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Thermo-optic coefficients of polymers for optical waveguide applications

Zhiyi Zhang *, Ping Zhao, Peng Lin, Fengguo Sun

Photonic Systems Group, Institute for Microstructural Science, National Research Council Canada, M-50, 1200 Montreal Road, Ottawa, Ont., Canada K1A 0R6

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Abstract

Polymers with diverse chemical structure were evaluated to establish an empirical relationship between their thermo-optic coefficients (dn/dT) and coefficients of thermal expansion (α) according to the Lorentz–Lorenz equation. The results have showed that, regardless their chemical structure and T_gs, all the evaluated polymers follow a single linear relationship between their dn/dT values and α values with the slope $(\delta n/\delta T)_\rho$ equal to 0.56 and the interception $(\rho\delta n/\delta\rho)_T$ equal to -3.7×10^{-6}. The relationship can be used to estimate the dn/dT value of a given polymer using its α value, which is widely available and can be easily measured using TMA and other conventional equipment, and the estimated dn/dT value is useful for developing polymers and evaluating device performance in optical waveguide applications.

Keywords: Thermo-optic coefficient; Optical waveguides; Coefficient of thermal expansion

1. Introduction

Planar polymer waveguides have attracted extensive attention for their applications in telecommunication and data communication [1,2], because of the low cost, simple processes, and high thermo-optic coefficient of polymers. Various photonic devices, such as the thermal optical switches (TOS) [3,4], variable optical attenuators (VOA) [4–6], optical couplers/splitters [7], and arrayed waveguide gratings (AWG) [8,9], were fabricated using polymer waveguides. While the basic optical properties of polymers, including optical loss, refractive index, birefringence, are critical for using polymers to fabricate quality waveguide devices, the thermo-optic coefficient of polymers plays a vital role in determining device's performance. A large thermo-optic coefficient favors the reduction of power consumption for both the TOS and VOA because it corresponds to a small temperature change and thus a small power input for causing the necessary change in the refractive index of polymer waveguides, which is required for optical switching or optical attenuation. Our research on the polymer/silica hybrid VOA showed that, when the coefficient of the cladding polymer was changed from -1×10^{-4} to -6×10^{-4} ($^\circ C^{-1}$), the power consumption of the device was reduced by 80% to settle at 10 mW/ch [10]. Only when the power consumption is reduced to a certain level, will the fabrication of the high channel-counting TOS and VOA, and the integration of the devices with AWG on one chip become practical. A large thermo-optic coefficient, on the other hand, is a disaster for AWG because its wavelength shifts with the change in the refractive index of waveguides and the associated wavelength shift is very sensitivity to temperature variation in this circumstance. Minimizing the coefficient is, in fact, necessary for fabricating AWG using polymers.

While the thermo-optic coefficient of polymers is so important for controlling device performance and should be properly selected for specific devices, there is extremely limited information about the thermo-optical coefficients of various polymers, possibly, because the measurement of thermo-optical coefficient requires dedicated equipment, which is usually unavailable to polymer laboratories and is often times unavailable to many optical laboratories, and the sample preparation for the measurement is very difficult. The situation has created a great difficulty in effectively developing the suitable waveguide polymers and using them in fabricating waveguide devices. Instead of measuring the thermo-optical coefficients of countless polymers to establish a sufficient database to meet the need, we have chosen to develop an empirical equation for estimating the thermo-optic coefficient of a polymer using its coefficient of thermal expansion, which can be easily measured using routine polymer testing equipment, such as TMA and dilatometer, and is available

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* Corresponding author. Tel.: +1 613 993 4198; fax: +1 613 993 0755.
E-mail address: zhiyi.zhang@nrc-cnrc.gc.ca (Z. Zhang).

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for almost all commercial polymers. As such, polymer scientists and optical engineers would have the basic information for selecting suitable polymer structure to develop desirable polymers and manipulate waveguide devices.

2. Experimental section

A multi-wavelength ellipsometer (J.A. Woollam, model VB-200) was used to measure the refractive index of various polymers as a function of temperature. Its temperature was controlled with a heating stage built in house, and the index measurement was done when the sample was equilibrated at the desired temperature, which was stepwise increased from room temperature. A thermal mechanical analysis (TMA, model 2940) from TA instrument was used to measure the linear coefficient of thermal expansion of the polymers. The testing was conducted under a temperature scan at the rate of 2° C/min and under the air flow at 50 ml/min. The tested polymers covered commercial polymers, including poly(methyl methacrylate) (PMMA) from canus plastics, polycarbonate (PC) from GE, poly(ethyl methacrylate) (PEMA) from Sigma–Aldrich, and specialty waveguide polymers, including epoxy formulated with bisphenol F epoxy and imidazole [11], sol–gel synthesized from 3-glycidoxypropyltrimethoxysilane and diphenysilanediethoxysilane [12], high-crosslinking silicone formulated from vinly-terminated dimethylsiloxy-diphenylsiloxane, and *tert*-butyl poly(ether-etherketone) (*t*B-PEEK) [13]. For index measurement, each of the polymers was first dissolved in a suitable solvent at a concentration of 2%, filtered, and spin coated on silicon wafers with a spin coater (Laurell, Model WS-400A-6NPP/LITE) to form uniform films, 2–3 μm thick, followed by an applicable thermal treatment. For thermal expansion measurement, the polymers were thermally processed or cast into blocks, around $8\times2\times3\ \mathrm{mm}^3$.

3. Results and discussion

It is known that the change in refractive index n of a polymer with temperature is due to the temperature-caused density change and temperature change itself as [14]

$$\frac{dn}{dT}=\left(\frac{\partial n}{\partial \rho}\right)_T\left(\frac{\partial \rho}{\partial T}\right)+\left(\frac{\partial n}{\partial T}\right)_\rho = -\left(\frac{\rho\partial n}{\partial \rho}\right)_T\alpha+\left(\frac{\partial n}{\partial T}\right)_\rho \qquad (1)$$

where n is refractive index, ρ is the density, α is the volume coefficient of thermal expansion of a polymer, dn/dT is the temperature-caused index change, i.e. thermo-optic coefficient, $(\delta n/\delta T)\rho$ is the index change under constant density, while $(\rho\delta n/\delta\rho)_T$ is a constant for a given polymer based on the Lorentz–Lorenz equation

$$\left(\frac{\rho\partial n}{\partial \rho}\right)_T=(1-\Lambda_0)\frac{(n^2+2)(n^2-1)}{6n} \qquad (2)$$

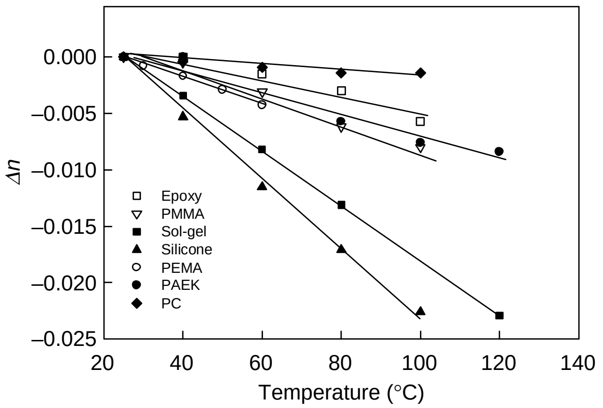

Fig. 1. Changes in the refractive indices of various polymers as a function of temperature.

where Λ_0 is the strain polarity constant related to effect of density change on atomic polarizability of the material.

With the equations, refractive index n, polarity constant Λ_0, and $(\delta n/\delta T)\rho$ value are required for calculating the thermo-optic coefficient of a polymer from its coefficient of thermal expansion. Instead of measuring all these parameters, which is, in fact, more difficult than measuring thermo-optic coefficient directly, we evaluated the relationship between the thermo-optic coefficients and coefficients of thermal expansion of many polymers with different chemical structure to see whether an empirical expression of Eq. (1) can be established and used to estimate the thermo-optic coefficient of a polymer.

Fig. 1 shows the temperature-caused changes in the refractive indices of these polymers at a wavelength of 1550 nm, which is the wavelength used in telecommunication applications. The slopes of the curves represent the dn/dT values of the polymers as summarized in Table 1. The volume coefficients of thermal expansion (α values) of the polymers are three times of the linear coefficient values that were directly obtained from the TMA measurement and are listed in Table 1. In the table, the literature available data for polystyrene [15], sol–gel synthesized from 3-glycidoxypropyltrimethoxysilane [16], and urethane acrylate elastomer [17] are also provided. The involved polymers were either tested within the temperature range below their glass transition temperatures T_gs (i.e. in glassy state) or above their T_gs (i.e. in rubbery state).

Table 1
Therm-optic and thermal properties of various polymers

Polymer type	Material state	$dn/dT\times10^4$ (°C^{-1})	$\alpha\times10^4$ (°C^{-1})
Epoxy	Glassy	−1.0	1.7
PMMA	Glassy	−1.3	2.2
Sol–gel with diphenysilane	Glassy	−2.3	3.9
Silicone	Rubbery	−3.1	5.9
PEMA	Glassy	−1.1	1.9
*t*B-PEEK	Glassy	−1.0	1.7
Polycarbonate	Glassy	−0.9	1.7
Polystyrene [11]	Glassy	−1.2	2.2
Sol–gel [12]	Glassy	−2.1	3.5
Urethane acrylate elastomer [13]	Rubbery	−4.2	7.2

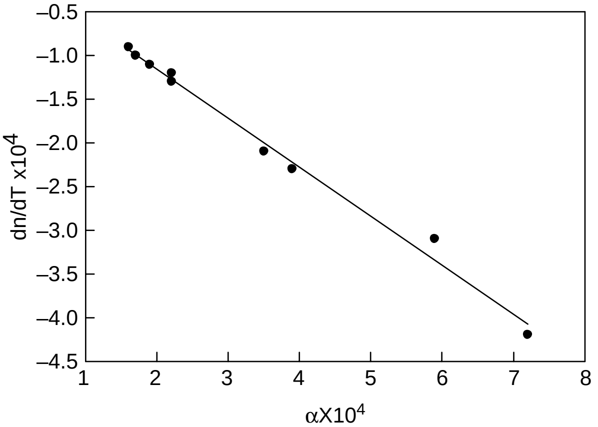

Fig. 2. Plots of thermo-optic coefficients of various polymers vs their coefficients of thermal expansion.

It can be seen that the glassy polymers have the absolute d*n*/d*T* values in the range of 1–2×10^{-4} (°C^{-1}) and the rubbery polymers have d*n*/d*T* values over 3×10^{-4} (°C^{-1}), which is in agreement with Eq. (1) since the thermal expansion of rubbery polymers is usually greater than that of glassy polymers.

Plotting d*n*/d*T* values of all the polymers vs their corresponding α values results in a straight line with a linearity of 99% as shown in Fig. 2. Although the involved polymer have very diverse chemical structure, and the refractive index *n*, polarity constant Λ_0, and non-density related index change $(\delta n/\delta T)\rho$ are theoretically related to the structure, these structure does not show a considerable effect on the plot. A possible reason for this result is that a large Λ_0 value corresponds to a high refractive index, which is intimately related to the material polarizability [18], compensating the effect of refractive index on the density-caused index change under a constant temperature (as seen from Eq. (2)). Meanwhile, the density-unrelated index change $(\delta n/\delta T)\rho$ is too small for polymers and a chemical structure-related variation is insignificant from one polymer to another one. This explanation is in agreement with the reported data that Λ_0 value of PC is greater than that of PMMA, and the $(\delta n/\delta T)\rho$ values of both the polymers are only in the order of 10^{-6} [14]. It is also in agreement with the widely accepted mechanism that thermal expansion is the principal reason for the temperature-related index change in polymers. Further more, since both the glassy polymers and rubbery polymers follow the same trend, the mechanism is believed irrelevant to the state of a polymer. In fact, there is no reason to suggest that the polarizability nature of a polymer is changed when it goes from glassy state to rubbery state, given that the mobility change in chain segments is the fundamental nature that a polymer experiences a transition from its glassy state to rubbery state.

With the obtained relationship between d*n*/d*T* values and α values in Fig. 2, $(\delta n/\delta T)\rho$ at 0.56 and $(\rho\delta n/\delta\rho)_T$ at -3.7×10^{-6} were obtained according to Eq. (1). Consequently, for a new polymer with similar chemical structure as listed in Table 1, one can easily measure its coefficient of thermal expansion using a conventional TMA or dilatometer and estimate its d*n*/d*T* value with the data, regardless of the state of the polymer. This relationship has confirmed our work of using silicone gel to maximize the d*n*/d*T* value of a polymer used in a low-power silica/polymer hybrid VOA [10]. Meanwhile, since the involved chemical structure as seen in Table 1 are very diverse and their effects on the $(\rho\delta n/\delta\rho)_T$ and $(\delta n/\delta T)\rho$ values are very small, it is suggested that the relationship be reasonably extended to the other types of polymers as an empirical equation. Given that thermal expansion is the dominated reason for temperature-caused index change, the estimated d*n*/d*T* value should be good enough for guiding material development and for selecting a proper polymer during device design. In addition to the convenience of using TMA or dilatometer for materials testing, coefficient of thermal expansion is, in fact, a widely available parameter for polymers. A rough estimation using the literature data can provide a basic idea for the purpose.

The estimated d*n*/d*T* value using the literature d*n*/d*T* value or measured one can be simply used as a necessary condition for developing a given polymer structure and evaluating its possibility in waveguide application. If it is off the range for a targeted waveguide device, there is on need to proceed with polymer synthesis or waveguide fabrication, both of which are time consuming and costing. This is especially true for polymer development since most polymer laboratories are not equipped the expensive instrument for precisely measuring the d*n*/d*T* value of a polymer and the sample preparation for such a type of measurement is difficult.

4. Conclusion

Polymers are used in fabricating planar waveguide devices deployed in telecommunication systems. In addition to their optical loss, refractive index, and birefringence, the thermo-optic coefficient of the polymers plays a vital role in dictating the device properties. This works tried to establish an empirical relationship between thermo-optic coefficients (d*n*/d*T*) and coefficients of thermal expansion (α) of polymers according to Lorentz–Lorenz equation. The results based on a group of 10 polymers with diverse chemical structure have showed that a single linear relationship between their d*n*/d*T* values and α values with the slope $(\delta n/\delta T)\rho$ equal to 0.56 and the interception $(\rho\delta n/\delta\rho)_T$ equal to -3.7×10^{-6} can be drawn for the involved polymers and the relationship is unrelated to the polymer's T_gs. Since the coefficients of thermal expansion (α) of polymers can be easily measured using TMA and other conventional testing methods and using the easily prepared samples, and in most case are widely available in literature, the obtained empirical relationship can be used to estimate the d*n*/d*T* values of polymers. This estimation is useful for guiding the material development and evaluating its possibility in waveguide applications.

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