

Investigation of Uv-Vis Characteristics of Pure/Doped Polystyrene Thin Films Prepared by Solution Casting Method

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Abstract

Minimizing the size of electronics to achieve thinner and lighter devices makes the shrinking of the components inevitable. The focus of this research is to incorporate dopants into the Polystyrene (PS) matrix to fabricate thin films with high efficiency and flexibility. Presented is a very simple approach of doping PS thin films with various dopants. The absorption spectra of the films were studied at the wavenumber range (300-700 nm). Effects of doping on optical properties such as, absorbance, transmittance, energy, absorption coefficient, extinction coefficient, and dielectric constant were derived. This study reveals that all these parameters have impact of dopants on PS.

Keywords: Polystyrene PS; UV-Vis Spectroscopy; organic polymer; solution casting; PZT; Lithium Tantalate; Lithium Niobate; Barium Magnesium Aluminate (Europium doped); Potassium Niobate; nanocomposite

Introduction

As the size of electronics continue to minimize, the size of components also decrease to maintain thinner and lighter devices. Prior to the age of dedicated scientific technological inquiry and innovation, metalsmiths made use of metal thin films to gild less-precious materials into thin layers of gold and silver. Building on that foundation, modern metal thin films are utilized in a variety of scientific and industrial applications, but fewer so in the optics world (Whiteside et al., 2016). The use of highly functionalized thin films in various electronic devices have made an increasing impact on social amenity, this due to the enhanced functional properties of materials at the nanoscale. Thus, leading to emergence of new and unique behaviors of such materials with optical, electrical, optoelectronic, dielectric applications - thin films (Jilani et al., 2017).

In recent years polymers with varying optical properties have attracted much attention due to their applications in sensors, light emitting diodes, and others. The optical properties of these materials can be easily tuned by manipulating the matrix with dopants (Mohammed, 2016). Conducting polymers have attracted much attention since the first report of electrical conductivity in a conjugated polymer. Researchers have made great efforts in fabricating nanocomposites consisting of organic polymers and inorganic nanoparticles. Independently, inorganic nanoparticles are emerging as very attractive nanomaterial for advanced applications in catalysis,

transistors, and sensors. Meanwhile organic conducting polymers are also explored for application in biosensors due to the considerable flexibility in their chemical structures and their redox characteristics. Researchers have investigated the results of combining the two possessing characteristics of both, improve their physical and chemical properties, and to introduce additional functionalities. Such nanocomposites can be useful. The nanoscale features can be achieved through polymer thin films are in the forerunners in polymeric devices in medical technology (Liu et al., 2008; Tsuruoka et al., 2013; Ellis et al., 2009).

Various methods have been developed to prepare nanocomposites, including incorporation of inorganic nanoparticles into polymer matrices, and incorporating dopants. Like most materials, the polymer structure is divided into amorphous or crystalline depending on the fabrication process (Jilani et al., 2017). PS has attracted attention of scientists for its amorphous structure, it's interesting features and its superior physical and chemical properties, and low cost. The many major characteristics include rigidity, transparency, high refractive index, good electrical insulation characteristics, low water absorption, and ease of coloring and processing which makes applicable for many applications (Mohammed, 2016; Ellis et al., 2009). While freestanding (pure PS) thin films are fragile and difficult to manipulate, when supported PS thin films are strongly influenced by the underlying substrate,

or dopant. It is traditionally considered as an excellent host material for composites (Ellis et al., 2009).

Although these ancient craftsmen didn't have the knowledge in the field of physiochemical processes involved in their procedures, and their contributions to metal film deposition techniques have inspired centuries of thin film innovation for applications that extend far beyond their artistic origins (Whiteside et al., 2016). Metal nanoparticles have been increasingly used in the fields of bioelectrochemicals and electrical applications owing to their extraordinary electrocatalytic activity potentially being employed as catalysts as well (Liu et al., 2008). They have been of great interest because they provide a good model system for studying experimentally interaction with inorganic and organic materials. By incorporating nanoparticles into polymer matrix even in the smallest amounts, many interesting optical properties including absorption, fluorescence, magnetic properties, and excellent mechanical properties may be obtained. This process may also considerably enhance their optical, electrical, mechanical, and thermal properties (Ellis et al., 2009; Acharya et al., 2017). For example, Zinc Oxide is an important semiconductor material with potential in numerous applications in the field of electronic components. Barium Strontium Titanate is suitable for capacitor materials. (Dewi, et al., 2019; Faraz et al., 2018).

In this study, the effects of dopants dispersed in the polystyrene matrix were explored. The impact on absorption was investigated for optical properties such as absorbance, transmittance, absorption coefficient, dielectric constant, extinction coefficient, etc. (France & Short, 1998).

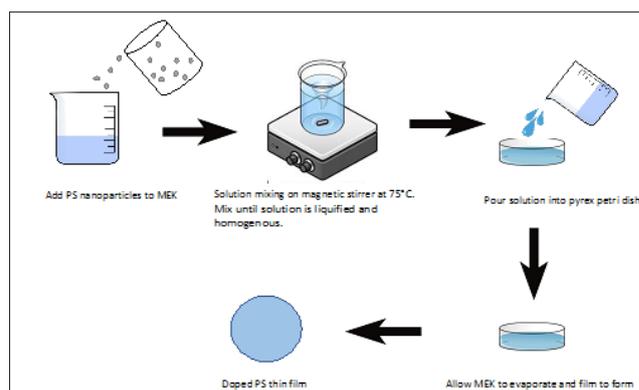
Materials and Methods

Chemicals

Methyl Ethyl Ketone (C_4H_8O) was purchased from Reagents. Polystyrene ($(C_8H_8)_n$) and all dopants were purchased from Sigma-Aldrich Chemistry as starting materials.

Pure Polystyrene film fabrication

Polystyrene ($(C_8H_8)_n$) was the polymer procured from Sigma Aldrich was used for these thin films. These PS latex beads are uniform in size and morphology. Methyl Ethyl Ketone (MEK) (C_4H_8O) was selected as the solvent. The PS-MEK solutions were prepared within the concentration range from 28.5 to 71.42 wt%. The thin films were fabricated utilizing the solution cast method, which can be seen in the schematic diagram 1. The PS nanoparticles were dissolved in MEK and stirred for 50 mins at 300 rpm utilizing a Stuart magnetic stirrer. The temperature was increased by 10° every 10 minutes to homogenize the solution. Because of the amorphous structure of polystyrene, dissolving PS is relatively simple. The rotation speed and time in oven were manipulated according to the thickness of solution. To increase the spread of the solution, the rotation speed was increased. The intermixed solution was removed from the stirrer at $75^\circ C$ & with a consistent pour transferred to a pyrex petri dish. The PS was annealed in an oven at $76^\circ C$ for at least 12 hours, then removed and cooled to ambient temperature.

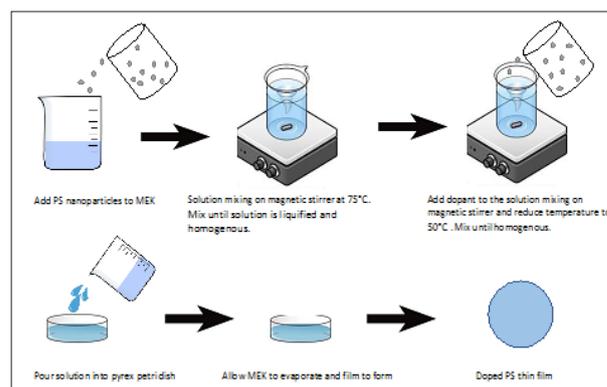


Schematic Diagram 1: Systematic representation of solution cast synthesis of pure polystyrene thin films

Three different concentrations of PS in MEK were developed to determine the concentrations effects on thickness and electrical properties. Solution casting a polymer dissolved in a solvent on a temporary substrate has many advantages. Solution casting technique may provide more uniformed thicknes distribution as well as higher dimension stability and optical purity.

Fabrication of doped thin film

Similarly, PS doped thin films were prepared utilizing the same system, shown in schema 2. The PS-MEK solution was mixed for 50 minutes using magnetic stirrer on hot plate with speed of 280 rpm beginning at room temperature ($\sim 25-30^\circ$) and increasing the temperature 10° every 10 minutes until $75^\circ C$. After stirring for 30 minutes, appropriate measurements of dopant is added to the solution and mixed at 300 rpm for 2 hours at $50^\circ C$. The intermixed then transferred to a Pyrex petri dish with a consistent pour for a homogenous mixture. The PS was annealed at $76^\circ C$ for at least 12 hours, then removed and cooled to ambient temperature. The PS thin film is removed completely from the glass substrate for all samples.



Schematic Diagram 2: Systematic representation of solution cast synthesis of doped PS thin films.

Results & Discussion

A variety of research has been performed in thin film optics due to their many technological and optoelectrical applications. The application of these thin films depends on important principals including: the wavelength of light absorbed, the thickness, and the optical properties of the film. These properties can be easily

tuned by controlling the dopant materials and optimizing dopant concentrations (Guggilla et al, 2017).

Characterization of the films including composition variations was done using Ultraviolet-Visible Spectroscopy utilizing a UV-Vis Cary 3E Spectrophotometer in the wavelength range of 300-700 nm. A spectrophotometer consists of two components: a spectrometer and photometer. Spectrophotometer produces light from spectrum with certain wavelength and photometer is a measuring tool of light intensity transmitted and absorbed. UV-Vis spectrophotometry provides a relatively quick and simple analysis of material optical properties (Dewi, et al., 2019; Tsuruoka et al., 2013; Whiteside et al., 2016).

The optical property of a material may give information regarding the composition of the material. Molecules absorb at different wavelengths of light depending on their structure. Data obtained from spectroscopy can help identify bonds between molecules as well as help calculate the optical properties such as: bandgap energy, optical density, dielectric constant, etc. (Guggilla et al., 2017).

Figure 1 shows the absorption spectra for prepared thin films consisting of PS with varying dopants. The graph shows an increase in absorbance from the pure PS sample. The wavelength of UV-Vis light depended on the process of electron transition. If electron transition corresponds with amount of photon energy, it will cause great absorption along with the amount of energy from photon (Dewi et al., 2019). When the wavelength increased, there were very small absorption bands in the visible region, because the samples are transparent.

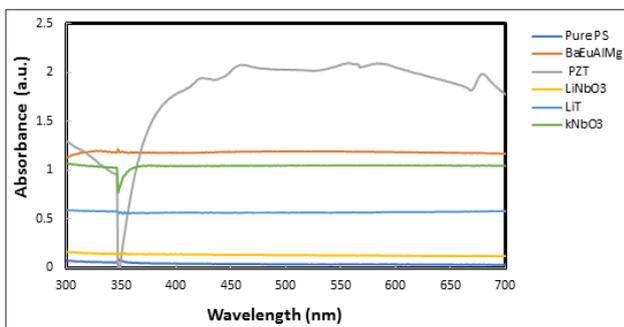


Figure 1: Optical absorbance spectrum of PS thin films with various doping

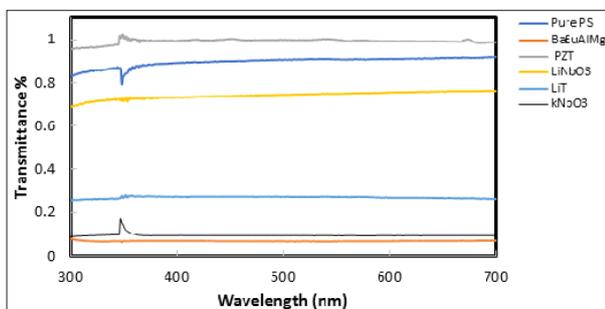


Figure 2: Optical transmittance spectrum of PS thin films with various doping

It is evident that with the incorporation of additives, the absorption increases in comparison to pure PS films. Enhanced absorption is a very important property for optoelectrical applications.

The transmittance percent decreases as there is a decrease in transmitting of incident light. The transmittance decreases with the addition of dopants, except for with PZT sample. Figures 1 and 2 also indicates a small peak in samples PZT and KNbO_3 around approximately 350 nm (seen in absorbance as well) to be explored through Xray Photoelectron Spectroscopy (XPS). The sample transmitted visible light in the UV spectrum possibly because in the UV wavelength, the sample absorbed energy hitting it (Dewi et al., 2019).

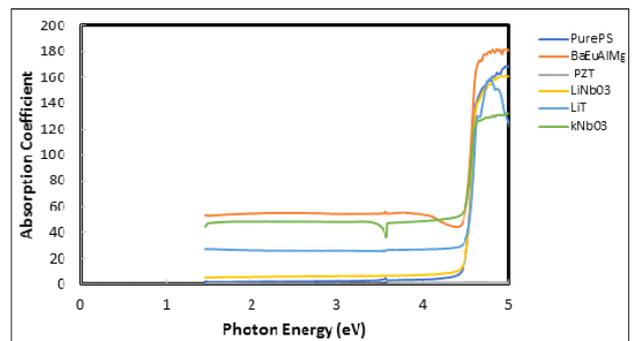


Figure 3: Absorption Coefficient (α) spectrum of PS thin films with various doping

From, we can also determine energy gap (E_g) and phonon energy (E_p) depending on α values; if $\alpha > 10^3$ that is lead to the direct transition and where $\alpha < 10^3$, these values lead to indirect transitions. Figure 3 shows the relationship between the absorption coefficient and photon energy of the PS/PS doped nanocomposite films. The gradient of absorption coefficient is from high photon energy to low photon energy. This means that the possibility of electron transition is little because the energy is not sufficient to move the electron from the valence band to the conduction band ($h\nu < E_g$) (Sangawar & Golcha, 2013).

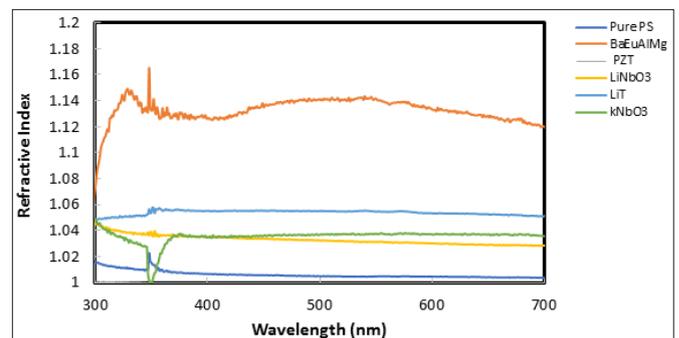


Figure 4: The refractive index of PS and doped PS thin films as a function of wavelength

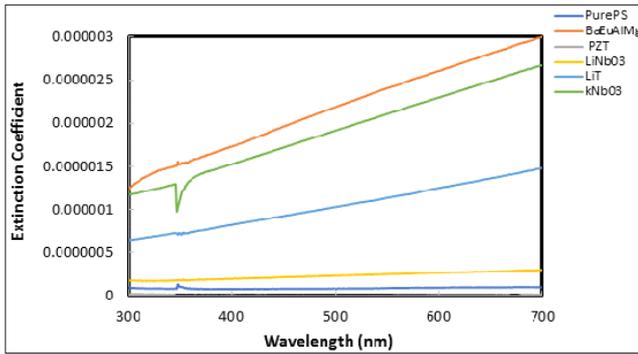


Figure 5: The extinction coefficient for PS and doped PS thin films as a function of wavelength

Figure 4 shows the refractive index of the samples as a function of wavelength. The refractive index increases when PS is doped with most dopants in this experiment.

The extinction coefficient, shown in figure 5 also increases with the addition of dopants. This may be due to the high absorption coefficient. The extinction coefficient is high at the longest wavelengths.

The dielectric constants in figure 6 are related to the absorption coefficients.

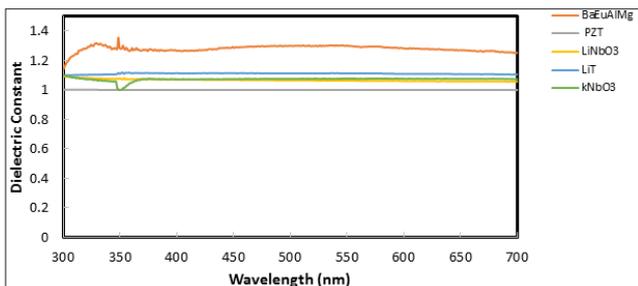


Figure 6: The dielectric constant for PS and doped PS thin films as a function of wavelength

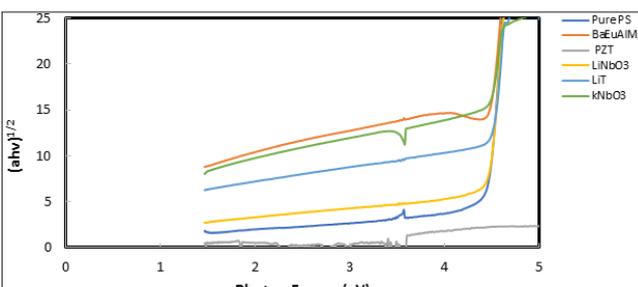


Figure 7: $(ahv)^{1/2}$ vs. $h\nu$ plots of PS and doped PS thin with energy gap of allowed transitions

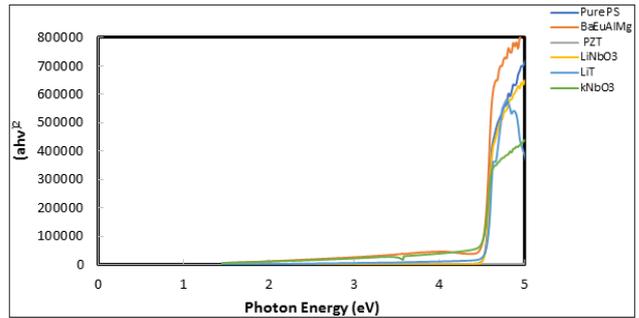


Figure 8: $(ahv)^2$ vs. $h\nu$ plots of PS and doped PS thin films

From figure 7 the relationship between absorption edge $(ahv)^{1/2}$ as a function of photon energy ($h\nu$). Figure 8 shows the dependence of $(ahv)^2$ on photon energy for direct allowed transitions. The value of the optical energy band gap was determined and plotted from the extrapolation curve of the linear portion of the plots to the abscissa yields the indirect allowed gap of transitions intersecting with the photon energy axis. A change in bandgap can suggest a change in degree of disorder in the films due to changes in the polymer structure.

Conclusion

Polystyrene doped nanostructures have been synthesized successfully and its application in achieving optimum optical properties is demonstrated. These thin films have been prepared by mixing various dopants with PS. The doped samples exhibited no significant change in energy bandgap in comparison to pure polystyrene. It may be necessary to implement some other process with the addition of dopants, possibly cold jet plasma treatment or incorporation of dyes to impact the energy bandgap. However, with the incorporation of Lead Zirconate Titanate the transmittance of the films showed an increase. Absorbance and transmittance peaks occurred around wavelength 350 nm. Typically, because the wavelength was UV area (200-400 nm) where the area would occur high absorbance process, and the photon energy produces were greater than the photon energy of visible light. All other measured parameters were affected with addition of dopants.

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