Temperature dependence of refractive characteristics of optical plastics

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Abstract. In this study we investigate the variation of refractive characteristics of optical plastics with temperature in the range of 10 to 50 °C. We have measured the indices of several optical polymers as Optorez 1330, Zeonex E48R, Polymethyl methacrylate, S-low styrene and Bayer by means of the deviation angle method. The obtained refractive index data is presented at five standard spectral lines in the visible region. A decrease of refractive index values with increasing temperature is observed. Dependence on measuring wavelength is also noticed. We have calculated the temperature coefficients of refractive indices of the studied optical plastics. Charts of refractive index of some of the materials versus temperature are presented. Temperature dependence of dispersion curves based on Cauchy-Schott’s approximation and Abbe numbers is also considered.

1. Introduction
Application of optical plastics (OPs) in the design of optical elements and devices requires the knowledge of their refractometric and dispersive characteristics. We have studied more than twenty types of plastic materials including principal and some new development polymers. Refractive index data has been obtained for both bulk and thin film samples [1-3]. Published refractive characteristics have been presented mainly at reference temperature of 20 °C which conforms to the European measuring standard [4] while the USA standard requires measuring temperature of 22 °C [1]. Usually, the most important operating temperature range for optical devices is between 10 and 40 °C though extreme conditions may sometimes exceed this interval.

Thermal properties of polymers are rather different compared to glasses. Service temperature limits for OPs (60 to 250 °C) are substantially less than for optical glasses (400 to 700 °C). The thermal expansion coefficient is about one order of magnitude greater than glass. For example, the linear thermal expansion coefficient of Acrylic has average value of \(7\times10^{-5} \text{ K}^{-1}\) [5] while for the N-BK7 glass the corresponding value is \(0.71\times10^{-5} \text{ K}^{-1}\) [4]. Another important parameter for optical materials is the variation of refractive index with temperature \(dn/dt\). The change of this parameter depends on two counteracting effects: the change in density caused by positive coefficient of thermal expansion and the increase in polarizability with temperature. Evaluation of \(dn/dt\) is possible by differentiation of the Lorentz-Lorenz equation with respect to temperature. The temperature gradient of refractive index \(dn/dt\) is referred in literature as a thermo-optic coefficient [6] or temperature coefficient of refractive index [4]. The absolute values of \(dn/dt\) of polymer materials are with orders of magnitude larger than
those for optical glasses and exhibit usually negative deviations compared to the positive thermo-optic coefficients for most of glasses. For example, the change of refractive index with temperature for Acrylic materials is approximately $-8.5 \times 10^{-5} \, \text{K}^{-1}$ [7] and for the N-BK7 glass with analogous refraction, the value is $1.6 \times 10^{-5} \, \text{K}^{-1}$ [4]. Though the analysis of $dn/dt$ is an essential issue for optical plastics’ applications in photonic devices and optical fibre communication systems, the literature data on their thermo-optic properties of OPs is rather limited.

In this paper we present measured refractive indices of some plastic materials at different temperatures in the range between 10 and 50 °C. Five spectral lines of illumination in the visible spectral region were utilized. Temperature variation of the refractive characteristics of the studied OPs had been analysed.

2. Measuring the refractive indices of optical plastics

2.1. Equipment and sample preparation

Refractive index measurements were carried out using the Carl Zeiss Jena Pulfrich refractometer PR2 with an accuracy of $2.10^{-5}$. The illuminating system consists of three spectral lamps: a mercury source with a green e-line 546.07 nm and a blue g-line 435.83 nm, a helium source for the yellow d-line 587.56 nm and a hydrogen source for the blue F-line 486.13 nm and red C-line 656.27 nm [8]. We have used the V-type SF3 prism (VoF3-prism) which is suitable to the shape of the examined samples. The VoF3-prism is produced as a glass block assembled into a massive metal body with thermostatic housing which assures stable temperature during the measuring. Besides that, the prism cap is made of stainless steel and has a mirrored internal surface, so temperature fluctuations are cut down and the matching liquid cannot evaporate. Measuring temperature was maintained by a MLW Thermostat U4 with waterbath, made in Germany. Water from the reservoir circulated through the prism block and temperature was monitored by a thermometer with accuracy of 0.2 °C.

Measuring with the VoF3 prism requires two mutually perpendicular surfaces of the examined solid body. The examined OPs samples were prepared as injection moulded plates with thickness varying from 1.5 mm to 2.5 mm and two adjacent surfaces were well polished to obtain a good refractometric data. We used a saturated aqueous solution of zinc chloride ($n_e = 1.51$), silicon oil ($n_D = 1.56$) and a saturated water solution of KHgJ$_3$ ($n_e = 1.73$) as a contacting liquid depending on the refraction of the examined material.

We have measured the transmittance of all examined plastic samples using the spectrophotometer SPECORD UV-VIS (VEB Carl Zeiss, Jena). The obtained results showed that these polymer materials are transparent in the considered spectral range, a normal dispersion is exhibited [1, 2] and the extinction coefficient can be neglected.

2.2. Principle of measurement

Determination of refractive index by means of the VoF3 prism of the Pulfrich refractometer is based on measurement of the deviation angle. The plastic sample is placed and covered into the prism (figure 1) and the desired temperature is adjusted. The collimated beam from the lighting system illuminates monochromatically the prism block and refracts by the examined material. The deviation angle $\gamma$ is determined and the refractive index $n_d$ of the examined plastic is calculated as follows:

$$n_d = \left( N^2_d - \cos \gamma (N^2_L - \cos^2 \gamma)^{1/2} \right)^{1/2}$$

where $N_L$ is the refractive index of the VoF3 prism. The value $N_d$ of the SF3 glass is calculated by the data published in [8] at standard spectral wavelengths applying our program OptiColor [2] involving the Caushy–Schott’s dispersion approximation. Each of the obtained results was corrected by involving the value of the temperature coefficient of the SF3 glass at the corresponding wavelength.
2.3. Measuring results
We have obtained five different OPs, namely: polymethyl methacrylate (PMMA) and S-low styrene produced by Eastman Chemical Company, and some trade-marks as Zeonex E48R®, Optores1330® and Bayer®. All of the samples were measured at five spectral lines at nine different temperatures in the interval between 10 and 50 °C which match the usual service temperatures of optical devices used in practice. The results for two of the samples are plotted in figure 2. A decrease of refractive indices with increasing temperature has been established for all of the samples. In figure 2-a) the results for the PMMA sample are presented. Graphs for all of the illuminating wavelengths show some nonlinearity especially at lower temperatures. Similar dependence has been obtained for the rest of the samples except for the Zeonex material which graph is almost linear – figure 2-b).

![Figure 1. Deviation of the illuminating beam in the sample.](image)

![Figure 2. Temperature dependence of refractive index for a) PMMA; b) Zeonex E48R.](image)

3. Discussion and conclusions

3.1. Variation of refractive index of optical plastics with temperature
Refractive indices of polymers are affected by temperature. Furthermore, the change of refractive index as a function of temperature depends on the specific material. For a better comparison among
studied plastics, these changes are evaluated as \( \Delta n(t) = n(t) - n_{20} \), where \( n_{20} \) is the measured refractive index at reference temperature of 20 °C which conforms to the European measuring standard. The obtained results for the e-line are plotted in figure 3. At lower temperatures (less than 20 °C) changes of refractive index are smaller in comparison to the values obtained at 40 °C or 50 °C. Greatest variation of refractive index is established for the S-low Styrene sample and lowest for the Bayer material. The dependence of \( \Delta n(t) \) for the PMMA and Zeonex E48R is quite similar at temperatures higher than 20 °C, and at lower temperatures the PMMA curve coincides with the Optorez 1330 and Bayer graphs. Nonlinearity of the presented curves is noticed especially for the Bayer, Optorez 1330 and PMMA. Almost a linear graph is obtained again for the Zeonex E48R.

![Figure 3. Changes of refractive index \( \Delta n \) at e-line with temperature.](image)

It is interesting to note that the magnitude of \( \Delta n \) in the considered temperature interval is of similar order to the refractive index deviation \( \Delta n \) due to dispersion. For example, in case of the S-low Styrene material the \( \Delta n \) value equals \( \Delta n_\lambda \) in the spectral range between 560 and 700 nm. In case of the high refractive Bayer polymer which shows much greater dispersion than rest of the plastics, lowest change \( \Delta n \) with temperature is established. Analysis of dispersion properties of more than twenty OPs has been published in our previous papers [2, 9].

### 3.2. Temperature coefficients of refractive indices

Linear approximation of the temperature dependence of refractive index is possible only in comparatively narrow temperature intervals. In figure 4 computed temperature coefficients \( dn/dt \) at e-line of the examined samples are presented. The obtained results for the Optorez 1330, Zeonex E48R, S-low Styrene and PMMA show that two temperature ranges in the considered interval can be distinguished. In case of the Bayer material the value of \( dn/dt \) is constant between 10 and 30 °C and drops down in the interval between 30 and 50 °C. The magnitudes of \( dn/dt \) for the examined samples are close and for the e-line they vary from 0.8\times10^{-4} for Bayer to 1.4\times10^{-4} for S-low Styrene. In case of the Zeonex plastic the \( dn/dt \) value is almost constant for the entire measuring temperature region.

The thermo-optic coefficient depends also on the wavelength. It decreases with increasing wavelength but the change of magnitude of \( dn/dt \) is considerably smaller than the deviation of the refractive index due to the wavelength variation \( dn/d\lambda \). Our results show that the variation of the
thermo-optic coefficient with wavelength in the visible spectrum has absolute values between $4 \times 10^{-6}$ and $2 \times 10^{-5}$. In table 1 some of the obtained thermo-optic coefficients at two wavelengths are presented.

| Optical plastics       | $d_n/dt \times 10^{-4}$ (K$^{-1}$) |
|-----------------------|-----------------------------------|
|                       | g-line (10 $\pm$ 20 $^\circ$C) | d-line (20 $\pm$ 50 $^\circ$C) | g-line (20 $\pm$ 50 $^\circ$C) |
| PMMA                  | -1.00                            | -0.90                           | -1.32                           |
| Optorez 1330          | -1.00                            | -0.96                           | -1.22                           |
| S-low Styrene         | -1.50                            | -1.40                           | -1.70                           |

3.3. Temperature influence on dispersion

The variation of refractive index values with temperature alters the dispersion characteristics of OPs. We have used the Cauchy-Schott approximation usable in case of normal dispersion and our program OptiColor for evaluation of the results. Dispersion curves of the Optorez 1330 material in the VIS range obtained at four of the measuring temperatures are presented in figure 5.

**Figure 4.** Change of the thermo-optic coefficient of optical plastics with temperature.

**Figure 5.** Dispersion curves of Optorez 1330 at different temperatures.

**Figure 6.** Change of the Abbe numbers $\Delta v_d$ as a function of temperature.
A change of the dispersive behaviour of the materials is noticed. As it can be seen a greater dispersion is observed at higher temperatures in the VIS region. Such dependence is observed for all of the studied materials. Usually the Abbe number is used to characterize the dispersive properties of optical materials. We have calculated $n_d$ at all measuring temperatures. A decrease of the $n_d$ values with increasing temperature is observed for all investigated OPs. For a better comparison among the results changes of the Abbe numbers are calculated in respect to the value at 20 °C: $\Delta n_d(t) = n_d(t) - n_{d_{20}}$.

Figure 6 illustrates variations of the Abbe numbers for the examined OPs. Deviation of $n_d$ in respect to $n_{d_{20}}$ also reveals nonlinearity. Lowest variation of the Abbe number, respectively dispersion, with the temperature is observed again for the Bayer material and greatest for the PMMA polymer.

3.4. Conclusions

Temperature dependence of refractive characteristics of five plastic materials has been investigated in the interval between 20 °C and 50 °C. Refractive indices of the polymer samples have been measured at 9 measuring temperatures at five spectral lines using the deviation angle method. A decrease of refractive indices with increasing temperature is established for all of the OPs. Nonlinearity of the obtained $n(t)$ curves at all measuring wavelengths is noticed (figure 2). Only the Zeonex material exhibits a linear dependence of $n(t)$ in the entire temperature interval. A better comparison of refractive index changes with temperature is achieved by calculation of $\Delta n(t)$ in respect to the indices at reference temperature of 20 °C (figure 3). The S-low Styrene shows greatest deviation of $\Delta n(t)$ and smallest value is obtained for the Bayer material. Changes of refractive index with temperature could be very substantial. For the S-low Styrene sample the value of $\Delta n(t)$ is almost equal to the change of refractive index due to dispersion beyond 560 nm in the VIS region.

Thermo-optic coefficients of the examined materials have been calculated. Only the Zeonex material has almost a constant value in the entire measuring interval. For the rest of materials more complex behavior of the thermo-optic coefficients is noticed. Their values could be estimated for much narrower temperature intervals (figure 4). A polynomial interpolation of $dn/dt$ dependence is possible when larger measuring temperature intervals are demanded.

Influence of temperature on dispersion properties of OPs is studied. The shape of dispersion curves at different temperatures varies substantially (figure 5). Abbe numbers values decrease with increasing temperature (figure 6). Greatest deviation of $\Delta n_d$ in respect to the value at 20 °C is observed for the PMMA plastic.

Our results show that temperature dependence of refractive characteristics of OPs can not be neglected in the design and construction of optical elements and devices when required service temperatures vary significantly. This dependence is specific for each optical polymer. Among studied materials the Bayer plastic shows best temperature stability of its refractive and dispersive properties. The Zeonex material could be also recommended for its almost constant value of the thermo-optic coefficient.

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