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Synthesis and Characterization of Polyethylene Vinyl Acetate / ZnSe Nanocomposite

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In the not too distant past, polymer scientists and technologists expanded their horizons from consumer products to the high technology arena, particularly notable in opto - electronic applications. Ethylene Vinyl Acetates (EVA) are popular because of their superior adhesion to most substrates as well as their ease of formulation. Its High transparency is a key attribute for photovoltaic cell encapsulation. It is expected that with the addition of ZnSe nano fillers, EVA becomes a high refractive index polymer (HRIP) with refractive index >2.5 and posses anti-reflective property. In this work, ZnSe nanoparticles were synthesised by solvo-thermal method. Nano – Composite matrices based on polyethylene vinyl acetate / ZnSe were prepared by chemical replacement mechanism. Refractive index of prepared polymer nanocomposites were calculated from dielectric study using Hioki 3532-50 LCR HITESTER at various frequencies and temperatures. The presence of nano filler enhanced the refractive index and it varied with frequency and temperature. UV-Vis-NIR Spectra of the samples enable to determine the bandgap and was found to decrease with increasing the concentration of nano fillers dispersed in polymer matrix. I-V characteristics of the nanocomposites were plotted at various concentrations of nano fillers and at various temperatures.

Keywords: EVA / ZnSe nanocomposite, XRD, UV-Vis-NIR spectra, Refractive index, I – V characteristics.

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1. INTRODUCTION

Studies on nanoparticles dispersed in polymer matrix is intriguing, because these materials provide tremendous options for combining characteristics stemming from both the nanometric inorganic components and the polymers[1-2]. The presence of nanoparticles in polymer improves the mechanical, electrical and optical properties of the material and it is possible to control these properties, including the refractive index, by concentration of the particles [1,6]. Most organic polymers show a limited refractive index, in the range 1.35 – 1.5. For optical applications, polymers with higher refractive index are required [1]. In the last years, High refractive index(> 1.65) polymer nanocomposites are targeted for optical applications, including planar waveguide devices, micro-optical elements and anti reflection coatings for solar cell materials[2-5, 9, 10].

Good flexibility, high transparency, chemical resistance, non-toxicity and environmental stability make polyethylene vinyl acetate[11,12] as one of the best polymers in optical as well as electrical studies. The choice of nanoparticles are influenced strictly in size and surface characteristics because dopants carry a major role in HRIP nanocomposites by limiting the optical loss, Rayleigh scattering and to increase transparency [7]. The ZnSe inorganic fillers with nanoscale exhibit high surface to volume ratio and thus expected to modify drastically the electrical, optical [8] and thermal properties of polymer. Hence, EVA / ZnSe nanocomposite is a potential candidate for photovoltaic applications.

2. EXPERIMENTAL

2.1 Synthesis of ZnSe nanoparticles

To prepare ZnSe nanoparticles, materials used are zinc acetate ($(CH_3COO)_2Zn.\ 2H_2O$) and sodium selenite (Na_2SeO_3) as the source of Zn and Se ion with preferable ratio 2 : 1 respectively. The solutions of 0.2 molar zinc acetate and 0.1 molar sodium selenite were prepared in 100 ml water and 30ml hydrazine hydrate mixed up at 50°C under vigourous stirring to allow ZnSe growth. These solutions were transferred into teflon lined sealed stainless steel autoclave and heated at 2400°C for 5 hrs in a muffle furnace. To remove any kind of unreacted chemicals and impurities it was washed in water several times and annealed at 1000°C. In essence, stringent symmetry of nano particles can be controlled by chemical of interest concentration,reaction temperature and kinetic control.

2.2 Synthesis of EVA / ZnSe nanocomposite

For the preparation of Ethylene Vinyl Acetate / ZnSe nanocomposite, the copolymer was obtained from copolymerisation of Ethylene and Vinyl Acetate and it was procured from DUPONT. Then it was dissolved in toluene and heated at 120oC. The next step carried out was the dispersion of ZnSe nanoparticles in EVA – Toluene mixture with varing concentrations. The dopants at the required ratio of 2% and 4% by weight of EVA were taken. For the proper and uniform dispersion, Magnetic stirrer and Ultrasonicator were used. The bond breaking was done by gradual stirring of magnetic stirrer and ultrasonicator allowed the uniform dispersion of ZnSe nanoparticles homogeneously throughout the matrix. Finally, the nano filled EVA was then transfered to a teflon coated glass mould and spread with uniform thickness. The solvent was evaporated by keeping in an air oven with a temperature of 100°C for one whole day to get a EVA / ZnSe nanocomposites of micrometer thickness.

3. RESULTS AND DISCUSSION

3.1 UV-Vis-NIR Absorption Spectra

Fig. 1 and Fig. 2 shows the UV-Vis-NIR spectra of EVA / 2%ZnSe and EVA / 4%ZnSe. The band gap of nanocomposites can be calculated using Tauc relation

$$\alpha h\nu = K(h\nu - Eg)^{n/2} \quad (3.1)$$

where K is a constant, Eg is the optical band gap and n is a constant = 1 for direct bandgap semiconductors. The plots of $(\alpha h\nu)^2$ vs. hν for EVA / 2%ZnSe and EVA/ 4%ZnSe are shown in Fig. 3 and Fig. 4. Extrapolating the straight line of these plots for zero absorption co-efficients provide the direct bandgap of nanocomposites. From the Fig. 3 and Fig. 4, it is clear that the band gap reduces from 4.67 eV to 4.21 eV as the percentage of ZnSe dispersed in the nanocomposites increases from 2% to 4%.

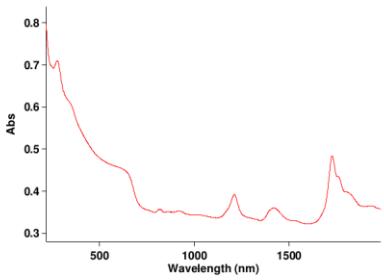

Fig. 1 – UV-Vis-NIR Spectra of EVA / 2% ZnSe nanocomposite

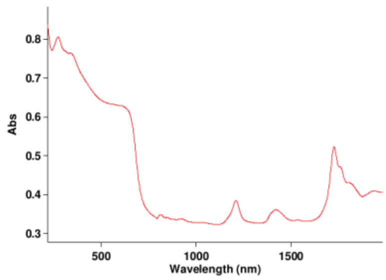

Fig. 2 – UV-Vis-NIR Spectra of EVA / 4% ZnSe nanocomposite

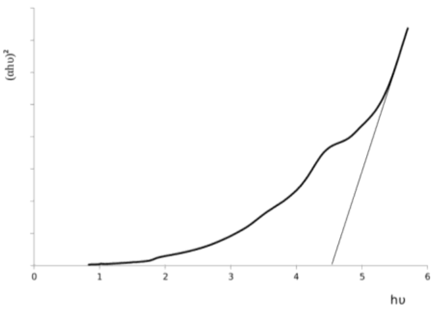

Fig. 3 – Tauc plot of EVA / 2% ZnSe nanocomposite

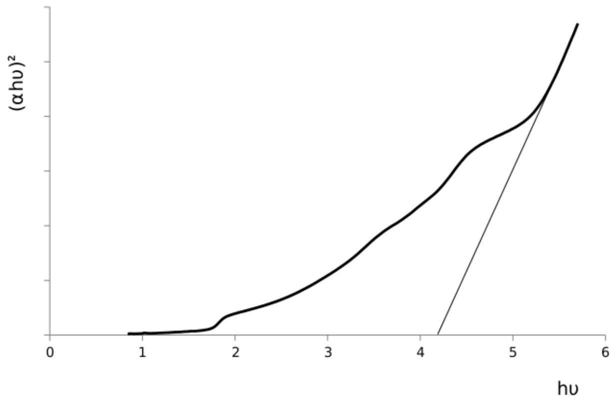

Fig. 4 – Tauc plot of EVA / 4%ZnSe nanocomposite

3.2 Refractive Index Study

Refractive index of polymer nanocomposites were calculated from dielectric study. According to Maxwell's Rule

$$n = \sqrt{\varepsilon_r \cdot \mu_r} \quad (3.2)$$

where ε_r is the dielectric constant and μ_r is the relative permibility. It is 1 for non-magnetic materials. The dielectric study was carried out by varing frequency (100 Hz to 1 MHz) and temperature(303 K to 353 K) using HIOKI 3532-50 LCR HITESTER. Fig. 5 shows the variation of refractive index with concentration of ZnSe nanoparticles dispersed. It is clear that the refractive index of pure EVA is 1.5 at room temperature and it increases to 2.26 as the concentration of ZnSe nanoparticles becomes 4% at high microwave region. But in the low frequency region, it showed huge dependance in refractive index and could be varied upto 5.7. Fig. 6 shows the variation of refractive index with frequency(100 Hz to 1 MHz) at different temperatures(303 K, 313 K, 333 K and 353 K) for EVA / 4%ZnSe nanocomposite. The refractive index is found to be almost stable within these ranges of frequencies and temperatures.

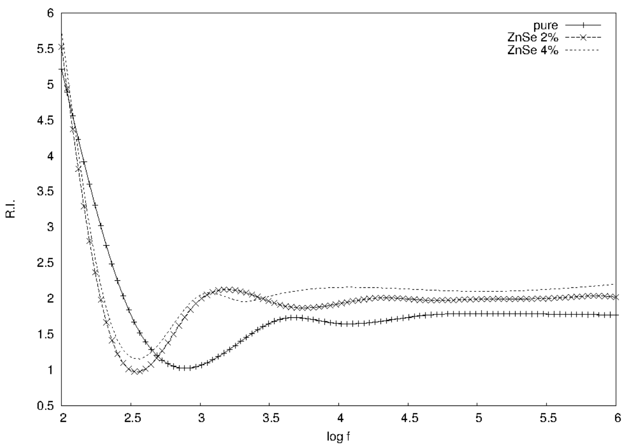

Fig. 5 – The variation of refractive index with frequency for different concentrations of ZnSe nanoparticles dispersed in EVA

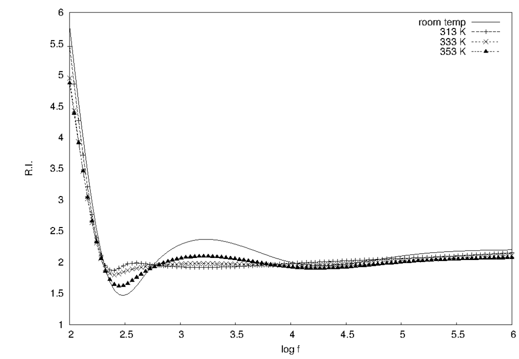

Fig. 6 – The variation of refractive index of 4%ZnSe / EVA nanocomposite at different temperatures

3.3 I – V CHARACTERISTICS

Fig. 7 shows the I – V plot of nanocomposites at room temperature with different concentrations of ZnSe nanofillers. The current is found to increase as a function of voltage with the increase of concentration of fillers.

Fig. 8 shows the I – V plot of EVA / 4%ZnSe nanocomposite at different temperatures. The current is found to decrease with the increase of temperature.

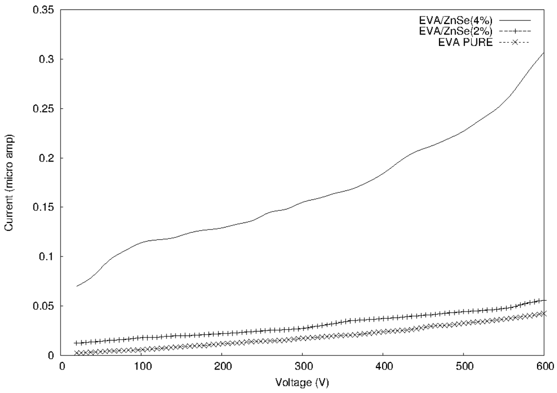

Fig. 7 – I-V plots of EVA with varing concentrations of ZnSe fillers added

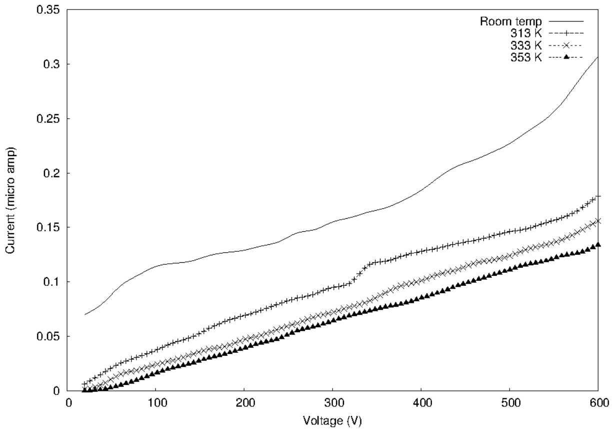

Fig. 8 – I-V plots of EVA doped with 4% of ZnSe nanoparticles at different temperatures

4. CONCLUSION

We successfully prepared ZnO nanoparticles by-solvothermal route and dispersed it in EVA polymer with various concentrations. Refractive index of polymer nanocomposites were studied by varying frequency and temperature. It was found that the presence of nano filler enhanced the refractive index and it varied with frequency and temperature. Band gap of the samples decreased as the amount of nano fillers increased. DC conductivity study showed that the prepared nanocomposites possess positive temperature co- efficient of resistance.

REFERENCES

1. Y. Wang, T. Flaim, R. Mercado, S. Fowler, D. Holmes, C. Planje, *Proceedings of SPIE* **5724**, 42 (2005).
2. J. Yang, X. Zhang, P. Wang, H. Ming, Y. Wu, J. Xie, J. Zang, *Chin. Opt. Lett.* **3**, 399 (2005).
3. R. Boyd, W.J. Korean, *Phys. Soc.* **43**, 603 (2003).
4. W.C. Cheong, X.C. Yuan, V. Koundriachov, W.X. Yu, *Opt Express*, **10**, 58 (2002).
5. W.S. Kim, K.B. Yoon, B.S. Bae, *J. Mater. Chem.* **15**, 4535 (2005).
6. D. Vollath, D.V. Szabo, *Adv. Eng. Mater.* **6**, 117 (2004).
7. H Althues, J Henle, S Kaskel, *Chem. Soc. Rev.* **9** No49, 1454 (2007).
8. S B Kondawar, *Archives of Applied Science Research* **2** No1, 247 (2010).
9. Z. Pasanovic, V. Gupta, R.K. Bhattacharya, *Rheol Acta* **43**, 99 (2004).
10. R. Prasad, Z. Pasanovic, V. Gupta, *Polym. Eng. Sci.* **44**, 1220 (2004).
11. G.C. Stael, M. Tavares, *Polym. Testing* **17**, 533 (1998).
12. D.S. Chaudhary, R. Prasad, R.K. Gupta, S.N. Bhattacharya *Thermochimica Acta* **433**, 187 (2005).