Study of Optical properties of stannous chloride ($SnCl_2$) doped Poly ether sulfone (PES) composite films

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ABSTRACT: This study investigates the optical properties of stannous chloride ($SnCl_2$) doped PES (poly ether sulfone) flexible thin films, prepared by casting method with different concentration (1%,2%, 5% and 10%) of $SnCl_2$ in PES. For this purpose the absorbance (A) and transmittance (T%) spectra of the synthesized films were recorded using UV-V-IS spectrophotometer in the wavelength range (300-1100) nm. The fundamental optical parameters viz. optical band gap energy, absorption coefficient (□), extinction coefficient (□), finesse coefficient (F), refractive index (n), real and imaginary parts of dielectric constant (□$_r$□and□□$_i$) and optical conductivity (□) have been evaluated. The optical conductivity, refractive index and dielectric constant in the doped samples are significantly affected by tin chloride concentration and are decisive for many applications.

Keywords —PES- $SnCl_2$ Composite films, Optical properties, Energy band gap, dielectric constants.

1. INTRODUCTION

Polyethersulfones are a class of engineering polymers with high thermal, oxidative and hydrolytic stabilitiy. They are amorphous, transparent thermoplastics that can be molded, extruded, or thermoformed into a wide variety of shapes.The high thermal stability is provided by the diphenylene sulfone group. It imparts high strength, high resistance to oxidation, and excellent flame retardancy but makes the polymer rigid. Flexibility in the backbone of the polymer is provided by ether linkages. These ether linkages also add to the thermal stability. Many commercial grades can tolerate high temperatures for a long period of time. Some grades, like polyphenylsulfone, are extremely tough and have very high impact strength, comparable to polycarbonate. Polysulfones are highly resistant to aqueous mineral acids, bases, and oxidizing agents and are fairly resistant to many non-polar solvents. However, polysulfones are not resistant to low polar solvents, such as esters, ketones, aromatic and chlorinated hydrocarbons.The usual grades have a good melt stability which permits fabrication by conventional thermoplastic processing methods.

Recently, metal polymer composites have received a considerable interest within the scientific community; as the introduction of the metal filler even in small quantities to the polymer matrix significantly enhances their thermo-physical properties. (Ramesan and Bijudas, 2016; Sharker et al, 2015; Gupta et al 2015; Ranganath et al , 2008; Hyodo T et al, 2005). This aids in development of novel materials of desired properties and applications. (Ajayi and Agunbiade, 2015; Marikkannan et al, 2015; Memarian et al , 2012; Deshmukh et al, 2008). The study of optical properties is significant in developing materials to be used in the advanced technological field of optoelectronics, optical lenses in cameras, optical fibers, plastic packaging, electro-chromic displays, rechargeable batteries, fuel cell etc. The changes in physical properties of the composite material depend on the chemical nature of the filler metal and on the interaction mechanism between the filler and the polymer matrix.

So in the present work, the authors used a simple solution cast technique to fabricate stannous chloride doped PES films with different concentration of metal particles and made an attempt to investigate the optical properties of these prepared sample films.

UV-VIS spectroscopy are the appropriate tool to grasp the interaction of metal chloride with the polar surface of the PES, the absorbance and transmittance spectra were recorded using double beam UV-VIS spectrophotometer in the wavelength range (300-1100) nm at room temperature. Sufficient information on energy band structure and an understanding of the optical transitions in materials can be obtained from the shape and shift of the absorbance spectra and transmission spectra of these composite films. From this recorded data, significant optical parameters like optical band gap, refractive index, extinction coefficient have been calculated.

2. METHODS AND MATERIALS:-

2.1 Materials:- Stannous chloride ($SnCl_2.2H_2O$ - analytical reagent grade , dehydrated purified) and Dichloromethane (purity of 99.8%) was purchased from Merck Specialties Private Limited, Mumbai; Poly ether sulfone (PES) granules were purchased from M/s Gadra Chemicals, Bharuch. All chemicals were used as received.

2.2 Sample preparation: - Films of pure Poly ether sulfone(PES) and its composites with different weight percent of $SnCl_2.2H_2O$ were prepared by solution casting technique. A predetermined amount of granular PES is measured and dichloromethane is added as a solvent. The solution is stirrer so that polymer and $SnCl_2.2H_2O$ dissolve completely to yield a clear solution. The solution was then poured into a glass petri dish of diameter 6 cm washed thoroughly with hot water and then cleaned with acetone. The solution spreads uniformly in all direction in the petri dish which is kept freely floating over a pool of mercury so as to achieve perfect levelling and uniformity in the thickness of the film. The solvent was allowed to evaporate slowly at ambient temperature under atmospheric pressure for almost twenty four hours. The dried samples are peeled off by tweezers clamp. Transparent flexible nanocomposite polymer films of thickness around 100 □m different concentration of $SnCl_2.2H_2O$ (1%,2%, 5% and 10% by weight) are obtained.

2.3 Characterization:

The transmission spectra and absorption spectra of composites have been recorded using EI 2375 UV-VIS double beam spectrophotometer. From the obtained data , the fundamental optical parameters *viz.* Optical band gap energy, absorption coefficient (□), extinction coefficient (□), finesse coefficient (F), refractive index (n), real and imaginary parts of dielectric constant (□$_r$□and□□$_i$) and optical conductivity (□) have been calculated.

3. RESULT AND DISCUSSION

3.1 *UV VIS Double beam spectrophotometer data and Band Gap Analysis*

UV-VIS Double beam spectrophotometer is a simplest tool to probe the optical properties to estimate band gap energy and to determine the types of electronic transition within the materials. When light of intensity (I) is incident on a film of thickness (t) then the penetrating light intensity (I_0) is given by :-

$I = I_0\ exp$ (-□ t)□□…. (1)

So that absorption coefficient □□□□□□□□□□□□□□□□□□□□2.303 ($A/\ t$) …. (2)

where □□is in cm^{-1} and the amount I/I_0 is defined as Transmittance so that log (I_0/I) is the absorbance (A).

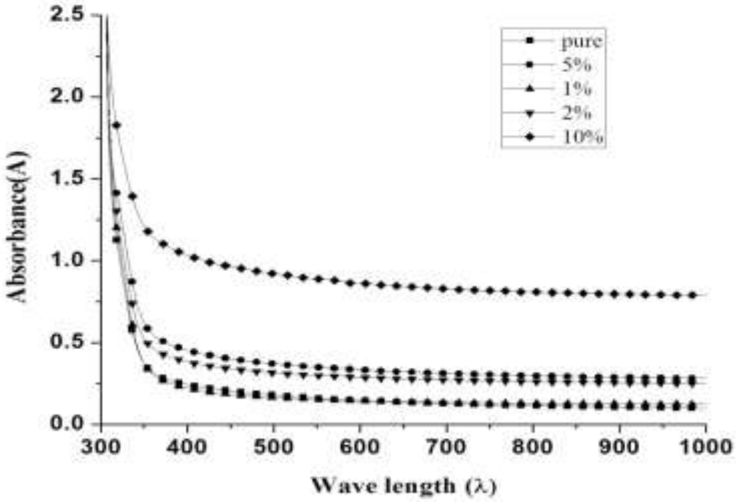

Fig.1: Absorbance as a function of wavelength for PES films with different concentration of $SnCl_2$.

Figure (1) shows the absorbance spectra as function of the wavelength of the incident light for PES film with different concentration of $SnCl_2.H_2O$. It is clear that increasing the concentration of $SnCl_2.H_2O$ in the polymer matrix leads to decrease in the absorption intensity.

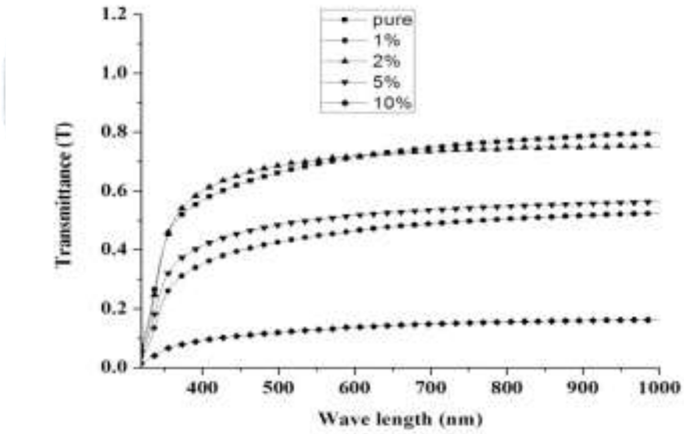

Fig.2: Transmittance as a function of wavelength for PMMA films with different concentration of $SnCl_2$.

From Figure (2) it is clear that the transmittance increases with the increase in the concentration of $SnCl_2.H_2O$. The pure PES has high transmittance because there are no free electrons (electrons are strongly linked to their atoms through covalent bonds) and the breaking of electron linkage and moving to the conduction band need photon with high energy. Similarly, $SnCl_2.H_2O$ molecules also do not contain free electrons to absorb photons of the incident light, thus transmittance increases with increasing concentration of $SnCl_2$.

The Mott and Davis relation (Abdullah et al, 2016;Ranganath and Lobo, 2008) is used to evaluate the optical energy gap :

□h□□□□□□□□□□□□□□□□C (h□□□□E_g)^m ………. (3)

where h□□□□is the photon energy, C is the proportional constant depending on the specimen structure, E_g is the allowed or forbidden energy gap of transition and the exponent m is an index which determines the type of electronic transition responsible for absorption. It can take values 1/2, 3/2 for direct and 2, 3 for indirect allowed and forbidden transitions respectively. Reported literature (Mohameda et al, 2008) suggests that if the amount of absorption (□□ > 10^4 cm^{-1} the electronic transitions are direct otherwise indirect one. If plotting □ vs E (i.e. h□□□shows an $E^{1/2}$ dependence, then plotting □^{2} with E will show a linear dependence. Therefore, if a plot of h□□versus □^{2} forms a straight line, it can normally be inferred that there is a direct band gap, measurable by extrapolating the straight line to the □ =0 axis. On the other hand, if plotting □ vs E (i.e. h□□□ shows an E^2 dependence, then plotting □$^{1/2}$ with E will show a linear dependence. So when a plot of □□$^{1/2}$ versus h□□□forms a straight line, it can normally be inferred that there is a indirect band gap, measurable by extrapolating the straight line to the □ =0 axis.

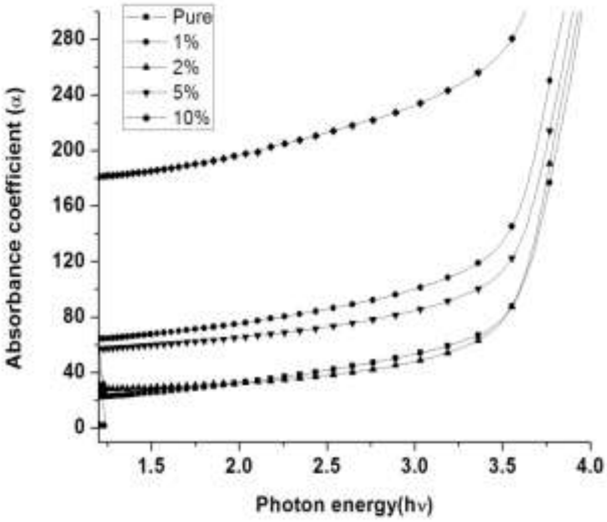

Fig.3 : Absorption coefficient (□) as a function of wavelength for PMMA films with different concentration of $SnCl_2$.

The absorption coefficient (α) shown in figure (3) has been calculated using equation (2). The coefficient of absorption for the PES - $SnCl_2.H_2O$ composites is more than 10^4 cm^{-1}, this explains that the electron transition is direct.

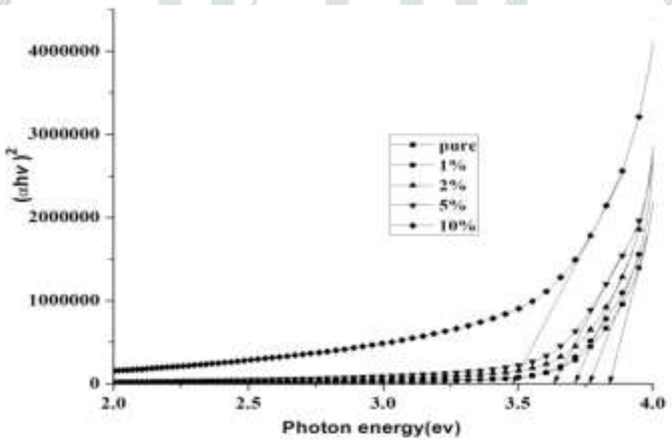

Fig.4: Absorption edges for composite films as a function of photon energy.

The intercept of the extrapolation of the linear portion of curves in figure (4) to zero absorption on h*v* axis, gives the value of optical band gap energy E_g listed in table 1. From Table 1 it can be inferred that the values of energy gap E_g increases with increase of the weight percentage of $SnCl_2.H_2O$. The decrease in E_g values suggest the loss of few energy levels (traps) between the HOMO and LOMO i.e. the decrease in density of localized states, due to the deformation taken place in the composite films.

Table 1: Optical Energy band gaps for PES: $SnCl_2.H_2O$ composite films

Samples	**E_g (eV)**
Pure PES	3.409
PES doped with 1% $SnCl_2$	3.765
PES doped with 2% $SnCl_2$	3.712
PES doped with 5% $SnCl_2$	3.626
PES doped with 10% $SnCl_2$	3.475

3.3 Refractive Index Study

The fundamental optical parameters like the extinction coefficient, refractive index and dielectric constant are necessary to be evaluated to understand the polarizability of the samples, and their consequent applications.

3.3.1 Extinction Coefficient

For incident wave of wavelength □□□the extinction coefficient is calculated using the relation:

k

□□.... (4)

From figure (5) it can be noted that *k* decreases with increasing $SnCl_2.H_2O$ content and incident photon energy. This can be ascribed to the variation of the absorption coefficient □ with increased doping percentages of added salt ions, as it is directly proportional to □□optical absorption coefficient and the incident wavelength described by equation (4).

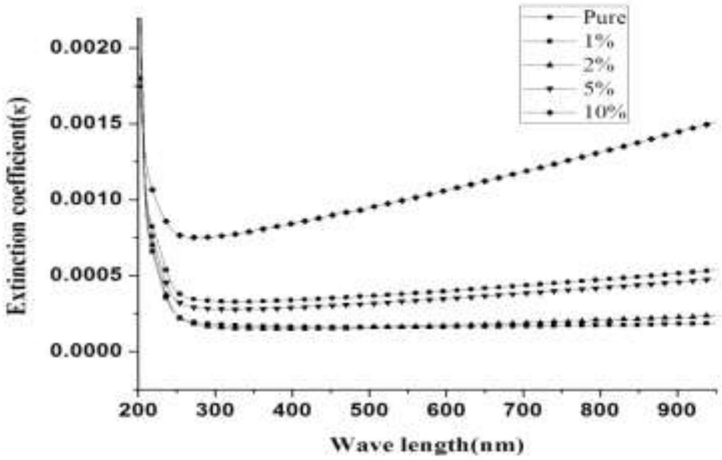

Fig 5: Extinction coefficient (*k*) as a function of wavelength for PES films with different concentration of $SnCl_2$.

3.3.2 *Refractive index*

The values of refractive index (n) can be obtained from the reflection coefficient R (which is *R* □□□□□□1-□□*A* □□*T*) and extinction coefficient (k) data using the below expression

$$n = (4R/(R-1)^2 - k^2)^{1/2} - (R+1/R-1) \quad \text{…. (5)}$$

Figure (6) shows that the refraction index for composite films decrease with wavelength and dopant concentration. The increase of refractive index (*n*) upon $SnCl_2.H_2O$ addition can be understood in view of the intermolecular hydrogen bonding between Sn+ ions and the adjacent ion of PES polymer chains.

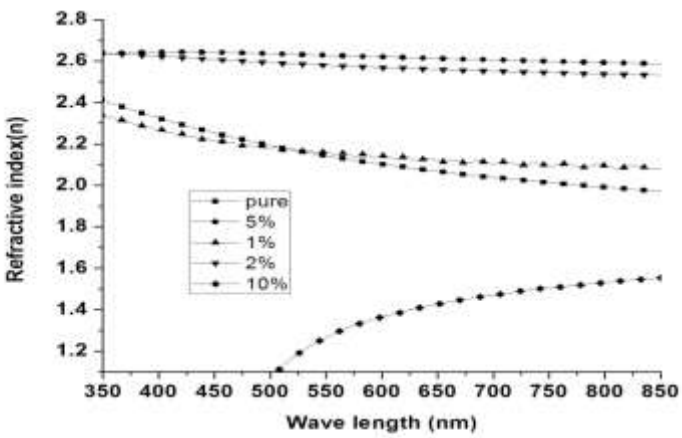

Fig 6: Variation of refractive index (*n*) as a function of wavelength for PES films with different concentration of $SnCl_2$.

3.2.3 *Finesse coefficient*

The finesse coefficient as calculated using the following expression:

□□F □□□□□□□□R □□□□□□R□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□…. (6)

and depicted in Figure (7) shows that it decreases with increasing in doping percentage because of doped additives that lead to changing in reflectance as F is dependent on R.

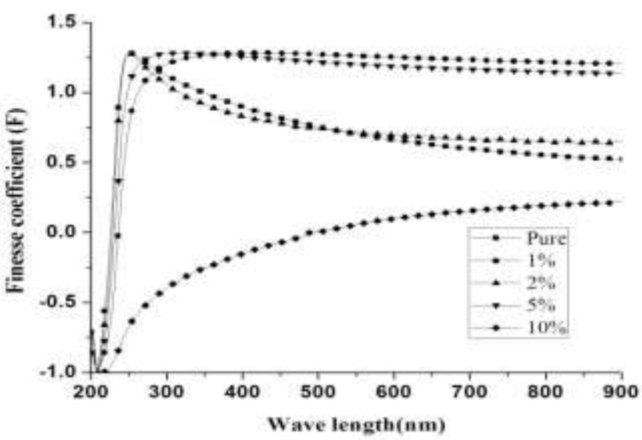

Fig. 7: Variation of Finesse coefficient (F) as a function of wavelength for PES films with different concentration of $SnCl_2$.

3.2.4 Dielectric Analysis

The real (ε_r) and imaginary (ε_i) parts of the dielectric constant are related to (n) and (k) values accordingly :

$$\varepsilon_r = n^2 - k^2 \quad \text{and} \quad \varepsilon_i = 2nk \quad \ldots..(7)$$

Figures 8 (a) and (b) show the change of these constants with wavelengths. The values of the real dielectric constant are high with respect to the imaginary dielectric constant and differ in their trend too. The real part decreases while imaginary part increases with increase in Wavelength

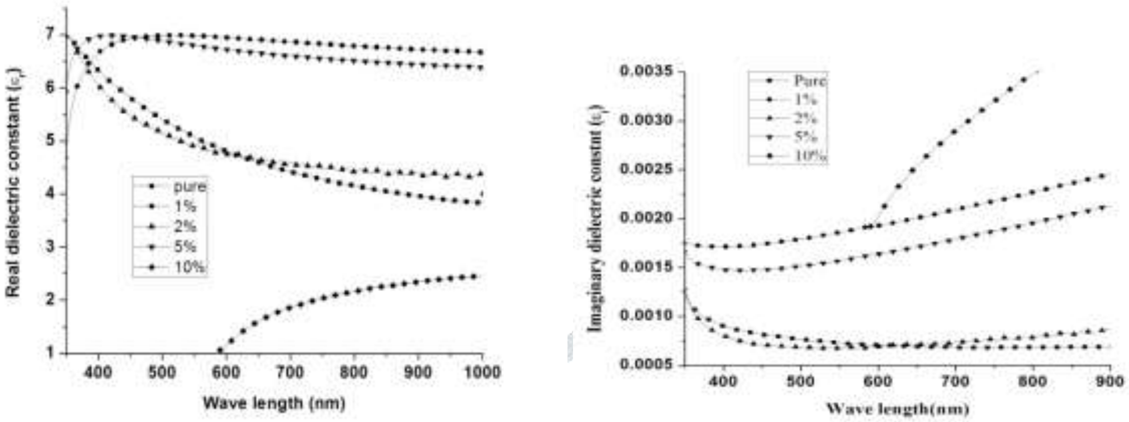

Fig.8: Variation of (a) real and (b) imaginary dielectric constant (ε_r) as a function of wavelength for PES films with different concentration of $SnCl_2$.

3.3 *Optical Conductivity Analysis*

The optical conductivity (σ) for pure PMMA and $SnCl_2.H_2O$ doped PES samples was calculated using the absorption coefficient α, and the refractive index *n* data using the relation expressed in equation (8).

$$\sigma_{opt} = \frac{\alpha n c}{4\pi} \quad \ldots. (8)$$

A decrease in optical conductivity is observed on increasing the doping percentages of stannous chloride. This means that on incorporation of the Sn ions in PES matrix suppresses the contribution of electron transitions between the valence and conduction bands, which leading to increase of energy gap.

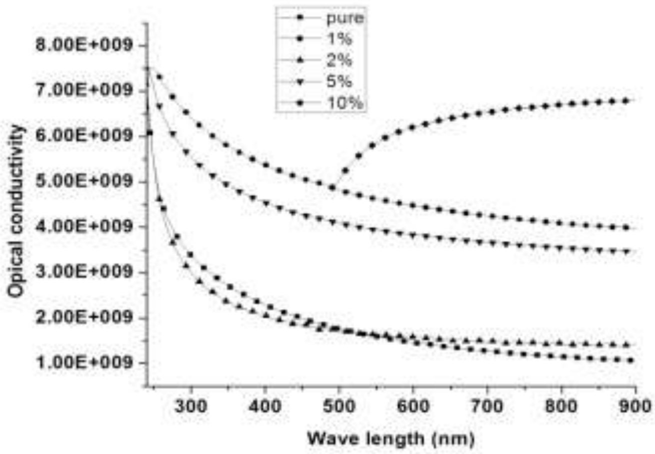

Fig.9: Optical conductivity (σ) as a function of wavelength for PES films with different concentration of $SnCl_2$.

4.CONCLUSION

In this work, composite sample films have been synthesized by adding tin chloride to PES using the solution casting technique. Determination of optical parameters has been done from the absorbance and transmittance (%T) spectra obtained. It is found that the absorption coefficient increases on addition of tin ions in PES matrix but there is a trend of decrease in absorption coefficient with increase in filler wt % content. The value of □ is indicative of direct electronic transitions. The increase in direct optical band gap energy with increasing tin chloride concentration suggests that the band gap can be plausibly tuned. The optical conductivity, refractive index and dielectric constant in the doped samples are significantly affected by $SnCl_2.H_2O$ concentration and are decisive for many applications.

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