

Material and optomechanical characteristics of polymers in optical design

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In addition to the optical requirements, polymers should be selected in the design on the basis of their material and mechanical properties. Stress-strain analysis requires knowledge of elastic moduli at static or dynamic loading. In this report results of acoustic measurements of different types of optical polymers are presented. Dynamic Young's, shear and volume moduli, as well as Poisson's ratio were determined on base of ultrasonic investigations. Some optomechanical, thermo-optical, and thermo-mechanical parameters were calculated which characterise deflection at constant thickness and constant mass, resonant frequency, linear thermal expansion coefficients, as well as thermal stress due to temperature differences. Presented results were compared to literature data for principal polymers and optical glass types.

Keywords: optical polymers, dynamic elastic moduli, optomechanical parameters, ultrasound velocities

INTRODUCTION

Polymers are preferred materials not only in consumer but in high quality optics for their excellent transparency in visible (VIS) and near-infrared (NIR) region, much lower weight in comparison to glass, high impact resistance, configuration flexibility, safety and low production costs because of the injection moulding technology [1]. Most important optical characteristics of plastics are their refractive indices at selected wavelengths, spectral transmission, as well as the consequent dispersive parameters. Precise refractometric data of various types of polymers have been obtained by means of different measuring techniques at many wavelengths between 406 and 1320 nm [2, 3]. Polymer properties are substantially influenced by temperature variations. Refractive indices (RIs) have been measured in the diapason 0 ÷ 50 °C and the thermo-optic coefficients have been estimated. On base of experimental RIs linear and volume thermal expansion coefficients are then calculated.

Rigidity of solids ensures their impact and shatter resistance and is a factor that determines safety in applications. Usually elastic moduli are reported to characterise rigidity. In [4] we have reported measured velocities of longitudinal ultrasonic waves but elastic moduli were estimated on base of literature data for Poisson's ratio. Velocities of shear waves are very difficult to be measured and there are some materials for which they are not reported due to high attenuations of the shear mode [5]. In this report a special emitter-

receiver was used to measure velocities of shear acoustic waves and obtained values were compared to literature data. On base of the ultrasonic results the dynamic Poisson's ratio was determined and Young's, shear and volume elastic moduli are reported. Some optomechanical and thermo-mechanical characteristics are calculated.

EXPERIMENTAL

Refractive index measurements

We have studied various types of American, German and Japanese optical plastics including principal polymers as polymethyl methacrylate (PMMA), polystyrene (PS), polycarbonate (PC), copolymers styrene acrylonitrile (SAN) and methyl methacrylate styrene (NAS), many trademarks as CTE-Richardson, Zeonex E48R, Optorez 1330, NAS 21 Novacor, Bayer, and some development materials, produced by the USA Eastman Chemical Company (ECC). Bulk samples were measured by means of an one-arc second goniometric set-up with a lighting module consisting of 250 W halogen lamp, condenser system and Carl Zeiss metal interference filters for VIS and NIR spectrum. Laser illumination was used, too. RIs in the VIS and NIR region were obtained within accuracy of $\pm 3.9 \times 10^{-4}$ for goniometric measurements and $\pm 3.6 \times 10^{-4}$ in case of laser illumination [6]. In the VIS area results were compared to RI values obtained by the classical Pulfrich refractometer with its V-shaped prism and coincidence better than ± 0.001 was obtained. Influence of temperature on refraction and dispersion was investigated on base

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of Pulfrich refractometric measurements in the range 0÷50 °C with a step of 2 degrees below 10 °C and 5 degrees at higher temperatures at the wavelengths of the spectral lamps of the instrument. The measuring accuracy was $\pm 2 \times 10^{-5}$. Thin polymer films were measured by means of a three- and four-wavelength laser microrefractometer. RI values of films differ in respect to layer thickness and bulk sample results.

Ultrasonic measurements

Velocities of longitudinal and shear waves with magnitudes higher than 1000 m/s were determined by means of a Krautkramer flaw detector USM 35XS. For lower values of velocities, a Panametrics apparatus was used. A pulse-echo contact method with a Krautkramer CLF5 transducer (10 MHz) for longitudinal waves and a specially designed sensor Sonic (5 MHz) for shear waves was applied. Thicknesses of the samples were measured by a Mitutoyo caliper with an accuracy of ± 0.01 mm. Single or multiple reflected echoes were registered to determine time propagation of sound waves and then velocities were automatically calculated. The receiver filtering was adjusted to pass the broadband frequency range and the attenuation was adjusted to produce a non-saturating signal on the A-scan display. Different values of input electrical impedance and pulse power were used to increase the resolution.

RESULTS AND DISCUSSION

Optical characteristics

Selection of polymeric materials (PMs) in lens design is based on knowledge of their optical and material properties. Most important optical characteristics are spectral transmission, refractive index and dispersion. We have measured spectra of many thin thermoplastic polymer films and the results show transmittance better than 85 % in the range 400 – 2000 nm [7]. Some weak absorption bands between 1660 and 1700 nm have been registered and a considerable transmission decrease has been found beyond 2200 nm due to the absorption of the functional groups.

Obtained refractive data are substantial. Refractive indices of polymer bulk samples and thin films were measured at 22 wavelengths in the interval of 406 ÷ 1320 nm. Usually RIs at the d-line of the helium source ($\lambda_d = 587.6$ nm) at standard temperature of 22 °C according to the USA standard are reported and RI values at the mercury e-line ($\lambda_e = 546.1$ nm) at 20 °C are used in the continental European standard. Many laser

emission wavelengths have been used not only in VIS but in NIR range, too. Abbe number is another important input parameter in lens design which characterises dispersion properties of optical materials in the applied spectral range. In Table 1 RIs and Abbe numbers of several polymers at d-line in VIS and the middle wavelength 879 nm of the measuring NIR range are presented. Values of v_{879} are determined by the equation:

$$v_{879} = \frac{n_{879} - 1}{n_{703} - n_{1052}} \quad (1)$$

and are used in case of the goniometric RI measurements of bulk samples. When laser microrefractometers were applied to measure thin polymer films the Abbe number at mean value of 1010 nm for the measuring range from 700 to 1320 nm was calculated as: $v_{1010} = (n_{1010} - 1) / (n_{700} - n_{1320})$. Random RIs at any wavelength can be computed by means of the Cauchy-Schott approximation [2].

Table 1. Refractive indices and Abbe numbers of PMs.

Polymer	n_d	n_{879}	v_d	v_{879}
PMMA	1.4914	1.4835	59.2	96.7
PS	1.5917	1.5756	30.5	55.9
PC	1.5849	1.5683	29.1	54.6
SAN	1.5667	1.5526	35.4	66.6
Zeonex E48R	1.5309	1.5224	56.5	100.5
Optorez 1330	1.5094	1.5017	52.0	71.7
Bayer	1.5857	1.5698	30.0	54.8

As seen, low-refractive polymers have higher values of Abbe numbers. Dispersion in NIR spectrum is not essential in comparison to VIS light. Relative partial dispersions are maximal in the short-range diapason [6].

RIs for all of the studied polymers decrease with increasing temperature which is opposite to the behaviour of most glass types. Our results show nearly linear dependence $n(T)$ in the regarded interval 0 ÷ 50 °C. There are some slight variations in respect to the wavelength and the measuring temperature. On base of our refractometric results, the thermo-optic coefficient dn/dT (TOC) for each polymer was determined at the respective wavelength. TOCs at d-line for some of the PMs are included in Table 2. As seen, polycarbonate materials as PC of ECC and Bayer show highest thermal stability in respect to the values of TOC and linear thermal expansion coefficient α . Thermo-optic coefficients are related to the thermal linear expansion coefficients by the Lorentz-Lorenz equation and α values in the second column of

Table 2 are determined on base of measured RIs by the equation:

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

Thermal linear coefficient α is related to the volume expansion coefficient as $\beta \approx 3\alpha$ which plays an important role for the dimensional stability of optical elements.

Table 2. Thermal parameters of PMs.

Polymer	dn/dT , $\times 10^{-4} \text{ K}^{-1}$	α , $\times 10^{-4} \text{ K}^{-1}$	α_{lit} , $\times 10^{-4} \text{ K}^{-1}$	S , $\times 10^{-4} \text{ K}^{-1}$
PMMA	-1.2	0.7	0.5±0.9	-0.86
PS	-1.3	0.6	0.6±0.8	-0.95
PC	-1.0	0.5	0.6±0.7	-0.73
SAN	-1.1	0.5	0.65±0.67	-0.80
Zeonex E48R	-1.2	0.6	0.6	-0.87
Optorez 1330	-1.1	0.6	0.7	-0.79
Bayer	-1.1	0.5	0.65	-0.80

Calculated expansion coefficients are compared in the table to literature data α_{lit} [1, 8]. Good coincidence can be established. Slight variations are noticed for each thermoplastic brand which may be due not only to measuring accuracy but to polymerization and moulding conditions, additives as plasticisers, mould release agents, etc. The expansion coefficients α of optical glasses for the internationally used temperature range for comparison purposes (-20 °C; 300 °C) are rather small and vary from 4 to $16 \times 10^{-6} \text{ K}^{-1}$ [9]. This fact explicitly confirms that temperature aberrations arising from geometrical alteration of plastic elements is a significant problem in the design. Hybrid glass-plastic optics should be applied to increase temperature stability of the systems [7].

Another thermal parameter is the thermo-optical constant defined as:

$$S = \alpha(n - 1) + \frac{dn}{dT} \quad (3)$$

in case of a plane-parallel plate which is an approximate measure of the sensitivity of the material to radial gradients and quantifies the optical path difference with temperature. Negative values of S show the same tendency as TOCs. In comparison to most glass types [9], TOCs of polymer materials are negative and their absolute values are with about two orders of magnitude larger. Thus, maintaining focus over a large range of temperature is a significant problem in plastic optics.

Acoustic and optomechanical characteristics

Low weight of polymer elements is a great priority in comparison to optical glass types. In Table 3 results for obtained densities ρ of studied polymers measured by the hydrostatic weighing method are presented. Density values are from 2 to 6 times smaller than those of glasses.

As known, dynamic elastic moduli of materials are related to sound velocities in solid bodies. In Table 3 measured values of velocities of longitudinal c_l , and transverse c_t waves are given. A comparison to velocities published by other sources [5] is presented. As seen, there can be significant differences for one and the same named material in respect to the measuring method, as well as to the processing conditions of the polymeric brand. Literature data were found only for basic polymer types. Velocities of shear waves are difficult to be measured and are rarely cited. Results show that longitudinal waves travel faster than shear waves and velocities of longitudinal waves are approximately twice the value of shear waves. Given values of densities and velocities of longitudinal waves determine the material acoustic impedance which is defined as the product of both quantities. Knowledge of material impedances enables the study of propagation of sound waves and phenomena at sample interfaces.

Table 3. Densities and ultrasound velocities of PMs.

Polymer	ρ , kg/m^3	c_l , m/s		c_t , m/s	
		meas.	lit.	meas.	lit.
PMMA	1187	2745	2724 2730	1356	1377 1430
PS	1040	2388	2346 2340	1152	1157 1143
PC	1195	2234	2250 2268	906	948
SAN	1160	2561	–	1176	–
Zeonex E48R	1007	2535	–	1035	–
Optorez 1330	1202	2648	–	1209	–
Bayer	1204	2221	–	824	–

Propagation of sound waves in isotropic solid bodies is determined by the material elasticity moduli. In case of samples which transverse dimensions are much greater than the sound wavelength, there are simple relations between sound velocities and the material elastic parameters:

$$c_l = \sqrt{\frac{E(1 - \mu)}{\rho(1 + \mu)(1 - 2\mu)}} \quad (4)$$

$$c_t = \sqrt{\frac{G}{\rho}} \quad (5)$$

As it can be seen, the velocity of the longitudinal wave depends on Young's modulus E , also known as tensile modulus, and it is a measure of the stiffness of an isotropic material. Velocity of shear (transverse) wave is related to shear modulus G in Eq. (5). Static and dynamic methods are applied for determination of elastic moduli of solids but they differ substantially. Experimental conditions such as magnitude of the external load, as well as of loading rate significantly affect measuring accuracy of the results obtained by static stress – strain measurements. The dynamic methods with a sinusoidal load are also applicable and they have a relatively high accuracy. According to the frequency range, the dynamic methods are classified as: acoustic for frequencies below 10^4 Hz and ultrasonic for frequencies between 10^4 and 10^8 Hz. The dynamic methods are widely applied to study elastic properties and determine the elastic moduli of glasses and glass-forming liquids [9]. Young's modulus of optical glass ranges from 51 GPa (SF66) to 126 GPa (N-LASF21). As seen from Table 4, tensile moduli of PMs vary between 2.3 and 5.8 GPa and their elastic properties are rather different. Large values of E for glasses and glass-ceramics correspond to their ideal brittleness and are matched by an equally ideal elastic behaviour up to the breaking point.

In Eq. (4) μ is the Poisson's ratio which is another important material characteristic used in elastic analysis. It is calculated by:

$$\mu = \frac{1 - 2(c_t / c_l)^2}{2 - 2(c_t / c_l)^2}. \quad (6)$$

Generally, “stiffer” materials have lower Poisson's ratio than “softer” materials. According to the results in Table 4, Poisson's ratio of PMs varies between 0.34 and 0.42 while for glasses is in the range 0.21 to 0.25.

There are also some other useful relations – shear modulus G and bulk modulus K depend on μ and tensile modulus E by the expressions:

$$G = \frac{E}{2(1 + \mu)}, \quad (7)$$

$$K = \frac{E}{3(1 - 2\mu)}. \quad (8)$$

The bulk modulus can be determined by static compression experiments but also and more easily by measuring the velocity of longitudinal sound waves. Different models are applied and K is the only mechanical quantity that can be calculated by means of additive quantities according to the group contribution theory [10].

Table 4. Elastic characteristics of PMs.

Polymer	μ	E , GPa	G , GPa	K , GPa
PMMA	0.34	5.8	2.2	6.0
PS	0.35	3.7	1.4	4.1
PC	0.40	2.7	1.0	4.7
SAN	0.37	4.4	1.6	5.5
Zeonex E48R	0.40	3.0	1.1	5.0
Optorez 1330	0.37	4.8	1.8	6.1
Bayer	0.42	2.3	0.8	4.8

Dimensional stability of optical components is influenced by many factors as varying temperature, moisture, pressure, stress, etc. Low values of Young's moduli of PMs confirm easy deflection of plastic elements by external loading or intrinsic mass. Structural stability in respect to both static and dynamic load is a basic requirement for most optical systems and can be characterised by the following parameters: resonant frequency, deflection at constant thickness, deflection at constant mass and mass at constant deflection [8]. All these quantities are functions of density and Young's modulus and are used to compare structural efficiency of materials [11]. Results for these characteristics are presented in Table 5. Deflection at constant thickness indicates the self-weight deflections of plastic elements with identical geometry and equal thickness. The figure of merit of this parameter is the specific stiffness E/ρ . Lowest possible ratio of ρ/E is preferred in order to minimize deflection. In the case where the deflections of components of equal mass but independent thickness are to be compared, deflection at constant mass, characterised by the ratio ρ^3/E , serves as an appropriate parameter and small values are preferred. This factor should be compared if mass is a specified parameter of the optical element and minimum self-weight deflection is desired [11].

Table 5. Optomechanical parameters of PMs.

Polymer	$\rho/E, \times 10^{-7}$ kg/(N.m)	ρ^3/E kg ³ /(N.m ⁷)	$(E/\rho)^{1/2}$ $\times 10^3$ m/s	σ , MPa
PMMA	2.0	0.3	2.2	30.9
PS	2.8	0.3	1.9	17.1
PC	4.3	0.6	1.5	11.5
SAN	2.6	0.4	2.0	17.3
Zeonex E48R	3.3	0.3	1.7	15.1
Optorez 1330	2.5	0.4	2.0	22.8
Bayer	5.2	0.7	1.4	10.0

For most applications, the resonant frequency of the optical element is an important figure of merit and is characterised by $(E/\rho)^{1/2}$ since natural frequency is proportional to the square root of the specific stiffness. High values of this parameter are appropriate for large plastic optical components with protruding parts, in order to get high resonant frequencies [8].

Thermal stress σ is another quantity used in polymer optics which combines mechanical and thermal properties of materials. This is the internal stress generated in a plastic piece due to a specified temperature difference ΔT . It can be estimated in first approximation using the following formula:

$$\sigma = \frac{E\alpha\Delta T}{1 - \mu} \quad (9)$$

The values in Table 5 represent the thermal stress factor, indicating stress over a temperature change ΔT of 50 °C which corresponds to usual variations of service temperatures in respect to environmental conditions. Results for PC and Bayer confirm their greatest stability in respect to temperature. Polycarbonate materials also have broadest service interval from -137 to +130 °C and possess more stable thermo-mechanical and physical-chemical properties in the limits from -30 °C to +125 °C [6]. The Japanese brand Zeonex E48R is a thermally stable polymer, too. Most of PMs, have much lower service temperature limits, in some cases no higher than about 60 °C. The maximal limit may approach 250 °C for some of the fluoropolymers.

As seen from Eq. (9), thermal stress is proportional to Young's modulus and to the coefficient of thermal expansion and reciprocal to the Poisson's ratio. Therefore, materials with a large thermal expansion coefficient and Young's modulus value are very sensitive to thermal shock and have to be processed very carefully. In comparison to glass, thermal stresses in PMs are lower because of

the small values of Young's modulus and higher Poisson's ratios though thermal expansion coefficient is larger [9]. Generally, 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. All of studied PMs in this report are thermoplastic.

Thermal stress is especially useful in coating of PMs with inorganic layers to compensate their imperfections as low abrasion or chemical resistance, hygroscopicity, etc. Since the temperature rises gradually during film deposition, large differences between the stress levels at the interface between the coating and the polymer occur and generated stress may be as high as 5–20 MPa/K [8].

CONCLUSION

Refractometric and ultrasonic measurements were accomplished to reveal material and optomechanical characteristics of PMs which are important in lens design. Though polymers have excellent transmission in VIS and NIR region, they have a much more restricted range of refractive index values between 1.49 and 1.59 at d-line (Table 1). There are some PMs with RIs of 1.47 (e.g. cellulose) and high refractive polymers of HOYA company and MITSUI Chemicals, etc. with $n_d > 1.7$ [6]. Results of RIs and Abbe numbers in NIR region are useful for the design of night vision optical systems. Presented values show lower dispersion of PMs in comparison to glasses in this part of the spectrum.

Thermal properties of PMs are studied on base of RI measurements in the interval between 0 and 50 °C. Temperature instability of refractive and dispersive properties of polymers should be regarded in the design of optical elements and devices. The large thermo-optic coefficients, linear and volume expansion coefficients and thermo-optical constants (Table 2) as well as thermal stress values (Table 5) result in arising of significant thermo-optical aberrations which should be minimised in the final construction by proper selection of optical glass-plastic and housing materials. On the other hand, thermal sensitivity of PMs may favour their utilization for dynamic control of refractive index in active waveguide components of photonic devices [7].

Dynamic elastic moduli and optomechanical characteristics of PMs are estimated on base of measured velocities of longitudinal and transverse ultrasonic waves. Comparison to literature data shows differences due to measuring method and

technology specifications of the polymer brands. In many cases published values are merely indicative for a given polymer in respect to the sample shape. Material parameters as moduli of elasticity, Poisson's ratio (Table 4), as well as parameters as resonant frequency, deflection at constant thickness, deflection at constant mass and mass at constant deflection which are responsible for structural stability (Table 5) are presented. Comparison to glasses gives higher values for factors of deflection at constant thickness and constant mass of PMs and lower values for the resonant frequency which result in lower structural stability of plastic components. PMs are suitable for optical fiber fabrication, because of their higher flexibility.

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