

Variation of Refractive Index of PMMA with temperature and different doping % of TiO₂

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Abstract: A simple and reliable method of measuring the refractive index of thin film is reported in the present paper. In this work, an experimental approach of Digital Abbe Spectrometer was used for measuring refractive indices of pure and doped PMMA at different wavelengths in the visible region. Refractive indices measurements at wavelengths of 405, 458, 492.2, 499, 546, 589, 632.8, 659.2, 670.2 nanometres were taken of Titanium di Oxide doped Poly (methyl metha acrylate) PMMA films. Also we explain with the help of graph refractive indices of PMMA increases with increasing doping percentage (0.0001%, 0.0005%, 0.001%, 0.005%, 0.01%, 0.05%) & we compare the refractive indices of un annealed and annealed polymer of doped PMMA at different temperatures (40°C, 60°C, 80°C, 100°C).

Keywords: PMMA-polymethyl methacrylate, refractive index, TiO₂, Wavelength.

1. Introduction

Refractive index is an important optical property of a medium. It plays an important role in many areas of material science with special reference to thin film technology [1]. The refractive index of a medium is changed with frequency. This effect, known as dispersion.

It is represented by the formula

$$\text{refractive index (n) of substance} = \frac{\text{speed of light in a vacuum}}{\text{speed of light in substance}} \quad (\text{Eqn 1})$$

Also Refractive index of a material is a measure of change in speed of light when it impinges on that material and enters into it. This happens due to absorption and reemission of light photons by the material atoms resulting

also in the change of propagation direction. One can measure the extent to which light is refracted from a material because of bending when it moves from air into the sample and information can quantitatively be extracted. It is also commonly used to compare experimental values to those of standard ones to confirm the identity of a sample, to test the purity of a sample by comparing its refractive index to the value for the pure substance and to determine the concentration of a solute in a solution by comparing the solution's refractive index to a standard curve. Refractive index depends on the wavelength of the electromagnetic wave, through dispersion relation. In materials where an electromagnetic wave can lose its energy during its propagation, the refractive index becomes complex. The real part is usually the refractive index (n) and the imaginary part is called the

extinction coefficient (K). For optical light, the refractive index is determined by the well-known Snell's law. By Snell's law in the visible region, when light travels in a material, the velocity of a material is distorted. The ratio of speed of light in a vacuum to speed of light in substance is called refractive index (n) [2].

$$\frac{n_2}{n_1} = \frac{\sin \theta_1}{\sin \theta_2} \quad (\text{Eqn 2})$$

where n1 is the refractive index of the medium 1 (here we take the medium 1 as air and therefore n1 = 1) and n2 is the refractive index of medium 2. In air the speed of light is equal to 3×10^8 m/sec and depending on the density of material 2 (polymer in present case), it is possible to determine the optical density of polymer.

The refractive index is dependent on the wavelength of the incoming light. In the design of optical devices, determination of refractive index of the polymer is an important property. Most organic polymers show a limited refractive index, in the range 1.35—1.5.

2. EXPERIMENTAL DETAILS

2.1 Materials

Among polymer materials, PMMA is well known as a polymeric glass with a wide range of applications. Use of PMMA offers two fold advantages such as availability to carboxylate functional group for a chemical bonding with the metal ions and high solubility of PMMA in solvent [3]. PMMA is a thermo plastic and transparent material. Chemically it is synthetic polymer of methyl methacrylate. The material was developed in 1928 [4-9]. Poly (methyl methacrylate) PMMA is a polymer with several interesting

physical properties, which are very useful in technical applications [10]. Formula of PMMA is " $C_5O_2H_8$ ". Molecular weight of PMMA is "114.14 g/mol". Poly(methylmethacrylate)(PMMA), which has a glass transition temperature Tg of about 100°C is one of the more brittle amorphous materials. The molecular mobility in the glassy state is low. Because of its transparency, PMMA is often used in applications that require good optical properties. The percentage transmittance of PMMA is 90.5 and for its blends, the transmittance value lies in the range of 84.2% to 86.8%. The solvent of PMMA is "n-Butyl, chloride and Benzene. Poly (methyl methacrylate) (PMMA) is a nonbiodegradable polymer with good transparency, mechanical strength, less weight, colorlessness, good insulating properties etc. [11].

The PMMA is almost insulating in nature with high elastic strength and its conducting property can be enhanced by adding either metal oxide or supporting agent.

2.2 Preparation of PMMA solution

The 2gm of PMMA was dissolved in 100ml of benzene, the solution stirring with the help of magnetic stirrer for 1-2 hrs. to allow polymer to dissolve completely to yield clear solution.

2.3 Preparation of dopent

For preparation of dopent the 0.0002gm of titanium dioxide was dissolved in 5ml of xylene and 5ml of alcohol, the solution magnetic stirring for 1 hrs. after that the solution kept on sonicator for 15 minutes.

Digital Abbe Spectrometer

An easy and precise method to measure the linear refractive index n in the visible region is provided by an Abbe refractometer. Commonly, such instruments are designed for the use at the wavelength of the sodium D line [12].

Measurement of refractive index using bending of the beam requires only simple and easy to operate instruments, which makes the technique suitable for wide spread uses. Abbe' refractometers are able to operate satisfactorily with white light by introducing a set of "compensating prisms" into the optical path after the refracting prism. These compensating prisms are designed so that they can be adjusted to correct (i.e., compensate for) the dispersion of the sample in such a way that they reproduce the refractive index that would be obtained with monochromatic light.

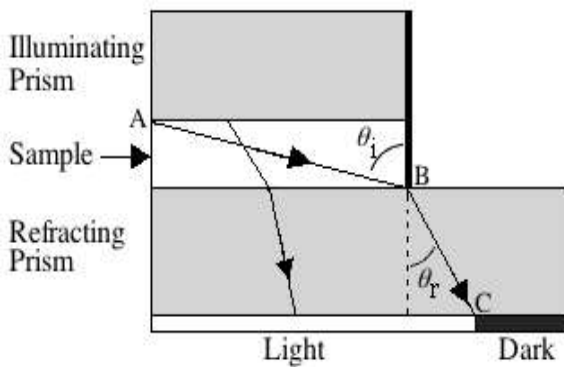


FIG 1 Cross section of part of the optical path of an Abbe refractometer. The sample thickness has been exaggerated for clarity.

2.5 Solution casting Method

There are various method used for preparation of polymeric thin films. Some of the methods are wet

chemical method, electrodeposition method, solution casting method etc. In the present work we will be using solution casting methods for film preparation. In this method desired amount of salt and polymer are dissolved in a polar solvent [13]. This is the method which includes evaporation of solvent in which the polymer and a dopant is dissolved. In this method the important things which should be kept in mind:-

- A stable solution with a reasonable minimum solid content and viscosity should be formed.
- Formation of homogenous films and release from the casting support should be must be possible [14].

This is one of the oldest technology in plastic film manufacturing which was developed more than a hundred years ago as a growing needs of emerging photographic industries. It has taken many years for the solvent casting manufacturing process to develop into a high precision technique.

Today this method is used in various field of engineering which includes the production of engineering plastics, optical films, medical films, and sheet forming for electronic applications. Some of the main advantages of this technique are:

- Homogenous thickness distribution
- Highest optical purity
- Excellent transparency
- Low optical retardation.

➤ Excellent flatness

The future of solvent cast technology will be closely linked to the need of optical films by the emerging liquid crystal display industry or other new optical applications which require polymer films with outstanding properties.

3 Procedure

Polymer thin films are a novel class of materials that have widely used in industrial and biomedical applications and are now an integral part of our everyday lives [15]. Thin films of approximately 80 micron thickness have been prepared by a solvent evaporation technique using PMMA solvent. PMMA solvent prepared by adding Benzene and PMMA. We used Titanium di Oxide as dopent. Because metal oxides, such as TiO₂ is a materials with high surface areas that exhibit exceptional chemical reactivity compared with commercial metal oxide. We have obtained films of different doping percentage (0%, 0.0001%, 0.0005%, 0.001%, 0.005%, 0.01%, 0.05%) by dissolving titanium oxide in PMMA solvent. Thin films were obtained by evaporating the solutions on glass substrates. Refractive indices measurements – at 405 ,458, 492.2, 499, 546, 589, 632.8, 659.2, 670.2 nm wavelengths were done by an Abbe's refractometer.

4 Results and discussion

For measuring refractive indices of the polymer we have used Abbe refractometer. A white light source was used with interference filters of wavelengths (405,458, 492.2, 499, 546, 589, 632.8, 659.2, 670.2 nm). The dispersion relations between refractive indices and wavelengths at certain temperature of PMMA doped with different doping percentage of titanium oxide were shown in **Figures**

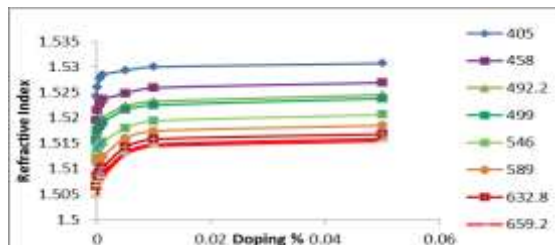


FIG 2 Refractive index Vs. Doping % at T = 0°C

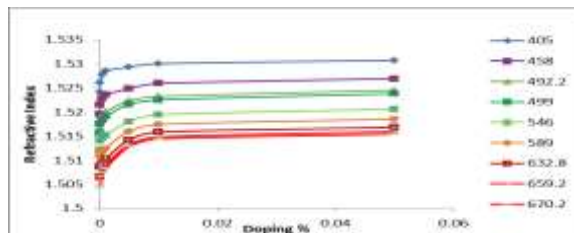


FIG 3 Refractive index Vs. Doping % at T = 40°C

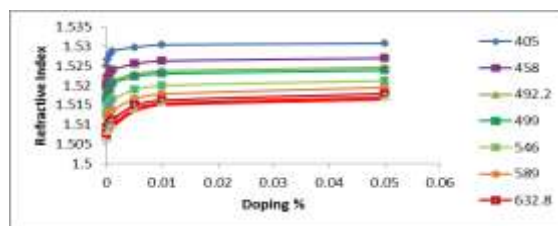


FIG 4 Refractive index Vs. Doping % at T = 60°C

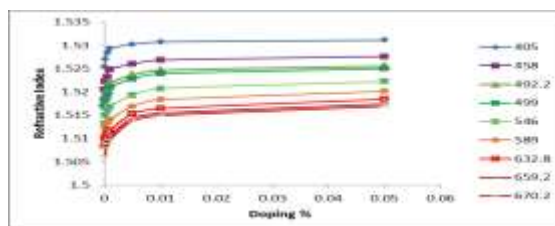
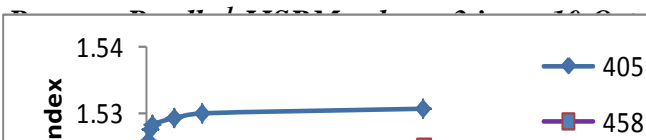


FIG 5 Refractive index Vs. Doping % at T = 80°C



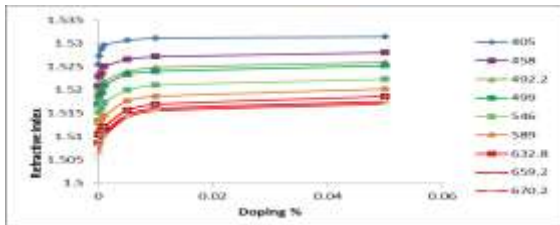


FIG 6 Refractive index Vs. Doping % at T = 100°C

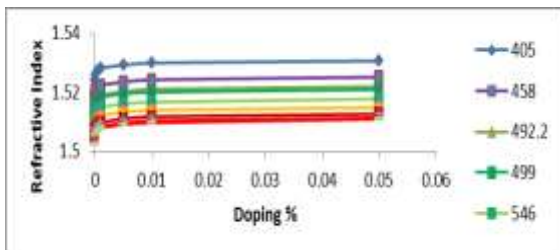


FIG 7 Refractive index Vs. Doping % of an annealed doped PMMA

So these figures (fig 2 to fig 6) shows the variation of refractive indices with wavelength for pure and doped PMMA samples at various temperatures (40°C, 60°C, 80°C, 100°C). For all the temperatures the refractive indices is found to be decreasing with increasing wavelengths. By increasing doping % its refractive indices also increases. Fig7 shows when we compare the refractive indices of un annealed and annealed doped PMMA with different doping % of titanium di oxide its shows refractive index of annealed doped PMMA is more than un annealed doped PMMA.

5 Conclusion

The presented methods provide an easy and accurate way to determine the refractive index of thin film. According to

the obtained results, the following conclusions had been achieved.

1] Inspection of these figures (fig 2 to fig 7) reveals that for all compositions refractive indices decreases with increasing wavelength but it increases as Titanium di oxide concentration increases.

2] The refractive indices of pure PMMA is less than the titanium oxide doped PMMA. Inclusion of titanium di oxide in PMMA increases the value of refractive index of the composite system. This is because pure PMMA is an amorphous substance with low density that increases with increasing the concentration of Titanium di oxide.

3] The refractive index of annealed PMMA increases when temperature of polymer increases.

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