# Effect of heat treatment on the refractive index of polymethylmethacrylate films

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Films of Polymethylmethacrylate (PMMA) of different molecular weights were deposited on microscopic glass substrate using spin coating technique at 1500 rps for 30 s. Refractive index of thin films has been determined using ultraviolet-visible- near infrared spectrometer in the spectral range 400-900 nm. Refractive index has been studied as a for PMMA at different temperatures (318 K, 328 K, 338 K, 348 K, 358 K) for different annealing times (1h, 2h, 3h,…., 10h). It has been observed that refractive index decreases with the increase in molecular weight of PMMA. It has also been observed that with increase in annealing temperature for different PMMA refractive index increases. Such films may be considered as prospective materials for fabrication of planar optical waveguides.

(Received August 12, 2009; accepted September 30, 2009)

*Keywords*: Polymethylmethacrylate, Refractive index, Transmission spectrum

## 1. Introduction

Polymers are being used in optical telecommunication applications and are in increasing demand for optical signal amplifying systems [1]. As polymers interfere with optical signals by absorbing part of their energy, transmission distance in polymer optical fibers is limited. To enlarge the transmission distance of optical signals in polymer optical fibers one must compensate for the loss of energy. By coupling the fibers to an optical amplifying device, a weakened optical signal is boosted and thus regenerated in strength. The properties of polymeric materials, intended for applications in electronic and optoelectronic structures, are affected especially by their physical aging and thermal aging. In the course of aging polymer films in a thermodynamically non-equilibrium state tend to an equilibrium state via spontaneously proceeding processes. The processes may proceed with different rates (with typical time constants from hundredth of second to few years) which can be influenced by external conditions, chemical and physical structure of polymer, its thermal history and molecular weight, the presence of dopants and the thickness of polymeric film [2-7]. By rapid cooling to the temperature of glassy transition (Tg) with simultaneous evaporation of solvent or under influence of an external force the oriented polymeric chains may pass into thermodynamically non-equilibrium state. After the external force is switched off relaxation processes tend to reorient polymeric chains back [8,9].

In our present work, we have analyzed the refractive index for spin coated films of Polymethylmethacrylate (PMMA) for different annealing temperatures. Also the effect of polymer molecular weight on the refractive index of PMMA has been examined.

## 2. Experimental details

Polymethylmethacrylate (I-PMMA) was synthesized in our laboratory by polymersising methylmethaacrylate using benzoyl peroxide. II-PMMA and III-PMMA were supplied by

GSFCL, India. The characteristics of PMMA used are given in Table 1. Fig. 1 shows the structure of PMMA. Spin coating technique (at 1500 rpm for 30 s) was employed for the deposition of PMMA films. Microscopic glass (Blue Star, India) slides were used as substrate. Films were dried at 40 $^oC$ in air. Films were annealed then at different temperatures (318K, 328K, 338K, 348K, 358K) for different annealing times (1h, 2h, 3h,…., 10h). Transmission spectra of annealed films were obtained using ultraviolet-visible-near infrared spectrophotometer (Perkin Elmer lambda 750) in the spectral range 400-900 nm. Optical spectra were taken at room temperature (300 K).

*Table 1. Materials characteristics of I-PMMA, II-PMMA and III-PMMA.*

| Material | Density (g/cc) | Molecular weight ($M_w$) | Polydispersity |
|---|---|---|---|
| I-PMMA | 1.1 | $5.26 \times 10^5$ | 2.34 |
| II-PMMA | 1.1 | $9.85 \times 10^5$ | 2.07 |
| III-PMMA | 1.1 | $13.67 \times 10^5$ | 1.53 |

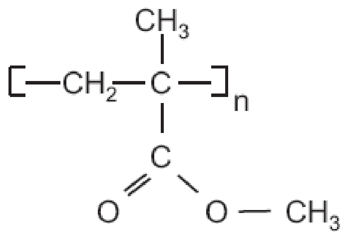

*Fig. 1. Molecular structure of PMMA.*

## 3. Results and discussion

Using the experimental data of optical transmittance of PMMA films the refractive index has been calculated. The film has thickness (*d*) and complex refractive index $n^* = n - ik$, where *n* is the refractive index and *k* is the extinction coefficient. The thickness of the substrate is several times larger than the thickness of the film. If the thickness of the film is constant, interference effect will give rise to oscillating curves as shown in Fig. 2. Fig. 2 shows the transmission spectra of I-PMMA (annealing temperature 338 K and annealing time 2h) as reference. Optical parameters are deduced from the fringes pattern in the transmittance spectrum [10,11].

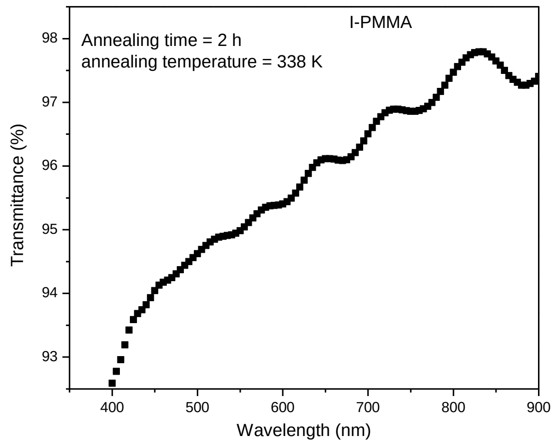


*Fig. 2. Transmission spectra of I-PMMA at annealing time 2 h and annealing temperature 338 K (as reference).*

According to Swanepoel [10] the value of the refractive index of the film can be calculated by using the following expression. In the transparent region where the absorption coefficient $\alpha \approx 0$, the refractive index (*n*) is given by

$$n = [N + (N^2 - s^2)^{1/2}]^{1/2} \tag{1}$$

where

$$N = \frac{2s}{T_m} - \frac{(s^2 + 1)}{2} \tag{2}$$

and $T_m$ is the envelope function of minimum transmittance and *s* is the refractive index of substrate. In the weak region where $\alpha \neq 0$ the transmittance decreases due to the influence of $\alpha$, equation (2) is given by

$$N = 2s\frac{T_M - T_m}{T_M T_m} + \frac{(s^2 + 1)}{2} \tag{3}$$

where $T_M$ is the envelope function of maximum transmittance. Refractive index can be estimated by extrapolating envelops corresponding to $T_M$ and $T_m$. If $n_1$ and $n_2$ are the refractive indices of two adjacent maxima or minima at wavelengths $\lambda_1$ and $\lambda_2$, then the thickness of the film is given by

$$d = \lambda_1\lambda_2 / 2(\lambda_1 n_2 - \lambda_2 n_1) \tag{4}$$

The refractive index of substrate used is 1.51. Thickness of the films was found to be 1800 nm, 1775 nm and 1840 nm for I-PMMA, II-PMMA, III-PMMA respectively with an uncertainty of ± 30 nm. Figs. 3, 4, 5 shows the variation of refractive index with annealing time corresponding to annealing temperatures (318K, 328K, 338K, 348K, 358K) for I-PMMA, II-PMMA, III-PMMA respectively.

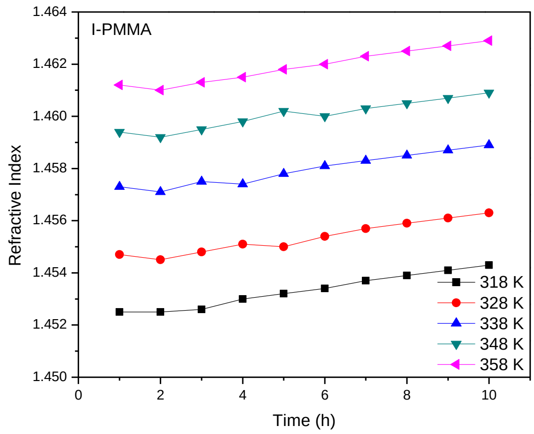


*Fig. 3. Variation of refractive index with annealing time for I-PMMA at annealing temperatures 318 K, 328 K, 338 K, 348 K and 358 K.*

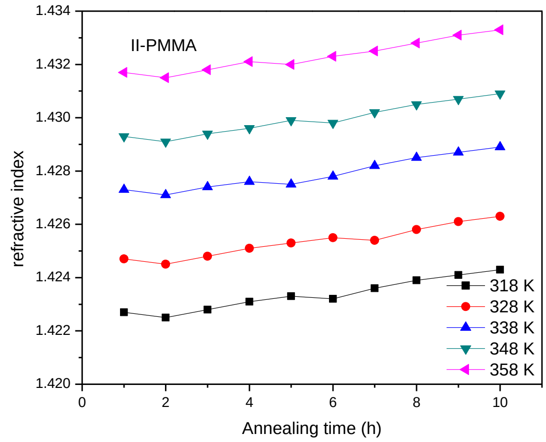


*Fig. 4. Variation of refractive index with annealing time for II-PMMA at annealing temperatures 318 K, 328 K, 338 K, 348 K and 358 K.*

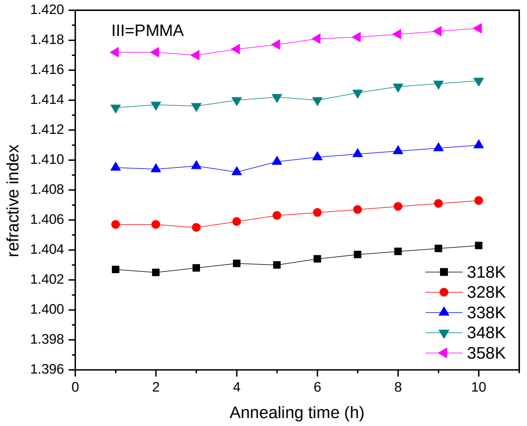


*Fig. 5. Variation of refractive index with annealing time for III-PMMA at annealing temperatures 318 K, 328 K, 338 K, 348 K and 358 K.*

This has been found that refractive index increases with increase in annealing time corresponding to all annealing temperatures. This has also been observed that refractive index increases with the increase of annealing temperature (Table 3).

*Table 2. Values of refractive index for I-PMMA, II-PMMA and III-PMMA at different annealing temperature corresponding to annealing time of 2h and wavelength 800nm.*

| | Refractive index for ageing time 2h at 800 nm | | | | |
|---|---|---|---|---|---|
| | n at 318K | n at 328K | n at 338K | n at 348K | n at 358K |
| I-PMMA | 1.4526 | 1.4544 | 1.4571 | 1.4592 | 1.4610 |
| II-PMMA | 1.4224 | 1.4246 | 1.4274 | 1.4291 | 1.4315 |
| III-PMMA | 1.4028 | 1.4057 | 1.4094 | 1.4137 | 1.4172 |

*Table 3. Values of refractive index for I-PMMA, II-PMMA and III-PMMA at different annealing time corresponding to annealing temperature of 338 K and wavelength 800 nm.*

| Time (h) | Refractive index at 800 nm (338 K) | | |
|---|---|---|---|
| | I-PMMA | II-PMMA | III-PMMA |
| 1 | 1.4574 | 1.4273 | 1.4095 |
| 2 | 1.4571 | 1.4274 | 1.4094 |
| 3 | 1.4575 | 1.4274 | 1.4096 |
| 4 | 1.4574 | 1.4276 | 1.4092 |
| 5 | 1.4578 | 1.4275 | 1.4099 |
| 6 | 1.4581 | 1.4278 | 1.4102 |
| 7 | 1.4583 | 1.4282 | 1.4104 |
| 8 | 1.4586 | 1.4285 | 1.4106 |
| 9 | 1.4587 | 1.4287 | 1.4108 |
| 10 | 1.4593 | 1.4291 | 1.4110 |

For temperature higher than room temperature there may have enough vibration energy to break some of the weaker bonds, thus introducing some translational degrees of freedom to the system and which in turn may lead to increase in refractive index with increase in annealing temperature. The values of refractive index were found to decrease with the increase in molecular weight of PMMA. This decrease in refractive index with increase in molecular weight may be due to spontaneous reorientation of PMMA dipoles during the specimen aging.

## 4. Conclusions

Refractive index of PMMA films has been determined using transmission spectra in the spectral range 400-900 nm. Refractive index has been studied as a function of PMMA at different temperatures (318K, 328K, 338K, 348K, 358K) for different annealing times (1h, 2h, 3h,…., 10h). It has been found that refractive index decreases with the increase in molecular weight of PMMA whereas it increases with increasing annealing temperature for different PMMA. This has been found that with annealing time refractive index also increases. Such films may be considered as prospective materials for fabrication of planar optical waveguides.

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