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RESEARCH ARTICLE

Investigation of Optical Properties of Tin Chloride ($SnCl_2$) Doped Poly Methyl Methacrylate (PMMA) Composite Films

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Abstract

Three solid composite films of Poly-methyl-methacrylate (PMMA) doped with various concentration (2%, 4% and 8%) of $SnCl_2$ of thickness (~100 μm) have been synthesized employing the solution cast technique. The FTIR studies of the prepared films ascertains that $SnCl_2$ nano particles are well dispersed in the polymer and are coordinated to carbonyl and methaoxy oxygen of the polymer. The incorporation of $SnCl_2$ in main chain of PMMA brings out a remarkable change in the optical properties of the composite films. For this purpose absorbance (A) and transmittance (T%) data of the synthesized films in the wavelength range 300-1100 nm were recorded using UV-V-IS spectrophotometer. The data so obtained were analysed and from them the fundamental optical parameters viz. optical band gap energy, absorption coefficient (α), extinction coefficient (κ), refractive index (n), finesse coefficient (F), real as well as imaginary parts of dielectric constant (ε_r and ε_i) and optical conductivity (σ) have been evaluated ; which revealed a clear dependence on the $SnCl_2$ content.

Keywords: Dielectric constants, Energy band gap, Optical properties, PMMA- $SnCl_2$ Composite films

Introduction

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. (Hyodo *et al.*, 2005; Ranganath and Lobo, 2008; Sharker *et al.*, 2015; Ramesan and Bijudas, 2016). This aids in development of novel materials of desired properties and applications. (Deshmukh *et al.*, 2008; Memarian and Rozati, 2012; Ajayi and Agunbiade, 2015; Marikkannan *et al.*, 2015). 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. Poly (methyl methacrylate) (PMMA) is versatile potential polymeric material used in wide range of applications as it has fascinating properties of being highly transparent, having good tensile strength, rigidity, insulating properties and dopant dependent optical and electrical properties. (Ranganath and Lobo, 2008; Ammar *et al.*, 2013; Khodair *et al.*, 2014; Al-Sulaimawi, 2015; Abdullah *et al.*, 2016; Gupta *et al.*, 2016).

So in the present work, the authors used a simple solution cast technique to fabricate stannous chloride doped PMMA films with different concentration of metal particles and made an attempt to investigate the optical properties of these prepared sample films. As FTIR and UV-VIS spectroscopy are the appropriate tool to grasp the interaction of metal chloride with the polar surface of the PMMA, the absorbance and transmittance spectra were recorded in the wavelength range 300-1100 nm using double beam UV-VIS spectrophotometer 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.

Materials and Methods

Materials

All the chemicals viz., stannous chloride ($SnCl_2.2H_2O$ - analytical reagent grade, dehydrated purified) and dichloromethane (purity of 99.8%) purchased from Merck Specialties Private Limited, Mumbai; Ethanol (99.9%)

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procured from Changshu Hongsheng Fine chemicals; the granular Polymethylmethacrylate (PMMA) purchased from M/s Gadra Chemicals, Bharuch, were utilized as received. Basically the materials used are PMMA as matrix and tin chloride as filler and dichloromethane as solvent.

Sample preparation

Films of pure PMMA and its composites with different weight percent of $SnCl_2.2H_2O$ were prepared by solution casting technique. A predetermined amount of granular PMMA is measured and dichloromethane is added as a solvent. The molten PMMA is stirred uniformly on a magnetic stirrer for four hours and to this prepared solution 5 ml of ethanol and different concentration of $SnCl_2.2H_2O$ (2%, 4% and 8% by weight) are added. 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 left to evaporate slowly at ambient temperature for almost twenty four hours. The dried samples are peeled off by tweezers clamp. Transparent flexible nanocomposite polymer films of thickness around 100 mm are obtained.

Characterization

The infrared (IR) spectra of the polymer metal complexes were recorded on a Perkin Elmer Spectrum Version 10.4.00 FTIR spectrophotometer in the region 500–4000 cm^{-1}. 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 (α), refractive index (n), extinction coefficient (κ), finesse coefficient (F), real as well as imaginary parts of dielectric constant (ε_r and ε_i) and optical conductivity (σ) have been calculated.

Results and Discussion

FTIR Analysis

FTIR spectra which represent the molecular fingerprint of the samples are depicted in figure 1 and 2 respectively for the pure PMMA and stannous composites of PMMA with different concentrations. As shown in figure 1, the structure of pure PMMA is characterized by the vibration modes at 1725 cm^{-1} ascribed to C=O stretching, other vibration mode appearing at 2951 cm^{-1} corresponding to the C–H stretching of the methyl group (CH_3). The vibration mode ascribed to C–H symmetric stretching mode is 1384 $cm^{-1}$and that to asymmetric stretching modes is 1435 cm^{-1}. The torsion of the methylene group (CH_2) is characterized by 1236 cm^{-1} band. The vibration of the ester group C–O corresponds to 1191 cm^{-1}, while C– C stretching bands are between 986-481 cm^{-1}. However with the incorporation of stannous chloride in composites of PMMA, appearance of a new peak is observed at 3456 cm^{-1} and it reveals that the chemical interaction has taken place. Further, the intensity of vibrational bands also decrease with increase in concentration of stannous chloride.

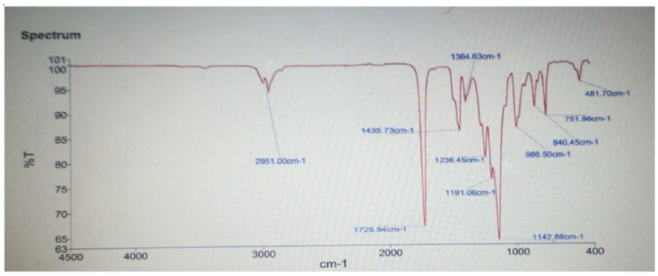

Fig.1. FTIR Spectrum for pristine PMMA

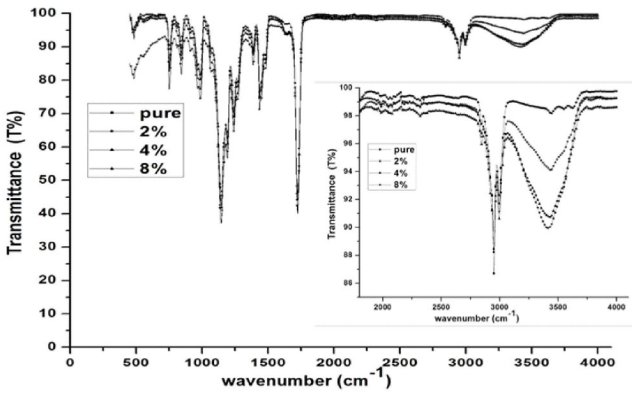

Fig.2. FTIR Spectra for PMMA and its composite films doped with different concentration of $SnCl_2$.

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_0) is incident on a film of thickness (t) then the intensity (I) of light coming out s given by :-

$$I = I_0 \, exp\,(-\alpha t) \qquad \text{…. (1)}$$

So that absorption coefficient

$$\alpha = 2.303\,(A/\,t) \qquad \text{…. (2)}$$

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

The absorbance data in the mentioned wavelength range for all synthesized PMMA composite films is depicted in figure (3). It is obvious that the increase in the concentration of $SnCl_2.H_2O$ into the polymer matrix decreases the absorption intensity. From Figure (4) it is clear that the transmittance increases when the concentration of $SnCl_2.H_2O$ is increased in the polymer. The pure PMMA shows high transmittance as it is devoid of free electrons. Photons of high energy are required to break the strong covalent bonding to release free electrons and move them to the conduction band. 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 $SnCl_2$.

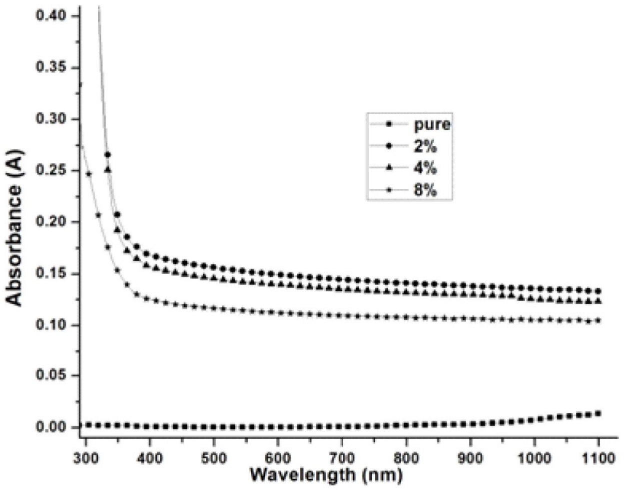

Fig.3. Variation of Absorbance with wavelength for PMMA composite films consisting different concentration of $SnCl_2$.

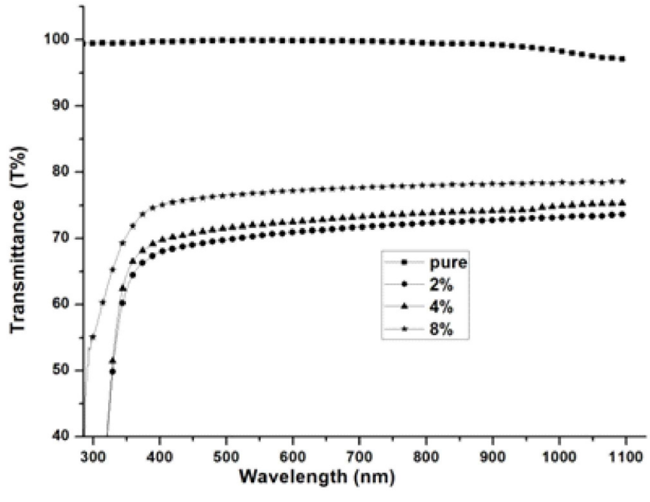

Fig.4. Variation of Transmittance with wavelength for PMMA composite films consisting different concentration of $SnCl_2$.

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

$$\alpha h\upsilon = C(h\upsilon - E_g)^m \qquad \text{.... (3)}$$

where the proportional constant *C* depends on specimen structure, $h\upsilon$ is the photon energy, E_g is the allowed / forbidden energy gap and the exponent m is an index which determines the mode of electronic transition responsible for absorption. The values of m = 1/2, 3/2 represent direct and m = 2, 3 represent indirect allowed and forbidden transitions respectively. Reported literature (Mohameda *et al.*, 2009) suggests that if the amount of absorption (α) > 10^4 cm^{-1} the electronic transitions are direct otherwise indirect one. If plotting α vs E (i.e. $h\upsilon$) shows an $E^{1/2}$ dependence, then plotting α^2 with E will show a linear dependence. Therefore, if a graph plotted between α^2 and $h\upsilon$ depicts a straight line then normally a direct band gap is inferred which is evaluated by extrapolating the straight line to the α =0 axis. Conversely, if plotting α vs E (i.e. $h\upsilon$) shows an E^2 dependence, then plotting $\alpha^{1/2}$ with E will show a linear dependence. So if the graph plotted between $\alpha^{1/2}$ and $h\upsilon$ depict a straight line then an indirect band gap can be inferred and can be evaluated by extrapolating the straight line to the α =0 axis.

The absorption coefficient (α) shown in figure (5) has been calculated using equation (2). As the value of α is more than 10^4 cm^{-1} for the PMMA-$SnCl_2.H_2O$ composites, we infer that the electron transitions are direct.

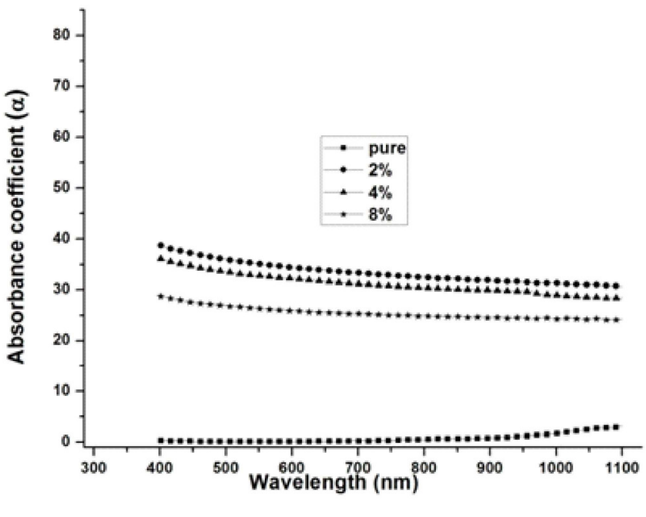

Fig.5. Variation of Absorption coefficient (α)with wavelength for PMMA composite films consisting different concentration of $SnCl_2$.

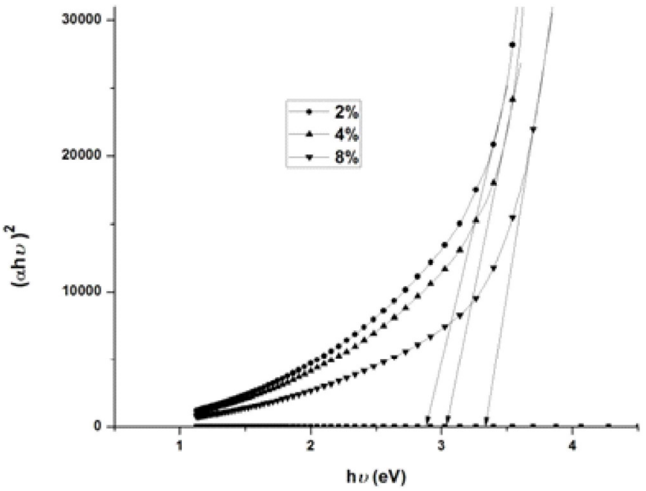

Fig.6. Absorption edges $(\alpha h\upsilon)^2$ for composite films as a function of photon energy. The direct allowed gap transition value is obtained on extending the curve to the values of $(\alpha h\upsilon)^2 = 0$.

The intercept of the extrapolated linear part of curves in figure (5) to zero absorption on hυ axis, gives the value of optical band gap energy E_g listed in Table 1. From Table 1 we conclude that the values of energy gap E_g increases on increasing the concentration of $SnCl_2.H_2O$ in PMMA. The decrease in E_g values suggest the loss of few energy levels (traps) between the HOMO and LOMO due to the deformation in the composite films.

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

Samples	E_g (eV)
PMMA doped with 2 % $SnCl_2.2H_2O$	2.881
PMMA doped with 4 % $SnCl_2.2H_2O$	3.037
PMMA doped with 8 % $SnCl_2.2H_2O$	3.340

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.

Extinction Coefficient

The extinction coefficient is evaluated using the relation:

$$k = \alpha\lambda / 4\pi \quad \text{.... (4)}$$

where λ is the wavelength of incident waves. From figure (7) 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 a and the incident wavelength λ described by equation (4).

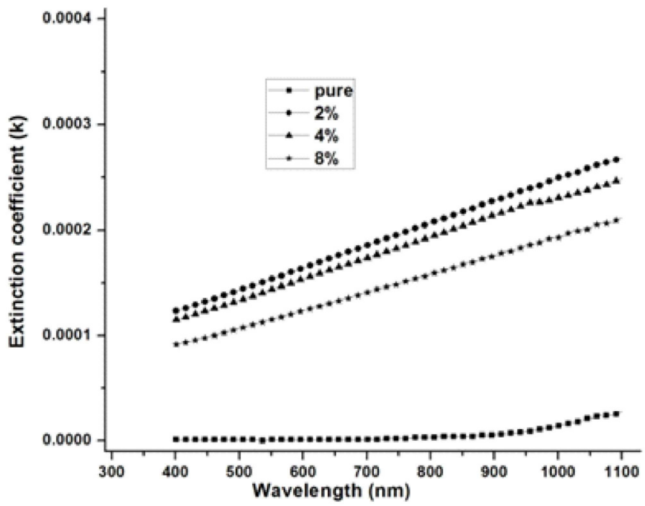

Fig. 7. Variation in Extinction coefficient (*k*) with wavelength for PMMA composite films consisting different concentration of $SnCl_2$.

Refractive index

The 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 (8) 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 PMMA polymer chains.

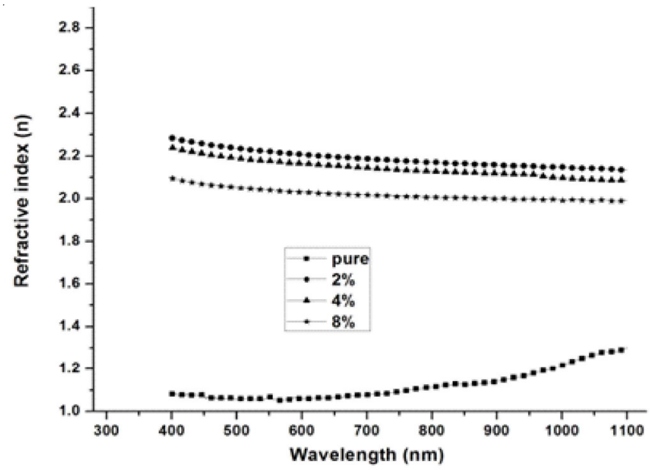

Fig. 8. Variation of refractive index (*n*) with wavelength for PMMA composite films consisting different concentration of $SnCl_2$.

Finesse coefficient

The finesse coefficient as calculated using the following expression:

$$F = 4R / (1-R^2) \qquad \text{.... (6)}$$

and depicted in figure (9) shows that it decreases with increase in tin chloride concentration. This occurs because the doped $SnCl_2$ lead to change in reflectance and F is dependent on R.

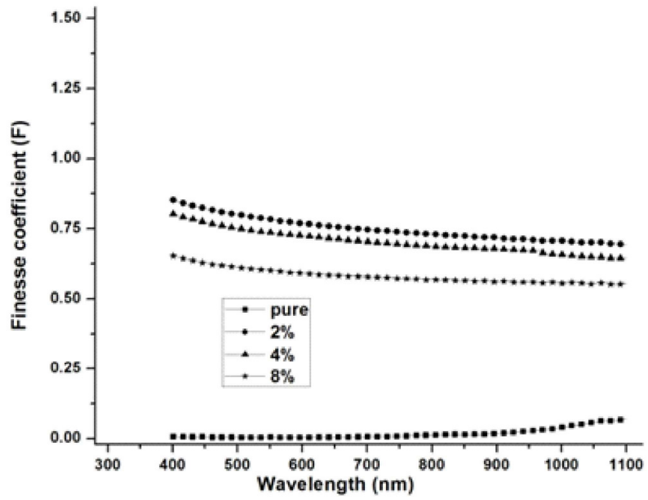

Fig. 9. Variation of Finesse coefficient (F) with wavelength for PMMA composite films consisting different concentration of $SnCl_2$.

Dielectric Analysis

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

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

Figures (10) and (11) show the variation in these constants with wavelengths. The values of the real dielectric constant are high compared to the imaginary dielectric constant and differ in their trend too. The real part decreases while imaginary part increases with increase in wavelength.

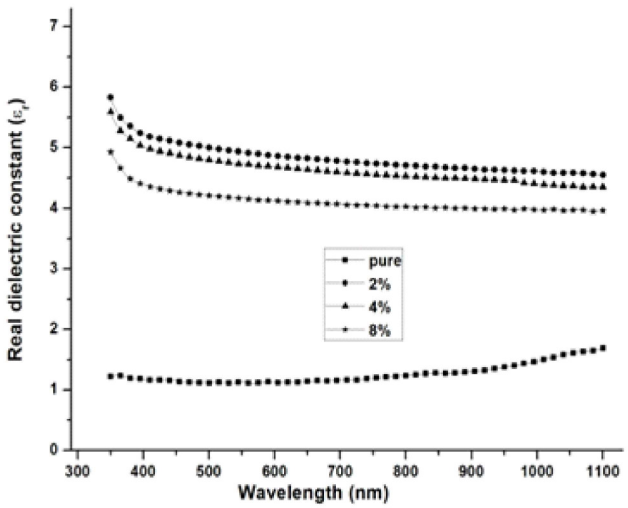

Fig.10 (a)

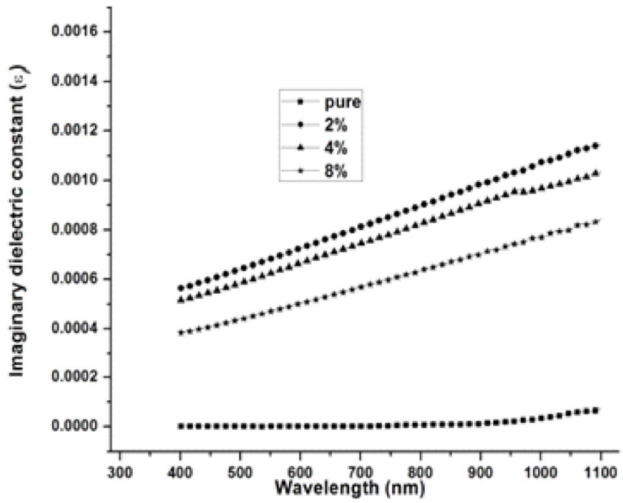

Fig. 10 (b)

Fig. 10. Variation of (a) real and (b) imaginary dielectric constant (ε_r) with wavelength for PMMA composite films consisting different concentration of $SnCl_2$.

Optical Conductivity Analysis

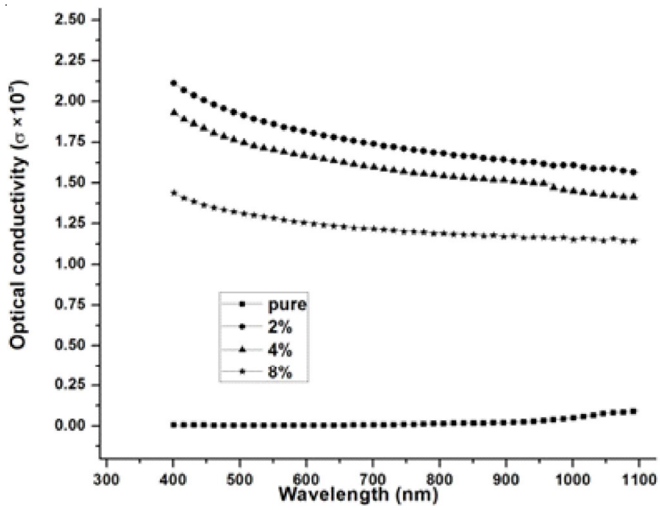

Fig. 11. Variation of Optical conductivity (σ)with wavelength for PMMA composite films consisting different concentration of $SnCl_2$.

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

$$\sigma_{opt} = nc\alpha \; / \; 4\pi \qquad \text{.... (8)}$$

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 PMMA matrix, the electron transitions between the valence and conduction bands is further suppressed, which leads to increase in energy gap.

Conclusion

In this work, composite sample films have been synthesized by adding tin chloride to PMMA 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 PMMA matrix but there is a trend of decrease in absorption coefficient with increase in filler wt % content. The value of α 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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