films has been obtained by different measuring techniques [1, 2]. Transmission spectra of OPs reveal normal dispersion of polymer materials in the entire visible (VIS) and NIR spectral regions up to 2200 nm. Dispersive characteristics are calculated on base of Cauchy-Schott and Sellmeier's approximations [3]. Polymers are more sensitive to temperature variations in comparison to glasses. Therefore, refractive index dependence with temperature has been studied and thermo-optic coefficients (TOCs) of OPs have been estimated in the range between 10 and 50 °C. Thermal expansion coefficients and thermal “glass” constants (TGCs) are derived on base of obtained values of TOCs. Mechanical characterization of OPs is carried out by means of ultrasonic measurements. Obtained values of Young’s and shear moduli are reported. Some additional physicomechanical characteristics as Poisson’s ratio, ultimate strength, hardness, impact resistance, thermal conductivity, etc. are presented.

Characterization of optical properties of polymer materials

Polymer materials transmit well in the VIS and NIR spectral regions. Typically, they are totally opaque in the ultraviolet (UV) and infrared regions beyond 2100 nm, though there are weak absorption bands at about 900 nm, 1150 nm, 1350 nm, and 1675 nm [4]. We have measured transmittance of thin polymer films prepared from solutions of ECC materials by means of a UV-VIS-NIR spectrophotometer Varian Carry 5E. In Fig. 1 results for the polycarbonate, polyarylate and copolyester layers with close thickness *d* are presented in the spectral range from 400 nm to 2500 nm. All studied OPs have transmission of about 90 % up to 1600 nm. Given spectra have weak absorption bands between 1660 and 1700 nm, due to the first overtone of the –CH group and a considerable transmission decrease is observed at wavelengths greater than 2200 nm where absorption of other C–H groups occurs. Results for transmittance (*TR*) of samples with thickness of 3.2 mm as well as spectral range (*SR*) of some of the studied OPs are included in Table 1 on base of literature data [3-5].

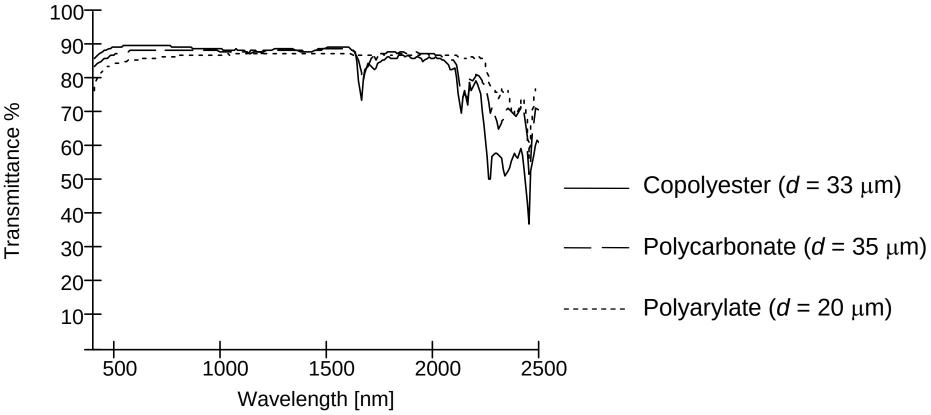


Fig. 1. Transmission spectra of different types of polymer films

Refractive index (RI) of optical materials is the most important parameter for their applications in optical and photonic systems and devices. Proper choice of RI measuring technique depends on the sample shape, size and thickness. Measurements of bulk polymer specimens are based on the deviation angle method. In the visible spectrum we have used the Carl Zeiss Jena Pulfrich-Refractometer PR2 with its V-type SF3 (VoF3 prism) glass prism. Samples were prepared as injection moulded plates or cubes with two fairly well polished, mutually perpendicular surfaces to obtain good refractometric data [1, 3]. Proper immersion emulsions with a suitable refractive index were used to ensure the optical contact between the specimens and the prism. Refractive indices of OPs have been determined at five emission wavelengths of the spectral lamps of the device: 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). Results for some of the examined polymers at 20 °C are presented in Table 1. Combined standard uncertainties of measured refractive indices were estimated and maximal value of $\pm 5.6\times10^{-5}$ was obtained.

Refraction of bulk polymer samples in the VIS and NIR regions up to 1052 nm has been measured by a goniometric set-up [1]. A lighting module consists of a 250 W halogen lamp and Carl Zeiss metal narrow band interference filters (IFs). A G5-LOMO goniometer with an accuracy of one arc second was used with the VoF3 prism-block of the PR2 instrument. A photo detector device including a plane silicon photodiode, operating amplifier and indicator was applied for RI investigation of OPs in the NIR area. Measurements are accomplished at wavelengths of maximal transmission of the IFs. In Table 1 results at 879 and 1052 nm are also presented. Combined standard uncertainty is ± 3.9×10^{-4} [3]. RIs at s- and t- spectral lines are calculated by the Cauchy-Schott approximation in the region of normal dispersion for input data consisting of six measured RIs [1, 3]. Additional RI laser measurements of thin polymer films at wavelengths up to 1320 nm have been accomplished [2].

Dispersion properties of optical materials are evaluated by their principal dispersion $n_F - n_C$ and Abbe numbers ν_d or ν_e (Table 1). Characterization in NIR spectrum is carried out by partial dispersion $\Delta n_{NIR} = n_{804} - n_{1052}$ which corresponds to the measuring interval and Abbe number, defined as: $\nu_{879} = (n_{879} - 1)/ (n_{804} - n_{1052})$. Materials in Table 1 are set in order of decreasing value of ν_d. The PC polymer is the most dispersive plastic in VIS as well in NIR region. However, this order is not preserved for materials as Zeonex which is less dispersive in NIR than in VIS spectrum in comparison to PMMA. NAS-21 and SAN polymers show the same tendency, too. Partial dispersion Δn_{NIR} is about one third of the principal $n_F - n_C$. First order dispersions $\left|dn/d\lambda\right|$ at d-line and 879 nm give more detailed information on dispersive properties of optical materials. In VIS region, values of $\left|dn/d\lambda\right|$ increase with the decrease of ν_d. This order is not the same as in NIR area – NAS-21 is the most dispersive material. PMMA and Zeonex E48R show least dispersion in the entire considered spectrum.

Table 1. General optical characteristics of OPs

	λ, nm	PMMA	Zeonex E48R	NAS-21	SAN	PS	Bayer	PC
n_g	435.8	1.5025	1.5431	1.5933	1.5882	1.6171	1.6121	1.6117
n_F	486.1	1.4973	1.5376	1.5835	1.5783	1.6056	1.5998	1.5994
n_e	546.1	1.4934	1.5333	1.5753	1.5705	1.5963	1.5905	1.5896
n_d	587.6	1.4914	1.5309	1.5714	1.5667	1.5917	1.5857	1.5849
n_C	656.3	1.4890	1.5282	1.5674	1.5623	1.5862	1.5803	1.5793
n_s	852.1	1.4837	1.5228	1.5575	1.5532	1.5762	1.5705	1.5690
n_{879}	879	1.4835	1.5224	1.5573	1.5526	1.5756	1.5698	1.5683
n_t	1013.9	1.4819	1.5209	1.5543	1.5504	1.5726	1.5669	1.5654
n_{1052}	1052	1.4813	1.5204	1.5544	1.5496	1.5718	1.5660	1.5645
$n_F - n_C$		0.0083	0.0094	0.0161	0.0160	0.0194	0.0195	0.0201
Δn_{NIR}		0.0030	0.0030	0.0050	0.0047	0.0057	0.0058	0.0058
ν_d	587.6	59.2	56.5	35.5	35.4	30.5	30.0	29.1
ν_{879}	879	161.2	174.1	111.5	117.6	101.0	98.2	98.0
$\left\|dn/d\lambda\right\|_d$ $\times10^{-5}$, nm^{-1}	587.6	5.75	6.06	7.58	10.13	11.19	10.64	11.59
$\left\|dn/d\lambda\right\|_{879}$ $\times10^{-5}$, nm^{-1}	879	0.97	1.07	3.03	1.70	2.34	2.54	2.37
TR, %		92÷95	92	90	88	87÷92	88	85÷91
SR, nm		360÷1600	360÷1200	300÷1600	360÷1600	380÷1600	380÷1600	380÷1600

Mechanical and thermal properties of optical polymers

In addition to the optical requirements, plastics should be selected on basis of their mechanical properties and environmental compatibility. The rigidity of a material ensures its impact or shatter resistance and is therefore a factor that determines safety. Evaluation of rigidity is based on examination of the polymer elastic modulus (Young's modulus). To obtain the values of elastic moduli of studied OPs we have accomplished ultrasonic investigations. As it is known, velocity c_l of longitudinal acoustic waves depends on Young's modulus E and Poisson's ratio μ in accordance to the relation:

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

where ρ is the material density. This equation is valid for propagation of elastic waves in solid objects which transverse dimension are much greater than the sound wavelength. On base of measured velocity c_l and ρ, and literature data [3, 6] on μ, E is estimated by Eq. (1), while shear modulus G is then derived from the expression: $G= E/[2(1+\mu)]$. Results are presented in Table 2. Some other mechanical characteristics, useful in applications of OPs, are also included as:ultimate tensile strength σ_m, impact resistance I in terms of the widely used Izod test, and hardness according Rockwell scale *HR M*. Strength as well as impact resistance of plastics are dependent not only on the type of the polymer, but also on the processing history of the product. It's worth noting that optical plastic elements should not be subjected to loads because of possible birefringence arising. Among all plastics, PC and Bayer, which is also a polycarbonate polymer, have the highest impact resistance. Though polycarbonates are relatively soft plastics [3], they are higher-temperature materials (Table 3) with higher elongation at break. For that reason, safety glasses, helmets, and systems requiring durability often are made from PC.

Table 2. Some mechanical and material characteristics of OPs

PMs	$\rho\times10^3$ kg/m^3	E GPa	G GPa	μ	I J/m	*HR M*	σ_m MPa
PMMA	1.187	4.17÷5.57	1.49÷2.06	0.35÷0.4	16÷32	92÷100	80
PS	1.040	3.69	1.37	0.35	19÷24	60÷90	30÷100
PC	1.195	2.78÷3.37	0.99÷1.23	0.37÷0.4	600÷850	70	55÷75
SAN	1.202	4.30	1.57	0.37	11÷21	75÷86	58÷79
Zeonex E48R	1.007	3.66	1.34	0.37	21	75	71
Bayer	1.204	2.98÷3.53	1.07÷1.30	0.36÷0.39	850	70	66

High temperature sensitivity is probably the weakest area of plastics. Polymer elements and systems should function well optically in a broad temperature interval between –40 °C and +130 °C. In Table 3 some important thermal characteristics are listed as maximal operating temperature $T_{\max}$, linear thermal expansion coefficients α_T, TOCs, TGCs, and coefficients of thermal conductivity κ. On base of measured RIs at different temperatures from 10 to 50 °C, TOCs which represent temperature gradient of RIs $\Delta n_d/\Delta T$ of polymers are estimated [7]. Most stable optically polymer is again the PC material while NAS-21 is the most temperature sensitive material. Obtained TOCs have been used to derive the linear thermal expansion coefficients using the well-known Lorentz–Lorenz equation [3] and then TGCs are estimated by the relation:

$$\gamma_{\lambda,T} = \frac{\mathrm{d}n_\lambda / dT}{n_\lambda - 1} - \alpha. \tag{2}$$

In comparison to glasses, TOCs of polymer materials are with about two orders of magnitude larger than those for optical glass types and are definitely negative. Thus, maintaining focus over a range of temperature is a significant problem in plastic optics. High temperatures also alter the geometric parameters of optical systems as focal lengths, radii of curvature of surfaces, lens thicknesses, air spaces, diameters, etc. Consequently, thermally-induced optical figure errors of polymer elements arise. Detailed analysis of thermo-optic aberrations of plastic devices could be accomplished in accordance with [6].

Thermal conductivity of OPs is relatively small and may be as much as one order of magnitude lower than for optical glass types and as a result plastics are good thermal insulators. Among presented OPs, the polycarbonate materials possess broadest service interval from –137 to +130 °C. Polymers as polystyrene and SAN have inferior thermal resistance as well as poor UV stability. The ability of plastics to withstand rapid changes of temperature is better than that of glasses. Thermoplastics allow variation of temperature below melting point without loss of optical quality [3].

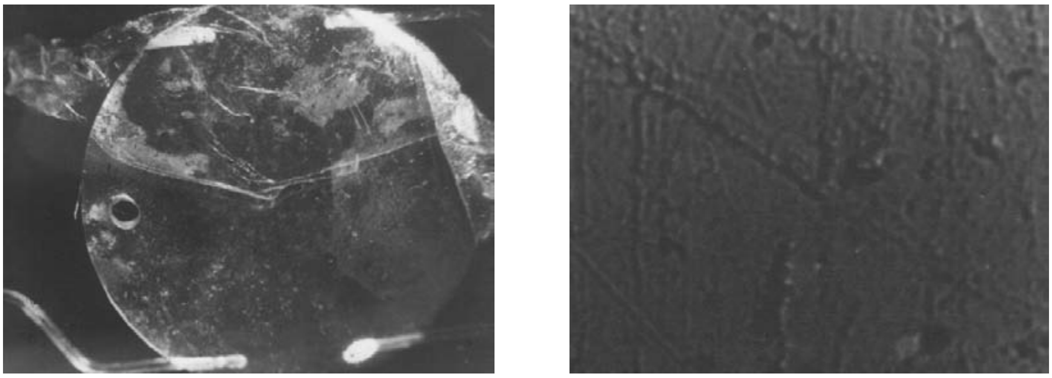
Table 3. Thermal characteristics of OPs

Polymer	Tmax °C	α_T $\times 10^{-4}$, K^{-1}	$\Delta n_d/\Delta T$ $\times 10^{-4}$, K^{-1}	$\gamma_{d,\,20°}$ $\times 10^{-4}$, K^{-1}	κ W/m.K
PMMA	86	0.7	–1.30	–3.4	0.21
PS	80	0.6	–1.31	–2.8	0.17
PC	130	0.5	–1.00	–2.2	0.2
SAN	79÷88	0.5	–1.10	–2.5	0.14
NAS 21	93	0.7	–1.40	–3.0	–
Zeonex E48R	123	0.6	–1.26	–3.0	0.17
Bayer	130	0.6	–1.20	–2.6	0.2

Micro- and nanometrology of polymer samples

Polymer products show imperfections as a result of the technological processing or exploitation history. Microdefects on polymer surfaces are controlled by means of optical microscopes which resolution ability (RA) is restricted by light diffraction according to the expression: $\delta = 0.61\ \lambda/A$ where A is the numerical aperture of the objective. This means that diffraction limit of the RA is about $\lambda/2$. For a given microobjective, with known A, the minimal distance δ between two resolved points estimates the minimal measured distance at the examined surface. The maximal magnification of optical microscopes is 1500x. In nanometrology of surface imperfections of OPs, transmission electronic microscopes (TEMs) are used. Wavelengths of electronic waves depend on the applied voltage of the accelerating field in the TEM device and are determined by the de Broglie wavelength: $\lambda = h/p$, where h is the Planck's constant and p is the momentum of the electron. In TEM devices, image sizes are in the interval 5 ÷ 100 μm and magnification is in the limits 50 000 ÷ 100 000x. Usage of CCD cameras increases linear magnification of microscopes with 2500x. In case of TEM systems, resolving power is limited by the diameter of the focusing electronic beam of about 0.1 nm. Limits of RA are restricted by the small apertures of the electronic lenses (down to 0.01) because of the residual spherical aberrations [7, 8].

In Fig. 2a) a photo of an American intraocular lens (Alcon type) with 40x magnification obtained by an optical microscope is presented. Protein fractals are observed at the surface of the enucleated patent's lens after usage. In Fig. 2b) a TEM image with 10800x magnification of an ophthalmic contact lens, made from a hydrophilic polymer, is illustrated. In the second picture cosmetic defects as scratches and ditches under 300 nm as a result of the physicochemical polishing, are perceived.



a) b)

Fig. 2. Photographs of: a) a microimage of a used intraocular lens; b) a TEM nanoimage of the lens surface

Birefringence is another imperfection developed by residual stresses in manufacturing of transparent plastics. It is due to the effect of variations in the index of refraction in different directions of the material and arises when polymer chains align during production procedures as extrusion, stretching, drawing, moulding, casting, joining, etc. [9]. Strains can be introduced by differential shrinkage, uneven cooling, or nonuniform flow of polymer melt. Birefringence Δn of OPs could be as high as 8×10^{-3} for PS components and less for the acrylic of about 6×10^{-5} [10]. By carefully controlling of temperature conditions and flow speed during the technological processes high quality of optical components can be achieved and birefringence can be smaller than 2×10^{-6} [9]. Polymer products and samples are checked for birefringence by refractometric and polarimetric measurements to eliminate low quality specimens.

Conclusions

OPs exhibit valuable optical, physical and mechanical properties. They are organic glasses which transmit well in the VIS and NIR regions. *SR* of transmittance depends on the structure of the material and sample thickness (Table 1). Some optical grade PMMA types have transmission down to 300 nm, but most OPs begin to absorb in the blue portion of the VIS light [4,5]. OPs have a limited range of RI values in comparison to glasses. Their optical properties may change with temperature and moisture. Generally OPs are more dispersive materials then glasses, but there are plastics as PMMA and Zeonex types which are less dispersive in NIR region. OP elements should not be subjected to loads because of possible birefringence arising.

The use of plastic optical elements is good for reduction of weight, due to the relatively smaller densities of polymers (Table 2). Impact resistance is one of the outstanding advantages of OPs in comparison to glass. PC and Bayer have the highest values of *I*. Low values of elastic moduli results in easy deflection of plastic elements by external loading or intrinsic mass. Insufficient abrasion and scratch resistance of OPs is a drawback in comparison to glasses. Both inorganic (vacuum deposited) and organic materials are used to reduce susceptibility to scratching. Among thermal characteristics, attention should be drawn to the maximal service temperature, linear thermal expansion coefficients, TOCs and TGCs (Table 3). Minimization of the temperature induced aberrations is achieved by usage of hybrid glass-plastic elements.

OPs are widely used in science and technology: night vision and laser systems, auto-building and military industry, optoelectronics, optical communications, etc. Some new applications of the plastic materials are hybrid and nanocomposite structures, used in the aerospace stations, military systems, optical information networks, etc. [6,8]. In aerospace apparatus engineering specialized materials as metal parts with integrated polymeric materials at the surface as well as polymeric components with metal atoms incorporated in the structure chains are used. OPs with nanotubes and nanometalic fibers which have excellent physicochemical and mechanical characteristics are used for the production of aero-illuminators, adaptive filters in remote controlled photo cameras, state-of-the-art colour displays and helmet displays, device-on-a-chip, etc. Up-to-date applications of OPs are metallic-organic and polymeric-semiconductors with multilayer structures used in the remote controlled optical electronic systems and aircraft complexes. In a DARPA (Defense Advanced Research Projects Agency) project a polymer membrane will be used which diffracts light like a Fresnel lens and because of light weight it can be fold up realizing a large telescope’s size.

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