

Evolution of the optical properties of Polystyrene thin films filled with Zinc Oxide nanoparticles

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Abstract: Thin films of Polystyrene (PS) with different concentrations (0, 0.5, 1, 3 and 5 wt. %) of ZnO nanoparticles (ZnO NPs) as a filler were prepared by using solution cast technique. Effect of ZnO NPs on optical properties of PS such as absorbance, transmittance, absorption coefficient, refractive index, extinction coefficient, and real and imaginary parts of dielectric constant have been investigated by measuring optical absorption spectra using UV-Vis spectroscopy. This study reveals that all these parameters are affected by increasing ZnO NPs percentage. The study has been also extended to include the changes in the optical parameters including the band tail width and band gap energies for the samples.

Keywords: Polystyrene, ZnO nanoparticles, solution cast technique, optical properties, filler effect.

1 INTRODUCTION:

In recent years, many efforts have been focused on the inorganic/organic nanocomposite materials with various compositions. By combining organic and inorganic materials, the resulting composites can possess advantages of both organic polymers (e.g. flexibility, ductility, dielectric) and inorganic components (e.g., rigidity, high thermal stability, strength, hardness, high refractive index) [1], thus creating extensive usages in many areas. By incorporating nanoparticles into polymer matrix even with a very little loading, many interesting optical properties including absorption, fluorescence, luminescence, nonlinearity, high reflex index (RI), magnetic properties, and excellent mechanical properties may be obtained [2].

In recent years, polymers with different optical properties have been attracted much attentions due to their applications in the sensors, light-emitting diodes, and others. The optical properties of these materials can be easily tuned by controlling the filler concentrations. Though a great deal of work has been reported on such materials [3-5], it is still meaningful to extend the research of these polymers.

Polystyrene has attracted the attention of scientists for its interesting features and its superior physical and chemical properties. Polystyrene (PS) is amorphous polymer with bulky side groups. Major characteristics of PS include rigidity, transparency, high refractive index, good electrical insulation characteristics, low water absorption, and ease of processing which makes important for many applications in industry [6, 7]. Moreover, PS is traditionally considered as an excellent host material for composites. In view of this increasing importance, the structure and conformation of polystyrene (PS) have received considerable attention in the recent literature.

Among the many inorganic materials, zinc oxide, ZnO, is a direct band-gap ($E_g = 3.37$ eV) semiconductor with a large exciton binding energy (60 meV) [8]. Recently it has been intensively studied as a promising material for optoelectronic devices such as light emitting diodes (LED) and flat display screens and as an interesting material for solar applications due to its unique combination of optical and semiconducting properties. ZnO has an optical band gap in the UV region and this makes it an extremely efficient UV absorber [9-11].

The optical study provides important information about the absorbance, transmittance and reflectance of the observed polymeric films. The optical absorption and especially the absorption edge present a useful method for the investigation of optically induced transition and for getting information about the band structure, the band tail and the energy gap of the polymeric materials under consideration [12-13].

In the present work, the absorption coefficient, refractive index, extinction coefficient and real and imaginary parts of dielectric constant were determined, and the effect of ZnO concentration on some of its optical properties is studied.

2 MATERIALS AND METHODS:

2.1 MATERIALS: Polystyrene used in this study was supplied by Polymer Chemical Industry, Mumbai. Toluene (AR Grade, E Merck India Ltd, Mumbai) was used as a solvent for PS. The hexagonal Wurtzite structured Zinc oxide nanoparticles (ZnO NPs) with average crystalline size about 80 nm, synthesized by a simple chemical solution method followed by combustion. Detailed preparation technique and properties of as-prepared NPs was reported

elsewhere [14]. This ZnO NPs were used as the filler in different weight % (0, 0.5, 1, 3 and 5).

2.2 SAMPLE PREPARATION: Thin films of ZnO/PS nanocomposites were prepared by using solution - cast technique [15]. PS was dissolved in toluene using hot plate magnetic stirrer at 50°C for 1 hr to obtain homogeneous solution. Then ZnO was added to the homogeneous solution of PS in different weight % (0, 0.5, 1, 3 and 5). For maximum dispersion the solution was further stirred for 2 hrs by keeping the temperature constant. Thin films were prepared by pouring the solution on a clean optically plane glass plate which was kept over the pool of mercury for perfect leveling, so as to ensure uniform thickness. The whole system was allowed to evaporate at room temperature in dust free chamber and after complete evaporation the film was detached from the glass surface.

The thickness of samples was measured by compound microscope in conjunction with n oculometer having least count 15.38 μm similar to the method reported by [16]. The thickness of all samples was kept constant and it is of the order of ≈ 61.52 μm.

The measurements of absorbance and transmittance spectra in the wavelength range (280-700) nm were carried out using SHIMADZU (visible spectrometer) UV-1700 series. The optical absorption and transmittance spectra were analyzed to determine the optical constants such as absorption coefficient α, refractive index n, extinction coefficient k and, real and imaginary parts of dielectric constant. Analysis of the absorption coefficient was also carried out to determine the optical band gap and nature of transitions.

3 THEORETICAL:

The valuable information such as the electronic band structure and the optical energy band gap can be obtained by absorption coefficient. The absorption coefficient α(v) can be estimated from the optical absorption spectrum owing to the following equation [17].

$$\alpha = 2.303 \frac{A}{d} \dots \dots 1$$

Where, d is the film thickness in cm and A is defined by log (I₀/I) where I₀ and I are the intensities of the incident and transmitted beams respectively.

Concerning the optical transitions resulting from photons of energy hv > E_g^{opt}, the present optical data can be investigated according to the following relationship for the near edge optical absorption. The absorption edge for direct

and non-direct transitions can be obtained in view of the models proposed by [18],

$$\alpha hv = C_0(hv - E_g^{opt})^r \dots \dots \dots 2$$

Where, α is the absorption coefficient, ν is the frequency, h is Planck’s constant, C₀ is a constant, E_g^{opt} is the optical energy band gap between the valence band and the conduction band and r is the power that characterizes the transition process. Specifically, r can take the values 1/2, 3/2, 2 or 3 for transitions designated as direct allowed, direct forbidden, indirect allowed, and indirect forbidden respectively [13]. The determination of the value of optical energy band gap E_g^{opt} involves the plotting of (αhv)^{1/r} against hv.

The reflectance (R) has been found from values of transmission (T), and Absorbance (A), using the relationship:

$$A+R+T=1 \dots \dots \dots 3$$

For normal reflectance, the refractive index can be determined from the relation:

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \dots \dots \dots 4$$

The extinction coefficient k is related to the absorption coefficient α by the relation:

$$k = \frac{\alpha \lambda}{4\pi} \dots \dots \dots 5$$

Where, λ is the incident photon wavelength.

The relation between the complex dielectric constant and the complex refractive index N is expressed by:

$$\epsilon = N^2 \dots \dots \dots 6$$

It can be concluded that

$$(n - ik)^2 = \epsilon_r - \epsilon_i \dots \dots \dots 7$$

The real (ε_r) and imaginary (ε_i) parts of the dielectric constant thus related to (n) and (k) values and can be calculated using the following formulas [19]:

$$\epsilon_r = n^2 - k^2 \text{ and } \epsilon_i = 2nk \dots \dots \dots 8$$

4 RESULTS AND DISCUSSION:

The obtained optical parameters of PS are found to be strongly affected by ZnO NPs used as filler. Figure 1

shows the absorption spectra of the prepared samples. The absorptions increases as the ZnO percentage increases, adding different concentration of the filler material to the polymer do not change the chemical structure of the polymer but new physical properties to the mixture will formed. There are no absorption bands in the visible region since the samples are transparent and this result agree with previous studies [20]

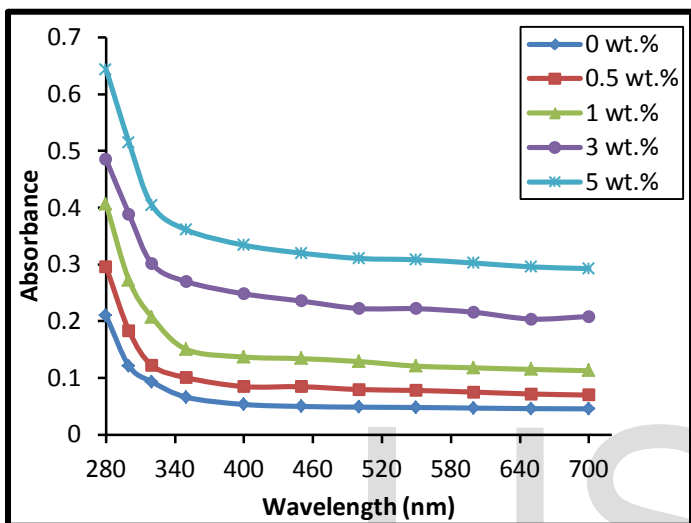


Figure 1: The absorbance as a function of wavelength of ZnO doped PS films at different concentrations.

Figure 2 shows an optical transmittance spectrum as a function of incident wavelength on ZnO doped PS films. The transmittance percent decreases with increasing filler concentration; this is because of layer of covalent bonds formed between polymer chains and additives that decrease the transmitting of the incident light especially at the shortest wavelengths. The electrons in the outer orbits have travelled to the higher energy levels and have occupied vacant positions of energy bands. Thus, part of incident light does not penetrate through it. However, the undoped PS has no free electron and the conduction band needs photon with high energy, after which it has high transmittance [21]

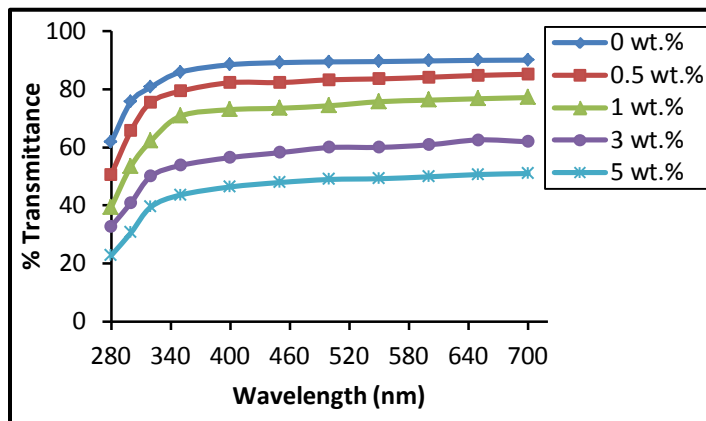


Figure 2: The transmittance for ZnO doped PS thin films as a function of wavelength at different concentrations.

Figure 3 shows the relationship between the absorption coefficient and photon energy of the ZnO/PS nanocomposites. The gradient of the 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 ($h\nu < E_g$). It was observed that at high energy, absorption is great and the forbidden energy gap is less which indicates the large probability of electronic transitions.

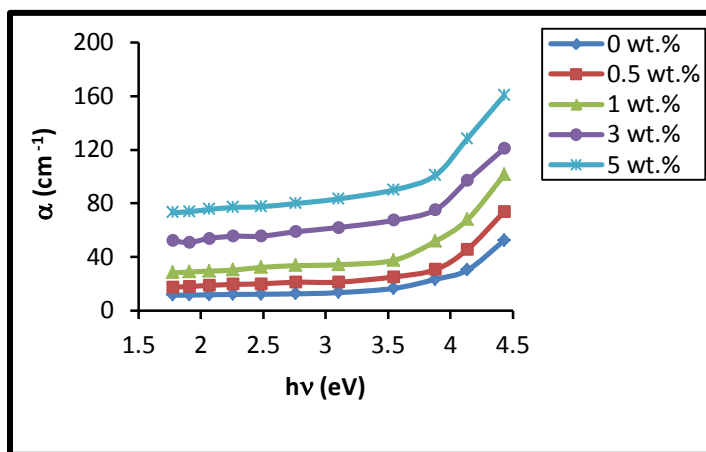


Figure 3: Optical absorption coefficient for pure PS and ZnO/PS nanocomposites

Figure 4 shows the variation of the refractive index of nanocomposites as the function of wavelength. The refractive index increase as a result of filler addition, this behaviour can be attributed to the increasing of the packing density as a result of filler content.

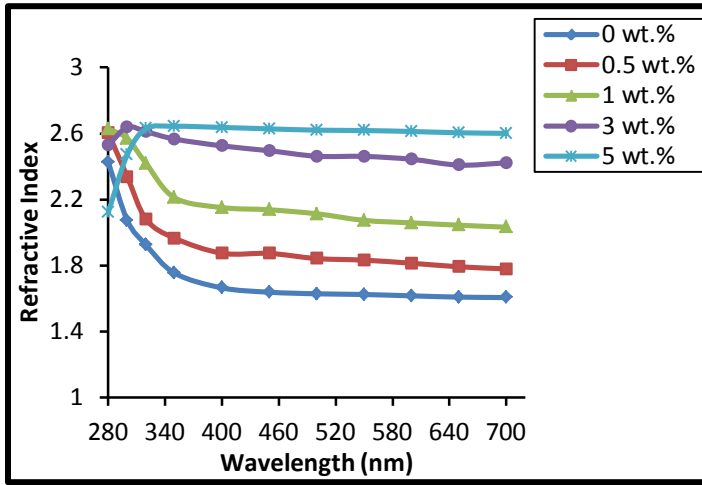


Figure 4: The refraction index of ZnO doped PS thin films as a function wavelength at different concentrations.

The variation of extinction coefficient (k) with wavelength for (PS-ZnO) nanocomposites is as shown in figure 5. The extinction coefficient increases with increasing of ZnO NPs concentration. This behaviour of extinction coefficient can be ascribed to high absorption coefficient. The extinction coefficient is high at the longest wavelengths and high concentration.

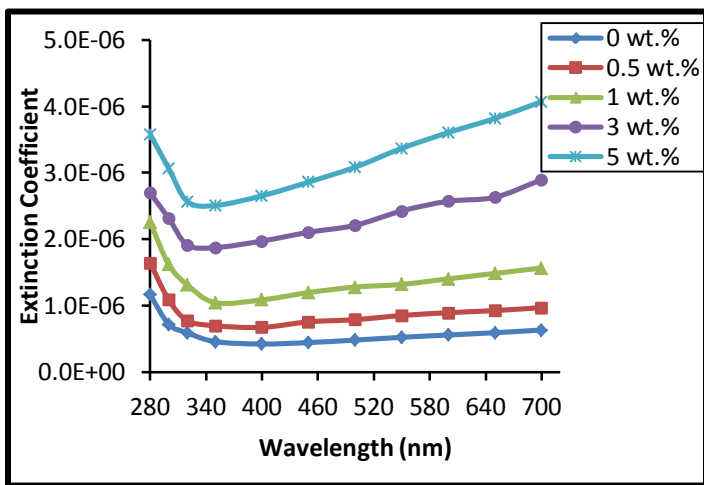


Figure 5: The extinction coefficient for ZnO doped PS thin films as a function of wavelength.

The real and imaginary dielectric constant (ϵ_r and ϵ_i) for PS-ZnO nanocomposites have been calculated from Equation 8. The variation of real and imaginary parts of dielectric constants of (PS-ZnO) nanocomposites with wavelengths is shown in figures (6, 7). It is concluded that the variation of ϵ_r mainly depends on (n^2) because of small values of (k^2), while ϵ_i mainly depends on the (k) values which are related to the variation of absorption coefficients. The values of the real dielectric constant are high with respect to the imaginary dielectric constant.

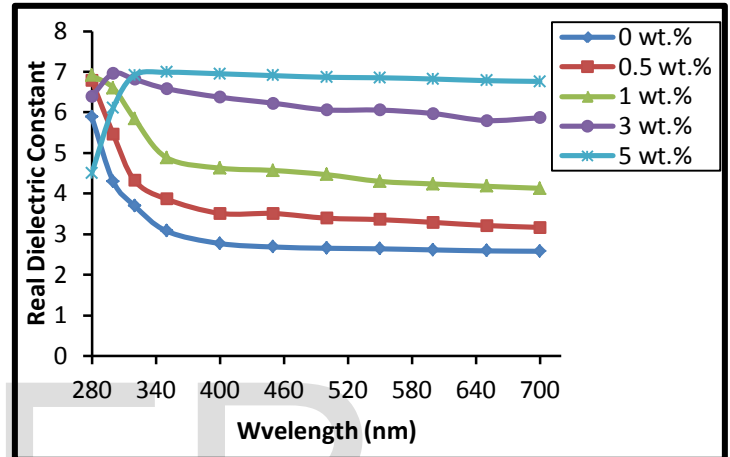


Figure 6: The real dielectric constant for PS-ZnO thin films as a function of incident wavelength.

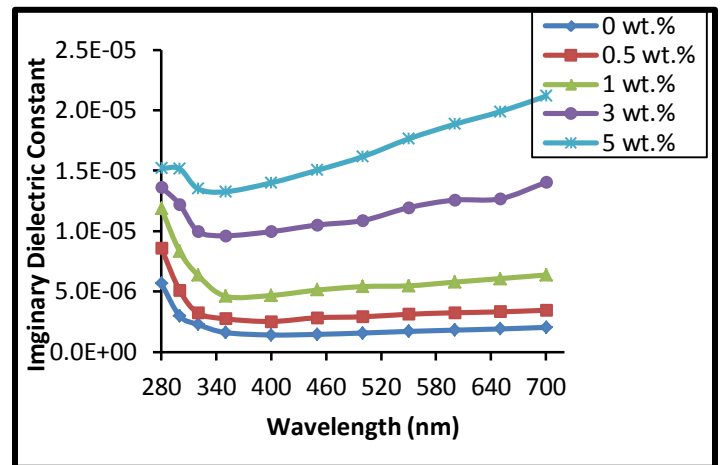


Figure 7: The imaginary dielectric constant for PS-ZnO thin films as a function of incident wavelength.

Figure 8 shows the relationship between absorption edge $(\alpha h\nu)^{1/2}$ for casting material as a function

of photon energy $h\nu$. Extrapolation of the linear portion of the plots to the abscissa yields the indirect allowed gap transition.

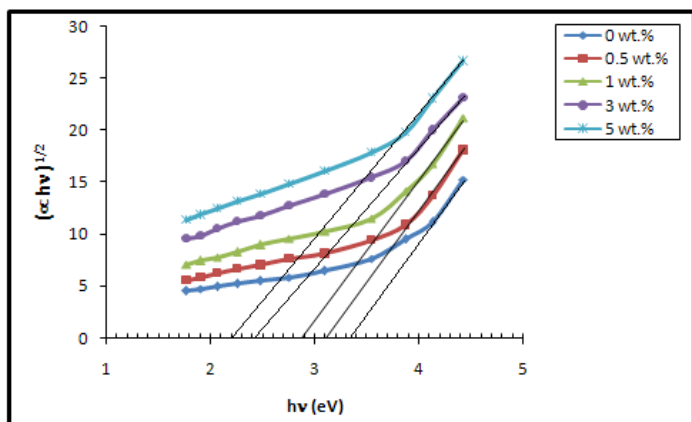


Figure 8: $(\alpha h\nu)^{1/2}$ vs. $h\nu$ plots of ZnO doped PS thin films for different dopant concentrations with energy gap of allowed indirect transitions.

Figure 9 shows the dependence of $(\alpha h\nu)^2$ on the photon energy ($h\nu$) for direct allowed transitions. The optical energy gap was estimated from the extrapolation of the linear portion of the graph to the photon energy axis. It is to be noticed that the curve is characterized by the presence of an exponentially decaying tail at low photon energy. It is observed that the E_g^{opt} slightly decreased with increasing dopant concentration.

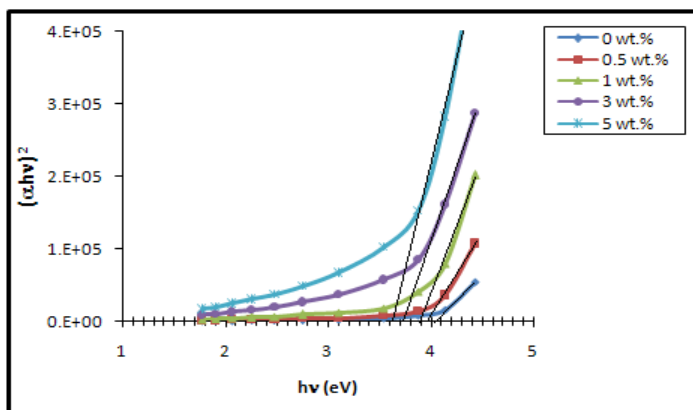


Figure 9: Relation between $(\alpha h\nu)^2$ vs. $h\nu$ for PS with different ZnO concentration

The Urbach plot is presented in Figure 10, in which the natural logarithm of absorption coefficient α is plotted as a function of photon energy ($h\nu$).

The magnitudes of the Urbach energy E_u were estimated by taking the reciprocal of the slopes of the linear portion of these curves. The origin of E_u can be considered as thermal vibrations in the lattice. The optical band gap and band tails of the localized state of the samples are tabulated in Table 1. The present experimental results concerning the direct and indirect optical energy band gaps and the Urbach energy tail E_u depict that filling significantly affects these optical absorption parameters.

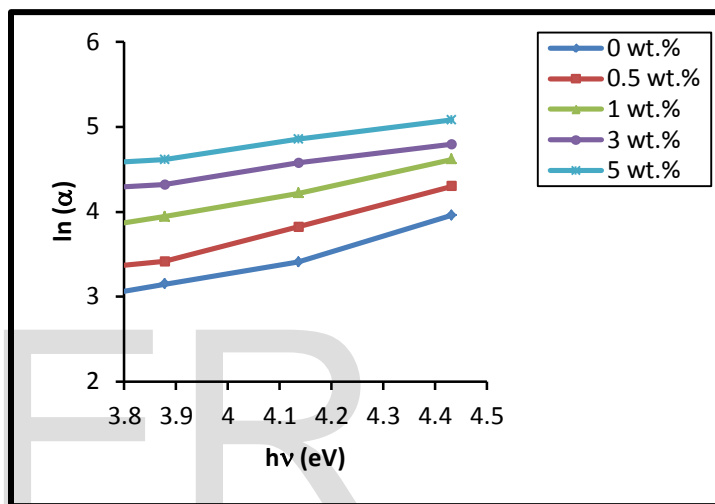


Figure 10: Relation between $\ln(\alpha)$ and $h\nu$ for PS at different ZnO NPs concentration.

Samples	Direct E_g^{opt} (eV)	Indirect E_g^{opt} (eV)	E_u (eV)
PS- 0 % ZnO	4.05	3.35	0.536421
PS- 0.5 % ZnO	3.97	3.12	0.613382
PS- 1 % ZnO	3.89	2.88	0.737052
PS- 3 % ZnO	3.72	2.43	1.334102
PS- 5 % ZnO	3.61	2.2	1.320392

Table 1: Direct, indirect optical energy gap, and band tail for PS doped with ZnO.

The variation of the calculated values of the optical energy gap may reflect the role of ZnO NPs in modifying the electronic structure of the PS matrix due to appearance of various polaronic and defect levels [13]. The decrease in the optical energy band gap with filling may be explained

on the basis of the fact that the incorporation of small amounts of dopant forms charge transfer complexes in the host matrix. These charge transfer complexes increase the electrical conductivity by providing additional charges, this result in a decrease of the optical energy gap. As the dopant concentration is increased, the dopant molecules start bridging the gap separating the two localized states and lowering the potential barrier between them, thereby facilitating the transfer of charge carrier between two localized states [22].

The increase of E_u values by increasing the concentration of ZnO NPs in ZnO/PS nanocomposites can be attributed to the effect of internal potential fluctuation associated with the structural disorder [23].

5 CONCLUSIONS:

Nanocomposite thin films of PS with different concentrations of ZnO NPs have been prepared by solution cast method and have been investigated for their optical properties. The absorbance, absorption coefficient, extinction coefficient, refraction index and reflectance of ZnO doped PS films increase with increasing of doping percentages, except the transmittance. The dielectric constant (real and imaginary) also increases with increasing doping content. The optical energy band gap and the Urbach energy tail were evaluated and their dependence on filling was investigated. The decreasing trend of the optical band gap with ZnO NPs concentration, which may be attributed to formation of charge transfer complexes, suggests the presence of the deep localized state in the band gaps.

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