Thermal variations of refractive and dispersive parameters of optical polymers

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Abstract. Temperature dependence of refractive and dispersive parameters of principal and some trade-marks of optical polymers has been studied. Refractive indices have been measured at several spectral lines in visible range at different temperatures between 0 and 50 °C. Thermo-optic coefficients have been determined and compared. We used the single-oscillator model of Wemple and DiDomenico to calculate oscillator energy and dispersion energy. These two quantities are related to the structure, charge distribution and chemical bonding of the material. Correlation to the dispersion properties of polymers is established. Variations of the two oscillator parameters with temperature are studied.

1. Introduction
Optical polymers (OPs) are widely used in a variety of industries for their low cost and weight, high impact resistance and ability to integrate proper mechanical and optical features [1, 2]. Great economies are possible through usage of polymers for reproducing aspheric and other complex geometric surfaces, integrated components with non-circular apertures or elements with very small dimensions, which are costly to produce in glass. Polymer fibers and waveguides have attracted extensive attention for their applications in telecommunication and data communication. Active optical polymer components as switches, attenuators, amplifiers, etc. are applied in compact high-density photonics circuits.

Thermal instability of OPs is, however, an essential restriction in their applications. In comparison to glasses, they show higher variation of refractive index with temperatures d\(n/dT\), large thermal expansion and limited service temperatures [1]. On the other hand, the high sensitivity of refraction to temperature favors utilization of OPs for dynamic control of refractive index in active photonic devices as switches, attenuators, modulators, amplifiers, controllers, waveguide components, etc. [3].

In this study, thermal variations of refractive and dispersive parameters of polymethyl methacrylate (PMMA), polycarbonate (PC), polystyrene (PS), styrene acrylonitrile (SAN), alicyclic methacrylate copolymer Optorez 1330 (Hitachi Chemical Co., LTD.), cyclo olefin polymer Zeonex E48R and styrenic material with low molecular weight (S-low styrene) are investigated. All of these materials are high transparent amorphous thermoplastics. On base of refractive index measurements at several spectral lines in the visible range, oscillator and dispersion energies, introduced by Wemple and DiDomenico [4], are determined. Refractive indices have been measured in an extended thermal interval from 0 to 50°C in comparison to our previous investigations [5]. Temperature dependence of oscillator and dispersion energy is examined.
2. Temperature measuring results and evaluation of optical parameters

2.1. Experimental

Polymers samples have been measured by the Carl Zeiss Pulfrich refractometer PR2 with its V-shaped prism (VoF3 prism). Plates with thickness varying from 2.5 to 5.5 mm and some cubic specimens of the American Eastman Chemical Company with two polished, mutually perpendicular faces have been used. Refractive indices of OPs have been determined on the principle of the deviation angle at emission wavelengths of the spectral lamps of the PR2 instrument in the visible (VIS) region: g-line (435.83 nm), F-line (486.13 nm), e-line (546.07 nm), d-line (587.56 nm) and C-line (656.27 nm). The instrumental error is $\pm 2 \times 10^{-5}$ [5]. The VoF3 prism is assembled into a massive metal body with thermostatic housing. Measuring temperature in the region from 0 to 50°C is maintained by a MLW Thermostat U4 with a water bath, made in Germany. Water from the reservoir circulates through the prism block and temperature is monitored by a thermometer with an accuracy of 0.2°C. At lower temperatures chilling liquids have been used.

All of the samples of studied OPs were measured at selected spectral lines at a 2 degree increment below 10°C and the step was 5 degrees at higher temperatures. Reading of the angle of deviation at each temperature has been accomplished after a delay of time from five to ten minutes in respect to sample thickness until thermal equilibrium was reached. Results were corrected taking into account its glass thermo-optic coefficient at the corresponding wavelength.

2.2. Temperature dependence of refractive indices

Obtained results show a decrease of refractive indices with increasing temperature for all examined OPs. Almost linear dependence is observed, though there are slight variations in respect to the wavelength and measuring thermal range. Results at d-line are plotted in figure 1 for low (figure 1a) and high (figure 1b) refractive polymers.

![Figure 1](image)

Figure 1. Temperature dependence of refractive indices of: (a) low refractive; (b) high refractive OPs.

Variation of refractive index $n$ with temperature $dn/dT$ is known in literature as thermo-optic coefficient (TOC). On base of measured results TOCs of studied polymers are determined by the slope of the graphs and obtained values are included in table 2. As it seen, TOCs of plastics are close and vary from $-1.0 \times 10^{-4}$ K$^{-1}$ for the PC sample to $-1.6 \times 10^{-4}$ K$^{-1}$ in case of S-low styrene. In comparison to glasses, the thermo-optic coefficients of OPs are always negative and their absolute values are with one or two orders of magnitude higher. There are some polymers, e.g. Bayer polycarbonate, which linearity occurs in a narrower temperature interval [6]. Estimation of TOC is then limited to the corresponding linear interval.
Negative values of TOCs for polymers are predictable. Evaluation of $dn/dT$ is possible by differentiation of Lorentz-Lorenz equation with respect to temperature [7]. The sign of the obtained expression depends on the sign of the difference between the temperature coefficient of the molecular polarisability and the thermal volume expansion coefficient. Since for polymers this volume coefficient is one or two orders of magnitude larger than the temperature coefficient of the molecular polarisability, polymers have always negative thermo-optic coefficients.

As we see, temperature is one of the most critical factors in application of OPs that affect not only optical but dimensional parameters of optical systems and cause thermo-optical aberrations. Thermal linear $\alpha$ and volume $\beta \approx 3\alpha$ expansion coefficients as well as thermal “glass” constants were estimated at different spectral lines in [8] again on base of the Lorentz-Lorenz equation. Our investigations on influence of temperature on dispersion of OPs show some alteration of Abbe numbers and dispersion curves depending on the type of material. In many cases chromatic correction of optical components are slightly influenced by temperature change [9]. Changes in the refractive index lead to differences in the optical path length and therefore to wavefront errors that are evaluated by the thermo-optical constant $G$. In case of a plane-parallel plate $G = \alpha(n-1) + dn/dT$. It is an approximate measure of the sensitivity of the material to radial gradients and is a responsible factor for image degradation.

2.3. Single-oscillator energy parameters

Wemple and DiDomenico developed the concept of a single-oscillator of the electronic dielectric constant [4]. The model can be used to describe refractive index dispersion at photon energies below the interband absorption edge. In case of the single-oscillator description, the frequency-dependent dielectric constant is used to define two energy parameters $E_o$ and $E_d$:

$$n^2 = 1 + \frac{E_o E_d}{E_o^2 - (h\nu)^2},$$

where $\nu$ is the photon frequency, $h$ is the Planck constant. Oscillator energy $E_o$ is the average excitation energy for electronic transitions, and $E_d$ is the dispersion energy which is a measure of the average strength of interband optical transitions.

Electronic structure of realistic models of polymers is difficult to be obtained but it is influenced by its chemical repeat unit and the structural arrangement of its atoms. On the one hand, the large-scale morphological disorders (due to semicrystalline or amorphous phases), present in a polymer, can alter its electronic structure by introducing band tail energy states, band edge position shifts, and band gap reductions [10]. Similarly, additives, ultraviolet (UV) and ionization radiations, as well as temperature, moisture and chemical treatment affect energy parameters [11-13].

According to equation (1), it is possible to determine the energy parameters of the oscillator by plotting $(n^2 - 1)/n$ versus $(h\nu)^2$. Values of $E_o$ and $E_d$ are obtained from the slope and intercept on the vertical axis of figure 2. Results are presented in table 1. Refractive indices at d-line $n_d$ and Abbe numbers $\nu_d$ of studied polymers are also included. OPs are set in order of decreasing values of $\nu_d$ which corresponds to growing dispersion. As it can be seen, an opposite tendency is observed for parameters $E_o$ and $E_d$ except for the Zeonex dispersion energy which is higher than that of PMMA. Low dispersive materials in VIS range have greater $E_o$ values which is connected with the location of the UV absorption bands. For example, the UV cut-off of PC is at 380 nm while for the PMMA material this cut-off occurs between 280 and 360 nm for different types of these materials [6]. Though PS is the most refractive polymer, its dispersion is less in comparison to PC and in consequence the oscillator energies are higher.

Oscillator energy is connected to the energy band gap $E_g$ by the relation $E_o \approx pE_g$ where parameter $p$ characterizes the optical absorption process and is theoretically equal to 2, 1/2, 3 or 3/2 for indirect allowed, direct allowed, indirect forbidden and direct forbidden transitions, respectively [14]. Our results show good coincidence with the literature data of $E_g$ for PMMA and PS [10]. For example, in our case $E_o$ of the PMMA is about 12 eV which is close to the double value of 5.6 eV in [13].
of PS, the approximation is better since band gap energy is given to be 4.4 eV [15]. According to [10], monomer chemistry and morphological disorder cooperate to create localized energy states and the formation of shallow/deep trap depths near the band edges, but tacticity has little effect on the band structure.

![Figure 2. Refractive index factor 1/(n² - 1) against (hv)² of OPs at 20 °C.](image)

**Table 1.** Refractive indices, Abbe numbers, oscillator and dispersion energies of OPs at 20°C.

| OP             | n<sub>d</sub> | v<sub>d</sub> | E<sub>o</sub>, [eV] | E<sub>d</sub>, [eV] |
|----------------|--------------|--------------|-------------------|-------------------|
| PMMA           | 1.4914       | 59.2         | 12.05             | 14.30             |
| Zeonex E48R    | 1.5309       | 56.5         | 11.86             | 15.43             |
| Optorez 1330   | 1.5094       | 52.0         | 11.49             | 14.19             |
| S-low styrene  | 1.5162       | 44.9         | 10.69             | 13.34             |
| SAN            | 1.5667       | 35.4         | 9.39              | 12.96             |
| PS             | 1.5917       | 30.5         | 8.81              | 12.73             |
| PC             | 1.5849       | 29.1         | 8.58              | 12.19             |

Energy oscillator parameters of studied polymers have been calculated at different temperatures in the region 0÷50°C. Constant value of TOC of each polymer in the measuring interval has been assumed. Results are plotted in figure 3 for PMMA and PS. Both energies E<sub)o</sub> and E<sub>d</sub> decrease with increasing temperature but the deviation is higher for dispersion energies (figure 3 b and d). For the rest of OPs a similar dependence is observed (table 2). According to calculated values of TOCs, there is no relation between thermal deviation of refractive indices and dispersion parameters of polymers. Obviously, thermal properties depend exclusively on the type of the material. As seen, the most dispersive polymer PC in our series (table 1) has lowest TOC value while PMMA and PS have close thermal coefficients, though represent different class polymer types. As known, acrylic materials correspond to the crown type glasses and PS and PC to flints.

Changes of energy oscillator parameters with temperature have been calculated and values are given in table 2. Higher values are observed for the dispersion energies. Though OPs are set in order of increasing dispersion, variation of temperature gradients of both energies is observed. Highest \(dE_o/dT\) and \(dE_d/dT\) values are obtained for the S-low styrene which corresponds to its highest TOC. For lowest oscillator energy values of PC minimal thermal variations are established, including TOC.
Table 2. Thermal variation of refractive index and optical parameters of OPs.

| OP               | \( \frac{dn}{dT} \), \( \times 10^4 \) [K\(^{-1}\)] | \( \frac{dE_o}{dT} \), \( \times 10^4 \) [eV.K\(^{-1}\)] | \( \frac{dE_d}{dT} \), \( \times 10^4 \) [eV.K\(^{-1}\)] |
|------------------|---------------------------------|---------------------|---------------------|
| PMMA             | –1.2                            | –11.9               | –56.0               |
| Optorez 1330     | –1.1                            | –10.0               | –49.3               |
| Zeonex E48R      | –1.2                            | –11.8               | –56.3               |
| S-low styrene    | –1.6                            | –13.2               | –66.6               |
| SAN              | –1.1                            | –7.0                | –40.9               |
| PS               | –1.3                            | –7.4                | –45.6               |
| PC               | –1.0                            | –5.6                | –34.0               |

The negative values of \( \frac{dE_o}{dT} \) correspond to the decrease of \( E_g \) with increasing temperature. The same dependence is observed for most semiconductors which can be explained with the change of electron energies with the volume (lattice thermal expansion) and influence of temperature on electron–phonon interactions [14]. In case of polymers, thermal alterations of their electronic structures also occur introducing band edge position shifts.

The dispersion energy is related to the charge distribution within each unit cell (chemical repeat unit) and is a quantity closely related to chemical bonding [4]. The smaller values of \( E_d \) correspond to the weak chemical bonding. According to [16], temperature dependence of \( E_d \) might be more influenced by lattice vibrations than by lattice expansion in case of solid state. For thermoplastics,
with increasing temperature intense thermal oscillations of atoms, molecule elements and chains occur and the balance positions of the oscillation segments are moving apart.

3. Summary and conclusions

In this report refraction and dispersion of optical polymers in respect to temperature are studied in the measuring interval from 0 to 50 °C. Our results for the principal and some trademarks of plastics show almost linear decreasing refractive index values with increasing temperature (figure 1). There are some polymers as Bayer which linearity occurs in a narrower temperature range. Therefore, temperature dependence of each material should be separately studied and TOCs should be carefully estimated for the adequate temperature interval.

Obtained TOCs are negative for all studied polymers while optical glasses may have positive as well as negative TOC values. This fact is important in the design of hybrid plastic-glass optical systems with reduced temperature aberrations. Passive athermalization of refractive lens systems should be designed with stable performance for the specified spectral range and service temperatures using the conditions for minimizing the thermal and achromatic defocuses by proper combination of the optical and housing materials. In table 2 obtained TOCs confirm that their values are not related to dispersion of the material (table 1). PC is the most dispersive polymer but its TOC is with lowest value. The PS polymer is another high refractive material with significant dispersion but its gradient is comparable to that of acrylics and cyclo olefins.

In the region of normal dispersion the single-oscillator model of Wemple and DiDomenico (equation 1) is applied. Its accuracy is lower than the Cauchy-Schott and Sellmeir’s approximations which give accuracy better than $10^{-5}$ if 6 dispersion coefficients are used [6]. In equation 1, single oscillator energy $E_o$ and dispersion energy $E_d$ are introduced which are related to the structure, charge distribution and chemical bonding of the material. In table 1 given values of $E_o$ and $E_d$ at 20 °C are determined on base of refractive index measurements at five spectral lines. Variation of energy parameters with temperature is studied. Both decrease with increasing temperature but values of $\frac{dE_d}{dT}$ are greater than $\frac{dE_o}{dT}$ (figure 3 and table 2). Correlation to the dispersion properties of OPs is established. Our results show that low dispersive materials have higher oscillator energy values.

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