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Research Paper

Optical Properties of ZnO/Low Density Polyethylene Nanocomposites

Science

KEYWORDS : LDPE, ZnO nanoparticles, solution cast technique, optical absorption, filler.

Vijaya S. Sangawar — Polymer/Nanomaterials Research Laboratory, Govt. Vidarbha Institute of Science and Humanities, VMV Road, Amravati -444602 India

Manisha C. Golchha — Polymer/Nanomaterials Research Laboratory, Govt. Vidarbha Institute of Science and Humanities, VMV Road, Amravati -444602 India

ABSTRACT

Thin films of Low Density Polyethylene (LDPE) filled with Zinc Oxide nanoparticles (ZnO NPs) for different weight percent (0, 0.5, 1, 3, 5 wt. %) were prepared by the solution cast technique. The Absorption spectra of thin films were taken in the wavelength range (200-700 nm). The changes in the band tail width and band gap energies for the samples were studied. It was found that the direct and indirect transitions values shifted to lower energies with the increase in ZnO NPs concentration.

1. INTRODUCTION

The synthesis of polymer nanocomposites is an integral aspect of polymer nanotechnology. By inserting the nano-metric inorganic compounds, the properties of polymers improve and hence this has a lot of applications depending on the inorganic material present in the polymer. Many research groups have focused on dispersing metal oxide nanoparticles into polymer matrix, as the hybrid nanocomposites not only inherit the functionalities of semiconductor nanoparticles but also possess advantages of polymers such as flexibility, film integrity, and conformity **[***Shuxiang Mu et al* **(2011)]**. Polymeric ZnO nanocomposite materials have attracted large interest because introduction of ZnO filler into polymeric matrices can modify the optical (e.g. shielding from UV and NIR radiation), electrical and mechanical properties.

Zinc Oxide is an important electronic and photonic material which possesses semiconducting and piezoelectric properties. It is a semiconductor, with a direct band gap of 3.37 eV and a large excitation binding energy (60 meV). This band gap value is equivalent to ultraviolet (UV) light energy, which means that ZnO has ability to absorb UV light [*Augustine S M et al* **(2010)**].

LDPE is a semi-crystalline polymer. Due to its excellent electrical and mechanical properties, is widely used as insulation material for electric power cables. Numerous studies have been performed to investigate the space charge distribution and electrical conduction in polyethylene systems. Combining ZnO nanoparticles with LDPE should enhance its optical and electrical properties.

The study of the optical absorption spectra in solids provides essential information about the band structure and the energy gap in both crystalline and noncrystalline materials. The lower energy part of the absorption spectra gives information about the atomic vibrations and higher energy part of the absorption spectra gives knowledge about electronic status in the materials.

2. MATERIALS AND METHODS

2.1 Materials

Commercial grade granular LDPE provided by Indothene (24 FS040) was used as it is without further processing and Xylene (AR Grade, E Merck) as a solvent for LDPE. 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 [*Golchha M C et al* **(2011)**]. 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/LDPE nanocomposites were prepared by using solution - cast technique [Sangawar V S et al (2006)]. LDPE was dissolved in Xylene using hot plate magnetic stirrer at 1000C for 2 hrs so as to obtain clear viscous solution. Then ZnO was added to the solution of LDPE 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. The melt was then poured on clean optically plane glass plate kept in pre-heated oven at 800C for 1 hr. The glass plate was perfectly leveled with the help of spirit level so as to ensure uniform film thickness. Then the solution was allowed to evaporate slowly and cool to the room temperature. After complete evaporation the film was detached from the glass surface.

The thickness of samples was measured by compound microscope in conjunction with n occulometer having least count 15.38 μm similar to the method reported by [*Sangawar V S et al* **(2012)**]. 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 were carried out using SHIMADZU (visible spectrometer) UV-1700 series in the wavelength range 200-700 nm. The optical absorption and transmittance spectra were analyzed to determine the optical band gap and nature of transitions.

3. RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of unfilled and ZnO (0.5, 1, 3, 5 wt. %) filled LDPE thin film samples recorded in UV-Vis wavelength region 200-700 nm using Shimadzu (visible spectrometer) UV-1800 series. This figure clearly indicates that absorption has been higher for ZnO filled LDPE samples than unfilled LDPE samples and found to be increased with increased loading % of ZnO NPs. Absorption spectra reveals that the chemical structure of the polymer is not changed by ZnO NPs, it remains in dispersed form but it changes the physical properties.

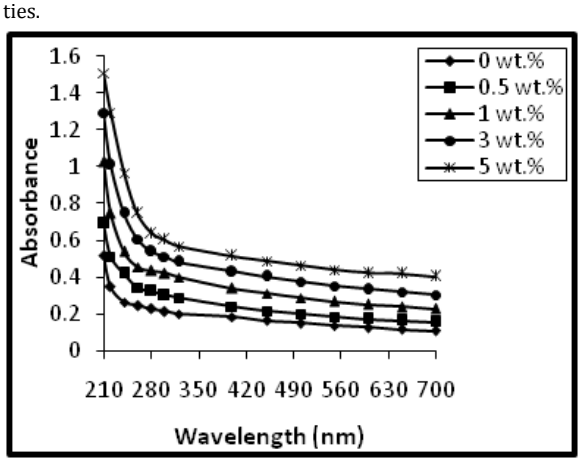

Figure 1: The optical absorption spectra of LDPE and ZnO/ LDPE films for different concentration of ZnO NPs in LDPE

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Figure 2 shows optical transmittance spectra of unfilled LDPE and ZnO filled LDPE thin films. From the figure 2 it is observed that with the increase in concentration of ZnO NPs, the percentage transmittance decreases remarkably indicating successful incorporation of ZnO in ZnO/LDPE nanocomposites.

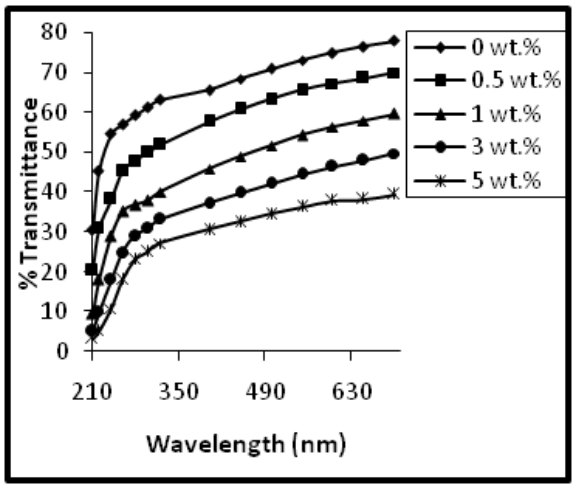

Figure 2: The optical transmittance spectra LDPE and ZnO/ LDPE thin films with different concentration of ZnO in LDPE

The optical absorption coefficient α which is the function of wavelength can be calculated from the optical absorbance spectra by using the relation [*Ballato J and Fougler S* **(2003)**].

$$log\left(\frac{I_0}{I_t}\right) = 2.303A = \alpha.d \quad .....1$$

Where, I_0 and It are the intensities of the incident and transmitted beams respectively, A is the optical absorbance and d is the film thickness and absorbance is defined by,

$$A = log\left(\frac{I_0}{I_t}\right) \quad .....2$$

Figure 3 shows the variation of the absorption coefficient (α) with photon energy (hυ) for all unfilled and ZnO NPs filled LDPE samples. Figure 3 shows that near the UV region the absorption coefficient increases exponentially. Also the absorption coefficient increases with the increasing concentration of ZnO NPs. This could be related to the extended states that are located inside the energy gap near the conduction. The absorption coefficient increases with the increase in photon energy. The remarkable change is observed at high photon energy indicating that the forbidden energy gap is less leading to large probability of electronic transitions.

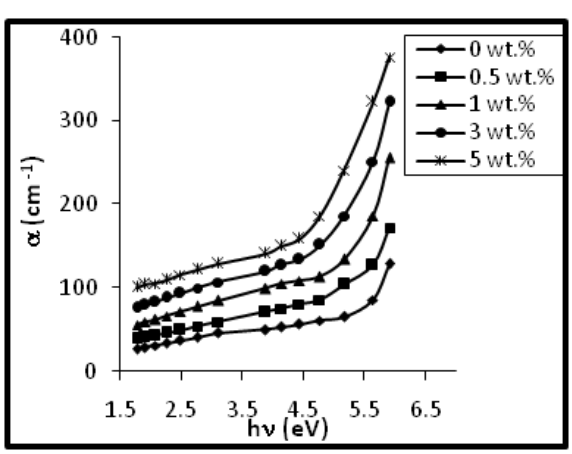

Figure 3: Optical absorption coefficient for unfilled LDPE and ZnO/LDPE nanocomposites

The optical edge for direct and non-direct transitions can be obtained in view of modals proposed by *Tauc et al* (1970),

$$\alpha h\nu = C_0\left(h\nu - E_g^{opt}\right)^n \quad .....3$$

Where, Co is an energy independent constant related to the properties of valence and conduction bands; hν is the photon energy; α is the absorption coefficient, is the optical energy band gap of the material and n=1/2, 3/2, 2 or 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions respectively [*Khare P K et al* **(2000)**]. The plot of $(\alpha h\upsilon)^{1/n}$ vs. hυ often yields a reasonably good straight line fit to the absorption edge and the extrapolated (hυ) at which $(\alpha h\upsilon)^{1/n}=0$ provides a convenient experimental benchmark for the optical band gap .

Figure 4 shows the dependence of (αhυ)1/2 on the photon energy hυ for indirect allowed transitions for all the samples of unfilled LDPE and ZnO filled LDPE thin films. From figure 4 it is noticed that the curves are characterized by presence of an exponentially decaying tail at low photon energy. The optical energy gaps were estimated from the extrapolation of the linear portion of the graph to the photon energy axis and are tabulated in table 1.

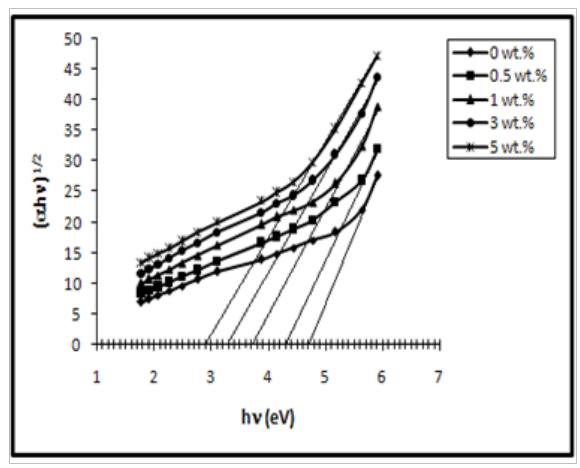

Figure 4: αhυ) 1/2 vs. hυ plots of LDPE and ZnO filled LDPE thin films for different filler concentrations.

For direct allowed transitions, the optical energy gap was estimated from the extrapolation of the linear portion of the graphs (αhν) 2 vs. photon energy (hν) to the photon energy axis, as shown in figure 5. The curve reveals the exponentially decaying tail at the low photon energy. It is observed that the slightly decreased with increasing filler concentration. The corresponding values are enclosed in table 1.

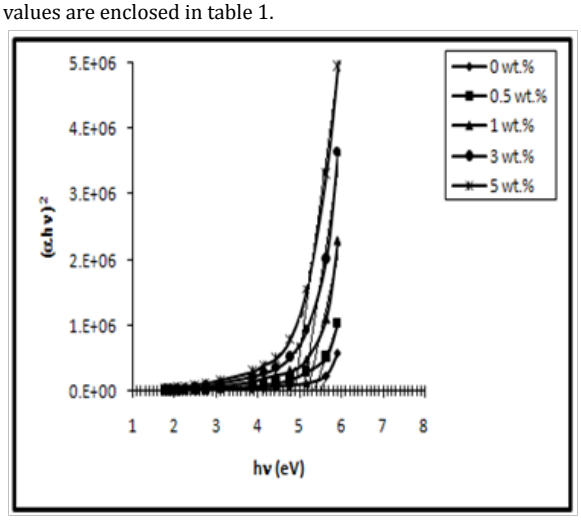

Figure 5: Relation between (αhν) 2 vs. hν for LDPE with different ZnO concentration

Table 1: Direct and indirect optical energy gap for LDPE filled with ZnO NPs

Samples	Direct $E_g^{opt.}$ (eV)	Indirect $E_g^{opt.}$ (eV)
LDPE- 0 % ZnO	5.53	4.71
LDPE - 0.5 % ZnO	5.35	4.4
LDPE - 1 % ZnO	5.13	4.75
LDPE - 3 % ZnO	5	3.3
LDPE - 5 % ZnO	4.9	2.9

From table 1 observations, the decrease in the optical energy band gap with ZnO NPs as the filler. The change of attributed to the change of induced energy states due to the change of intercalation mode. This confirmed the formation of 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 filler concentration increases, the dopant molecules start bridging the gap separating the two localized states and lower the potential barrier between them, thereby facilitating the transfer of charge carrier between two localized states. Our results are in good agreement with *Sultan S et al* **(2012).**

The optical absorption coefficient α(ν) near the band edge shows an exponential dependence on photon energy (hν) and obeys an empirical relation by *Urbach F* **(1953),**

$$\alpha(\nu) = \alpha_0 \exp\left(\frac{h\nu}{E_u}\right) \qquad \ldots\ldots\ldots 4$$

Where, α_0 is constant and E_u is related to the width of the band tails of localized states in the forbidden band gap.

Figure 6 is the plot of natural logarithm of the absorption coefficient α (ν) vs. photon energy (E= hν) for LDPE and ZnO/LDPE thin films. The values of the Eu were calculated by taking the reciprocal of the slopes of the linear portion of these curves. The origin can be considered as thermal vibrations in the lattice. The optical band tails of the localized state of the samples are tabulated in Table 2. The experimental results concerning the Urbach energy tail Eu reveals the loading % of ZnO NPs significantly affects the optical absorption parameters of LDPE. The Urbach energy Eu values are enclosed in table 2.

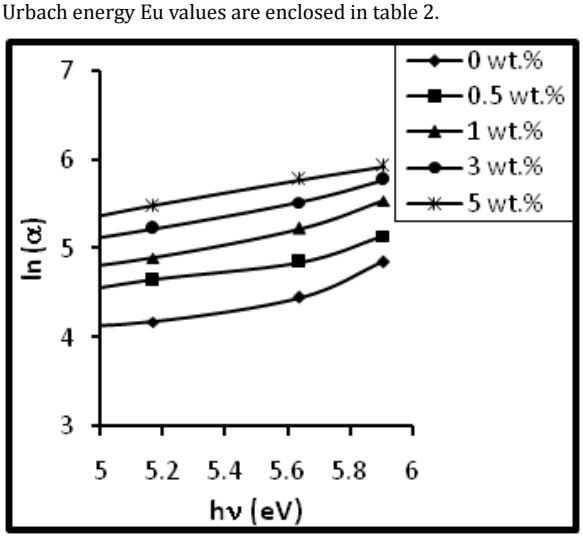

Figure 6: Relation between ln (α) and hν for LDPE at different ZnO NPs concentration

Samples	Eu (eV)
LDPE- 0 % ZnO	1.09
LDPE - 0.5 % ZnO	1.12
LDPE - 1 % ZnO	1.14
LDPE - 3 % ZnO	1.34
LDPE - 5 % ZnO	1.65

Table 2: Band tail energy values for LDPE filled with ZnO NPs

The increase of Eu values by increasing the concentration of ZnO NPs in ZnO/LDPE nanocomposites can be attributed to the effect of internal potential fluctuation associated with the increase in disorder. It is apparent from the table 2 that there is increase in Urbach's energy corresponds to the decrease in optical band gap. Such an observation supports the increase in the number of traps as a result of increasing concentration of embedded ZnO nanoparticles which results in the lower energy transitions feasible and thus, reducing the values of optical band gap [*Abdelrazek E M et al* **(2013)**]

4. CONCLUSION

Nanocomposite thin films of LDPE with different concentrations of ZnO NPs have been prepared by solution cast technique and have been investigated for their optical properties. The Absorption (A) increases while Transmittance (T) decreases with increasing the concentration of ZnO NPs. The optical energy band gap and the Urbach energy tail were evaluated and their dependence on concentration of ZnO NPs was investigated. The increase in Urbach's energy was attributed to the decrease in optical band gap due to formation of charge transfer complexes and increase in the number of traps as a result of increasing concentration of embedded ZnO nanoparticles.

REFERENCE

Abdelrazek E M, Ragab H M, Abdelaziz M, Plastic and Polymer Technology (PAPT) 2(1), 2013, p. 1-8. | Augustine S M, Jayalekshmi S, International Conference on Advances in Polymer Technology, Feb. 26-27, 2010, p. 148-152. | Ballato J and Fougler S, J. Opt. Soc. Am. B 20(9), 2003, p.1838-1843. | Golchha M C, Bhagat R N and Sangawar V S, International Journal of Nanotechnology and Applications 5(2), 2011, p. 109-116. | Khare P K, Gaur M S, Singh R, Ind J Phys 68A, 1994, p. 545-552. | Sangawar V S and Moharil N A, Chem Sci Trans. 1(2), 2012, p. 447-455. | Sangawar V S, Chikhalikar P S, Dhokane R J, Ubale A U and Meshram S D, Bull. Mater. Sci., 29(4), 2006, pp. 131-116. | Shuxiang Mu, Dezhen Wu, Shengli Qi, and Zhanpeng Wu, Journal of Nanomaterials Volume 2011, p. 1-10. | Sultan S, Khan M S and Hymuyan M, Turk. J. Chem 36, 2012, p. 709-716. | Tauc J, Menth A and Wood D (1970) Phys. Rev. Lett., 25, 749. | Urbach F, Phy. Rev.Lett. 92, 1953, p. 1324. |