

# SYNTHESIS AND CHARACTERIZATION OF PEO: CuO/ZnO/SnO POLYMER NANOCOMPOSITE FILMS AND STUDY OF THEIR OPTICAL AND ELECTRICAL PROPERTIES

Hosaholalu Balakrishna Uma, Sannaiah Ananda and M.S.Vijaya Kumar\*

Department of Studies in Chemistry, Manasagangotri, University of Mysore, Mysore-570006, India

**ABSTRACT:** PEO and PEO:CuO/ZnO/SnO nanocomposite films have been prepared by well known solution casting method. The structural studies of the polymer films are studied by X-Ray diffraction, SEM and FTIR techniques. The optical property is studied by recording UV-Visible spectroscopy. The structural properties of polymer films characterized by X-ray diffraction measurements confirm semi crystalline nature of PEO which contains crystalline and amorphous regions. The SEM images of PEO:CuO/ZnO/SnO films exhibit characteristic patterns on the film surface depending upon the % wt of dopant nanoparticle. Photo-voltaic activity of the PEO and PEO:CuO/ZnO/SnO nanocomposite films are studied.

**KEYWORDS:** PEO:CuO/ZnO/SnO polymer nanocomposite films, solution casting method, photo-voltaic activity

## I. INTRODUCTION

Polymer nanocomposite materials have attracted the attention of many researchers due to their unique optical, electrical, thermal, mechanical, magnetic and dielectric properties. Nanoparticles exhibit size-related properties that differ significantly from bulk materials. The high surface reactivity and large surface to volume ratio of the nanoparticles make them superior over traditional fillers. One of the advantages of nanofillers as polymer additives compared to conventional additives is that the loading requirements are quite low [1]. Polymer blending is one of the most important contemporary ways for the development of new polymeric materials and it is a useful technique for designing materials with a wide variety of properties [2]. Polymer metal nanoparticle composites are promising functional materials in several fields such as optical, electrical, thermal, mechanical and antimicrobial properties [3-7]. Many reports in the literature show attempt for the synthesis of metal nanoparticles based polymer nanocomposites with the possibility of variation in their optical and electrical properties for their application in high-performance capacitors, conductive inks and other electronic components [8,9]. Nanocomposites play a significant role in tailoring the properties of polymeric materials to suit any technology [10,11]. The incorporated nanoparticles inside the polymer matrix will also affect the properties of the host matrix. Polyethylene oxide (PEO) is known for its interesting properties such as relatively high melting point, good structural integrity, low glass transition temperature, low toxicity and biocompatibility [12]. PEO offers a number of important physicochemical properties even though it has a very simple linear structure. PEO layers have ability to avoid non-specific protein adsorption on surfaces [13]. This behavior is generally observed as a consequence of the hydrogen bonding between ethylene oxide segments and surrounding water molecules which induces local order at the molecular interface [14]. The introduction of CuO/ZnO/SnO nanoparticle dopant into the PEO matrix reduces the crystallinity of the polymer and enhances the mobility of the ions resulting in the enhanced property of the polymer. The SEM images of PEO:CuO/ZnO/SnO films exhibit characteristic patterns on the film surface as the concentration of nanoparticles in polymer film increased.

## II. EXPERIMENTAL

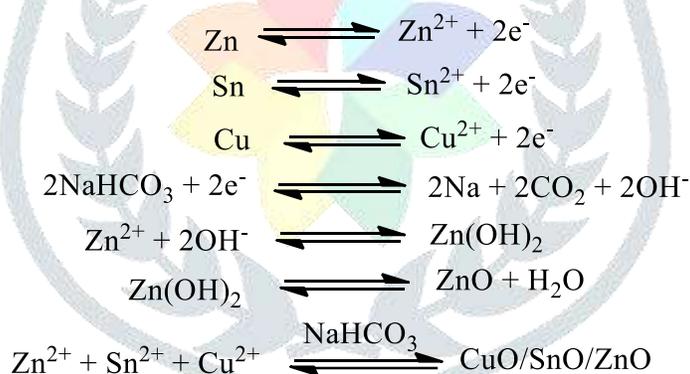
### Materials and methods

All chemicals are of analytical grade and they are used without any further purification. Polyethylene oxide (PEO) from Alfa-asear Pvt Ltd., and CuO/ZnO/SnO nanoparticles prepared by the electrochemical method were used for the preparation of polymer nanocomposite films. Deionized water produced from PURELAB ultrawater purification system was used for all experiments.

### Preparation of CuO/ZnO/SnO nanoparticles by electrochemical procedure:

Nanocomposites of CuO/ZnO/SnO were synthesized by the electrochemical process using copper, zinc, stannous and platinum electrode in an aqueous system containing 0.5 % NaHCO<sub>3</sub> as conductive salt. The electrodes are fixed in a holder so that they are surrounded by electrolytic solution and they are separated by 1cm apart. The electrolysis was carried out by taking 20 ml of NaHCO<sub>3</sub> for 3 hrs at room temperature without stirring. The potential has been adjusted so that the current reaches 20 mA. During the electrolysis zinc, tin and copper electrodes act as anodes and start to dissolve giving Zn<sup>2+</sup>, Cu<sup>2+</sup> and Sn<sup>2+</sup> ions which are electrochemically reacted with sodium bicarbonate solution to give CuO/ZnO/SnO nanoparticles. As the redox potentials of Zn<sup>2+</sup>, Cu<sup>2+</sup> and Sn<sup>2+</sup> ions are different, the rate of the electrochemical reaction is not the same for Zn<sup>2+</sup>, Cu<sup>2+</sup>, and Sn<sup>2+</sup> ions. Since the dissolution potential of zinc (-0.76 eV) is more negative than tin (-0.14 eV) and copper (+0.34 eV), the formation of ZnO takes place faster followed by the formation of SnO and CuO respectively. The synthesized nanoparticles are washed repeatedly with distilled water so that sodium bicarbonate is completely removed, centrifuged and calcinated for 2 hrs at 800 °C so that the sodium and hydroxide impurities formed during the electrolysis are completely removed.

The electrochemical formation of CuO/ZnO/SnO takes place according to the following mechanism.



**Scheme 1: Mechanism of the electrochemical formation of CuO/ZnO/SnO nanoparticles**

### Preparation of PEO:CuO/ZnO/SnO polymer nanocomposite films:

Polymer nanocomposite films of PEO dispersed with different concentrations of CuO/ZnO/SnO nanoparticles were prepared by solution casting method [15]. A known quantity of PEO (1.5%) was dissolved in double distilled water and then heated gently using a water bath to prevent thermal decomposition of the polymer. The hot solution was stirred until the polymer is completely dissolved and forms a clear viscous solution. This is called polymer stock solution. Different quantities of CuO/ZnO/SnO nanoparticles (0.025%, 0.05%, 0.075% and 0.1%) prepared by the electrochemical method were added to the PEO stock solution, stirred thoroughly with a magnetic stirrer. The resulting viscous solution then casted into plastic Petri dish and kept in dry atmosphere at 60 °C about 48 hrs. After drying the films were peeled off from the Petri dish and kept in vacuum desiccators until use.

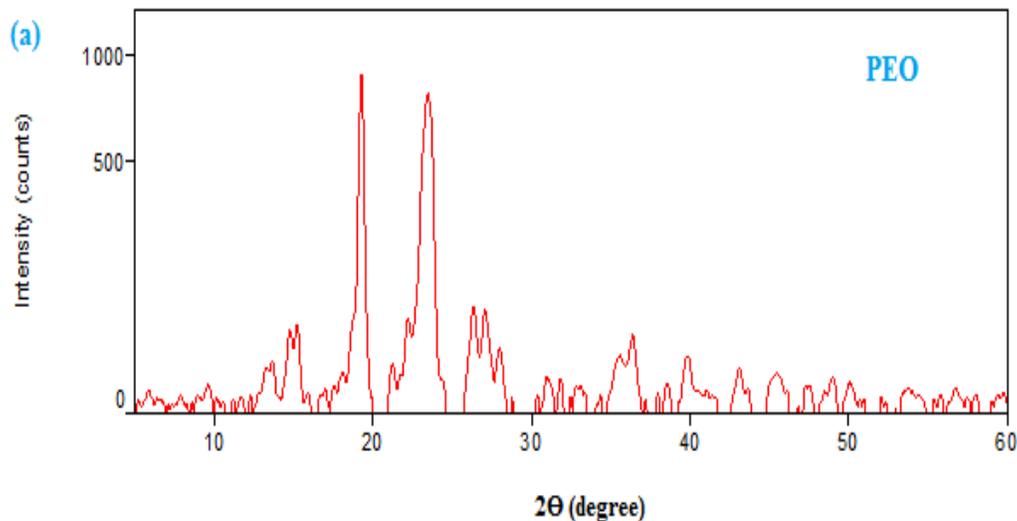
## Characterization

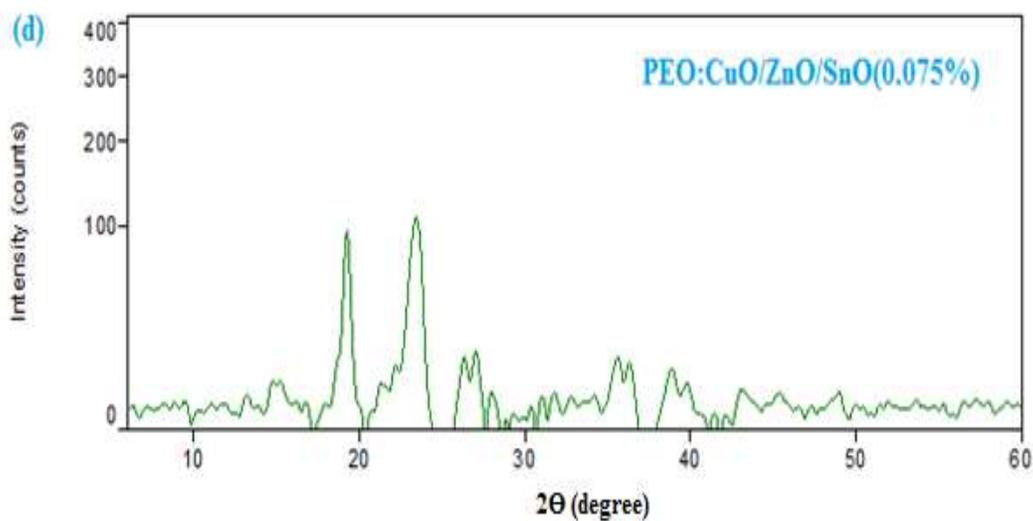
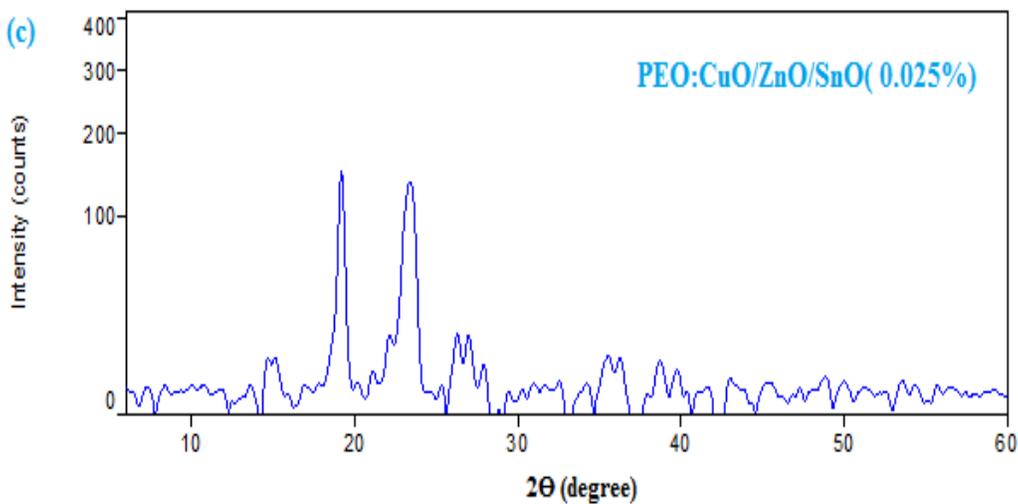
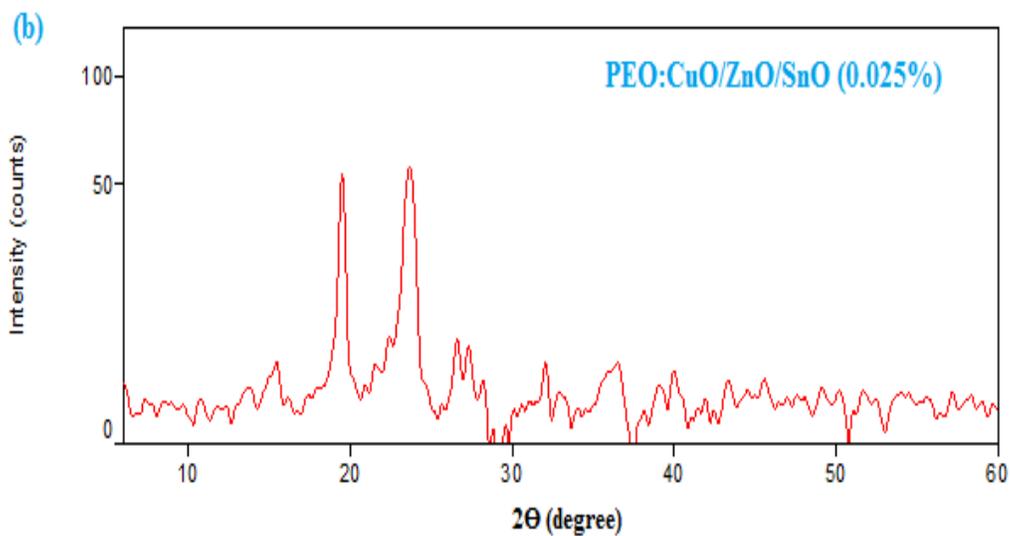
FT- IR spectra were recorded using JASCO FT-IR with wave number ranging from 4000 - 400  $\text{cm}^{-1}$ . The SEM images of the sample were recorded on ESEM Quanta - 200 FEI- Netherlands scanning electron microscope. The powder X ray diffractions were recorded using Rigaku miniflex II desktop X ray diffractometer (Cu-K radiation,  $\lambda = 1.54\text{\AA}$ ) scan rate of 0.02°/S range from 0° to 60°. The optical absorption spectra have been observed by UV-Vis spectrophotometer at room temperature with JASCO-UV Vis spectrometer.

## III. RESULTS AND DISCUSSION

### X-ray Diffraction (XRD):

The crystallographic interpretations are performed by X-ray diffractometer using Cu  $\text{K}\alpha$  wavelength ( $\lambda = 1.5406\text{\AA}$ ) in the scan range from 0° to 60°. Fig.1 represents the XRD pattern of pure PEO and PEO nanocomposite films doped with different concentrations of CuO/ZnO/SnO nanoparticles (0.025%, 0.05%, 0.075 % and 0.1%). The diffraction pattern of pure PEO indicated by fig.1(a) shows broad peak in between  $2\theta$  values equal to 15° and 25°. This indicating the semicrystalline nature of PEO polymer which contains both crystalline and amorphous regions. The semicrystalline nature of PEO is due to the presence of intramolecular hydrogen bonding in individual monomers and intermolecular hydrogen bonding between the monomers [16]. There is a decrease in the relative intensity of broad peak which is corresponding to PEO after embedding the CuO/ZnO/SnO nanoparticles into PEO matrix which is represented in fig.1(b) – fig.1(e). As the percentage of doping increases there is a decrease in peak width and also peak height indicating the decrease in crystallinity of the films [17]. The degree of crystallinity of the polymer was found to be decreased after doping with CuO/ZnO/SnO due to the decrease in number of hydrogen bonds.





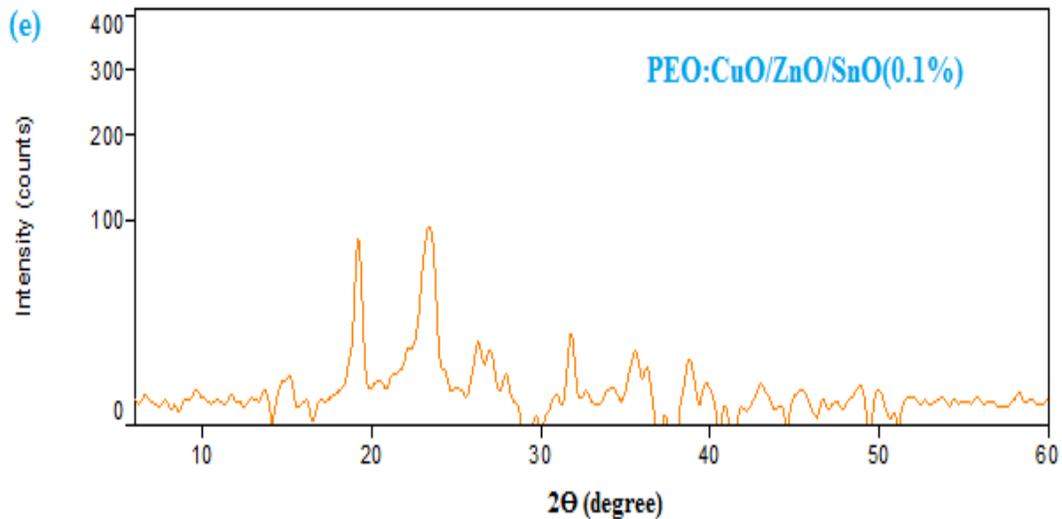
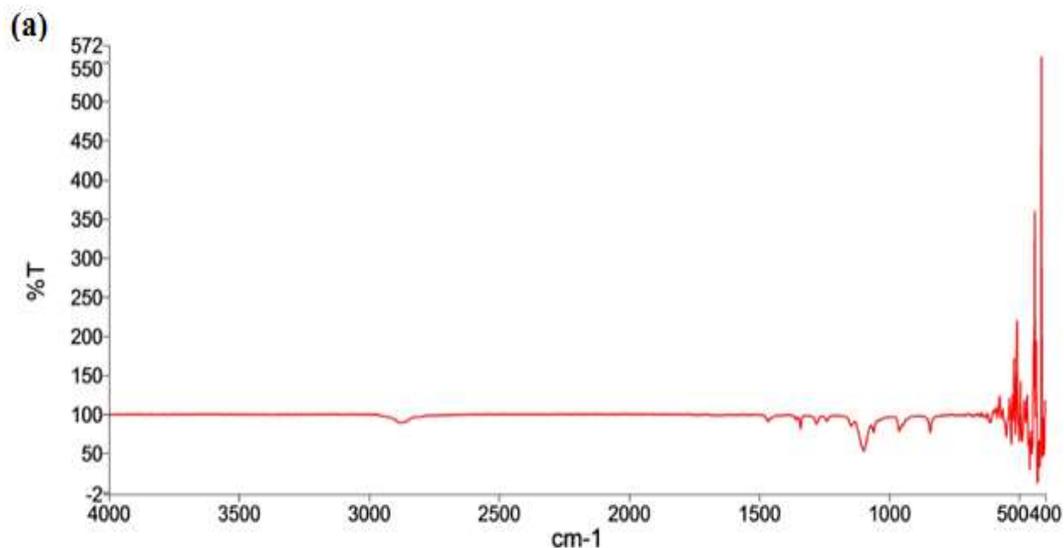
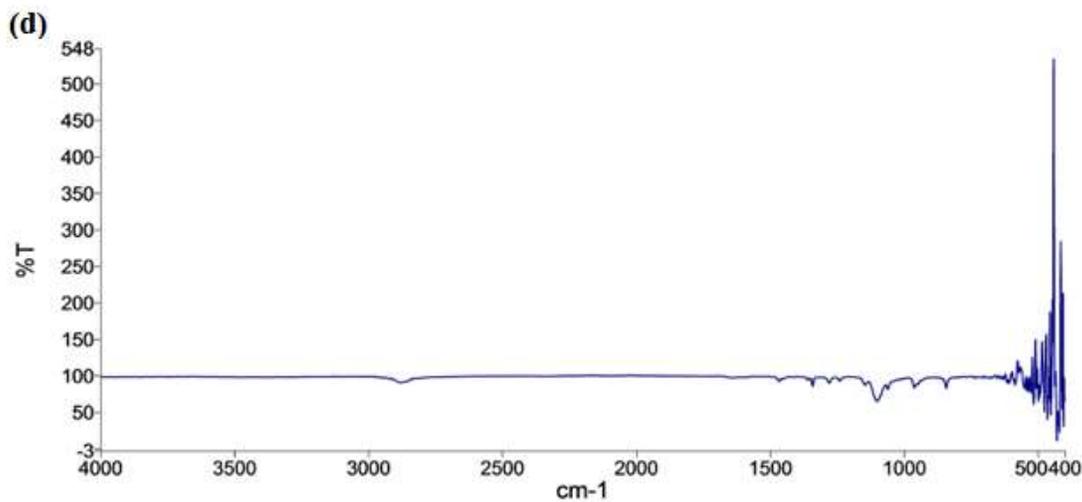
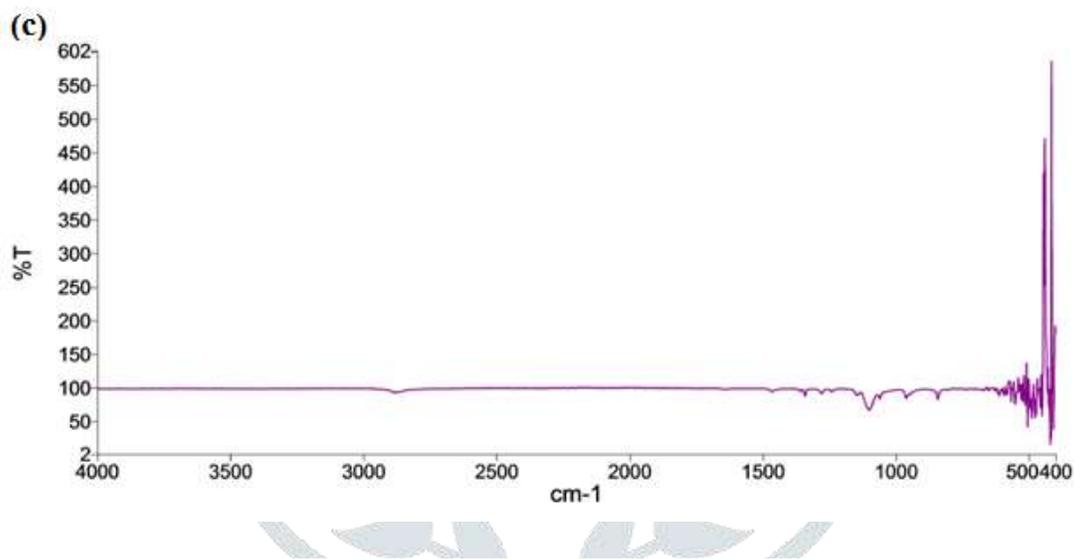
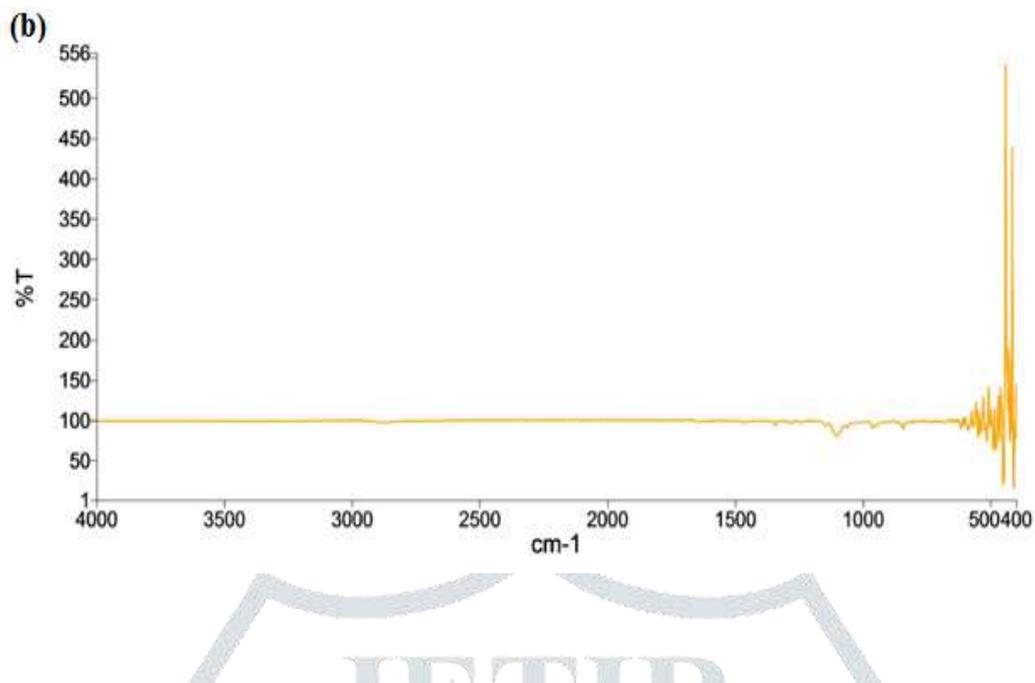


Fig.1: XRD of (a) undoped PEO film and PEO film doped with (b) 0.025%, (c) 0.05%, (d) 0.075 % and (e) 0.1% CuO/ZnO/SnO nanoparticles.

#### Fourier Transform Infrared analysis (FT-IR):

Fig.2 represents the FT-IR spectra of pure PEO and PEO nanocomposite films doped with different concentrations of CuO/ZnO/SnO nanoparticles (0.025%, 0.05%, 0.075 % and 0.1%). The spectra consists of several stretching and bending vibrational bands like C-H, C=C, C=O, C-O, C-O-C and CH<sub>2</sub> of PEO. The doping of nanoparticle into polymer films affects the height and the position of certain IR absorption peaks. The structural modifications can be identified by investigating the CuO/ZnO/SnO doping level dependence on the height and position of IR absorption peaks. According to Hooke's law, the shifting of the wavenumbers is related to the force constant and hence the shifting to the higher wavenumbers indicates an increase in the force constant [18]. Further the variations in the intensity of the bands at 940 cm<sup>-1</sup>, which characterized the syndiotactic structure of PEO, 1145 cm<sup>-1</sup>, a u(CO) mode in the crystalline region of PEO, and 1469 cm<sup>-1</sup>, which was assigned to the bending of CH<sub>2</sub> vibration, are related to the strong interaction between the dopant and the polymer. The new absorption bands at 428 cm<sup>-1</sup>, may be correlated to defects induced by the charge transfer reaction between the dopant and the polymer molecular chain [19].





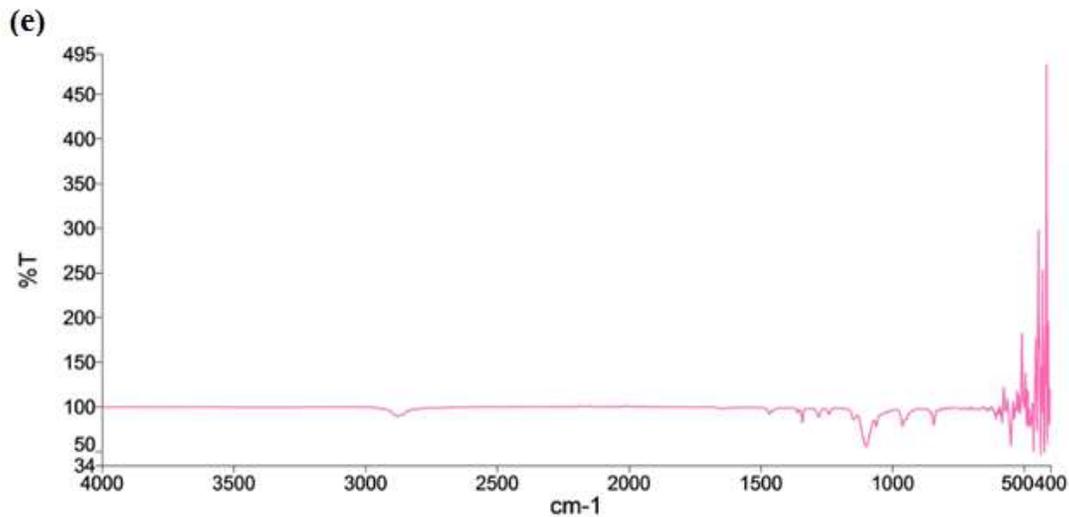


Fig.2: FT-IR spectra of (a) undoped PEO film and PEO film doped with (b) 0.025%, (c) 0.05%, (d) 0.075 % and (e) 0.1% CuO/ZnO/SnO nanoparticles.

#### Ultraviolet-Visible spectroscopy:

The UV-visible spectra of the polymer nanocomposite films were recorded at room temperature in the wavelength range 200-800 nm and it is shown in fig.3. The PEO:CuO/ZnO/SnO polymer composite films showed absorption peak in UV region while no absorption peak in visible region. It is evident that the films exhibit very small transmittance in the UV region and very high transmittance in the visible region. Consequently these materials are considered as optically transparent in the visible region. Meanwhile the PEO:CuO/ZnO/SnO films showed higher absorbance compared to the pure PEO film.

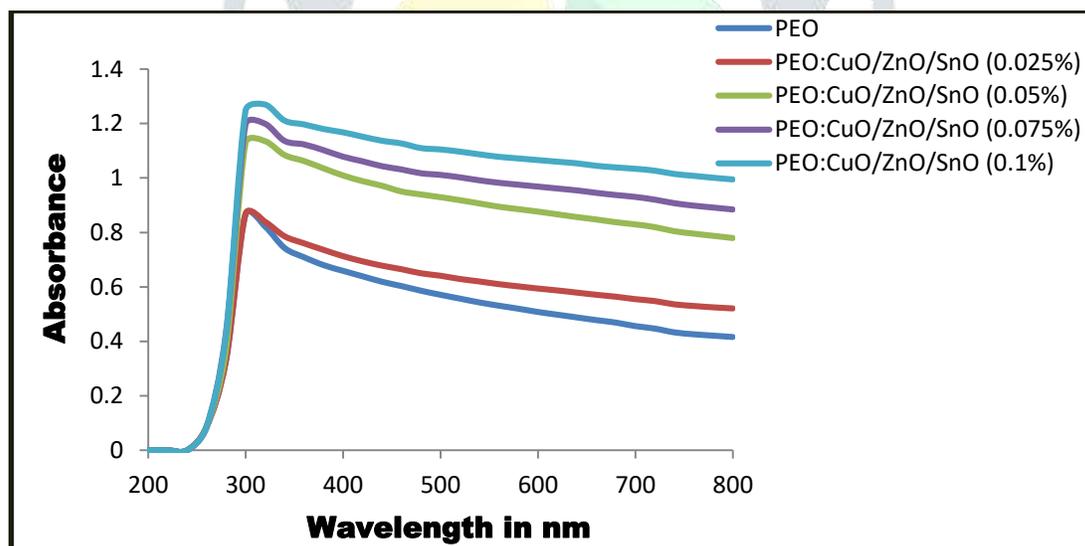
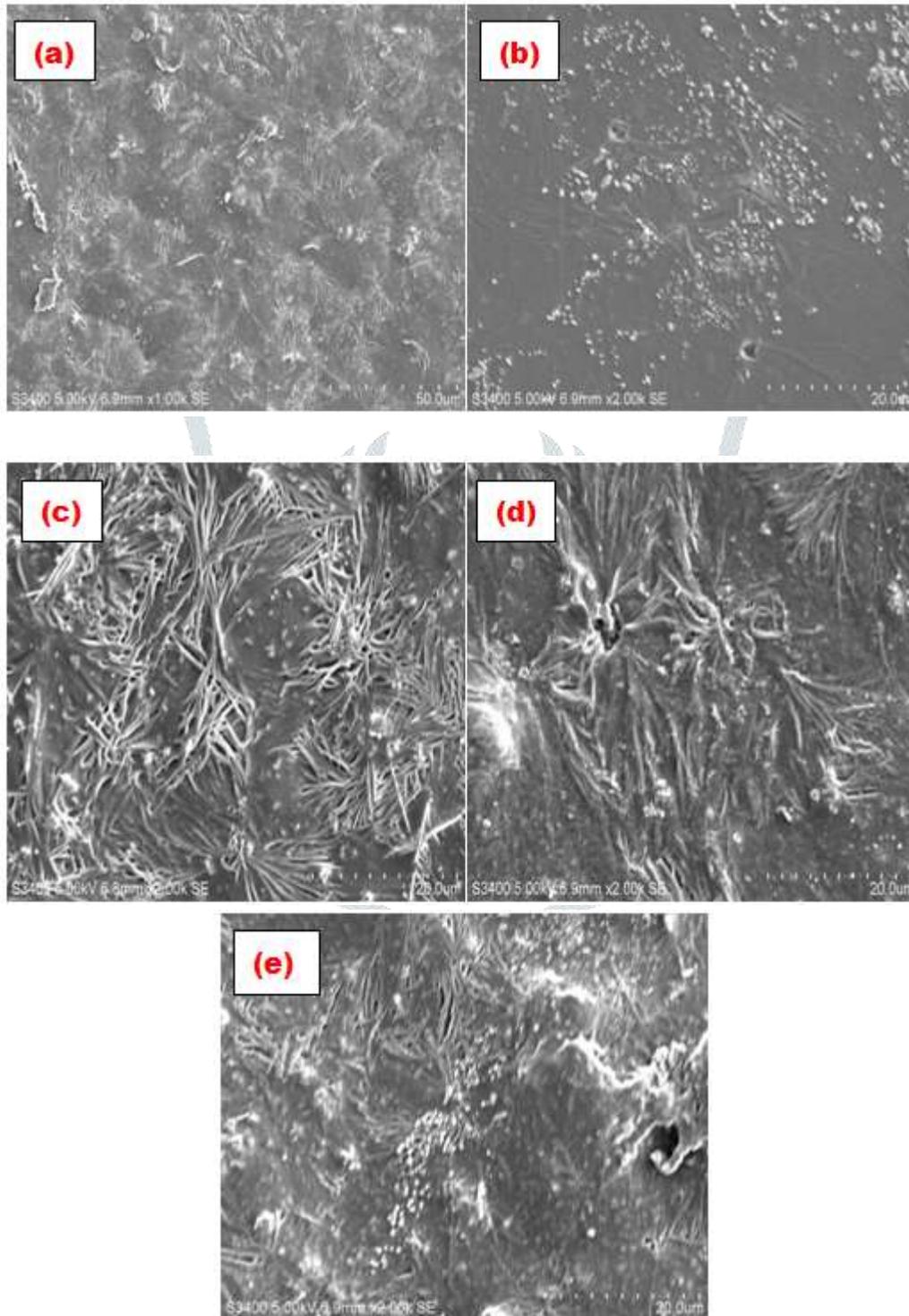


Fig. 3: UV-Visible spectra of (a) undoped PEO film and PEO film doped with (b) 0.025% , (c) 0.05%, (d) 0.075 % and (e) 0.1% CuO/ZnO/SnO nanoparticles.

#### Scanning Electron Microscopy:

The morphology of the samples is studied by FE-SEM analysis. SEM is used to investigate fully the effect of CuO/ZnO/SnO nanoparticles content and to examine the dispersion of nanocomposites particles in the polymer matrix. Fig.4 shows typical SEM

images of PEO films undoped and doped with different concentrations of CuO/ZnO/SnO nanoparticles. The SEM image represented by fig.4(a) for undoped PEO film is found to be harder, homogeneous and coherent. It is flat and compact with very sparsely distributed small particles without any phase segregation. It is apparent that the addition of CuO/ZnO/SnO nanoparticles in PEO blend films exhibits changes in the surface morphology of the system and exhibit characteristic patterns represented in fig.4(b)–fig.4(e). CuO/ZnO/SnO nanoparticles are dispersed within PEO matrix in the blend film with relatively good interfacial adhesion between the two components.



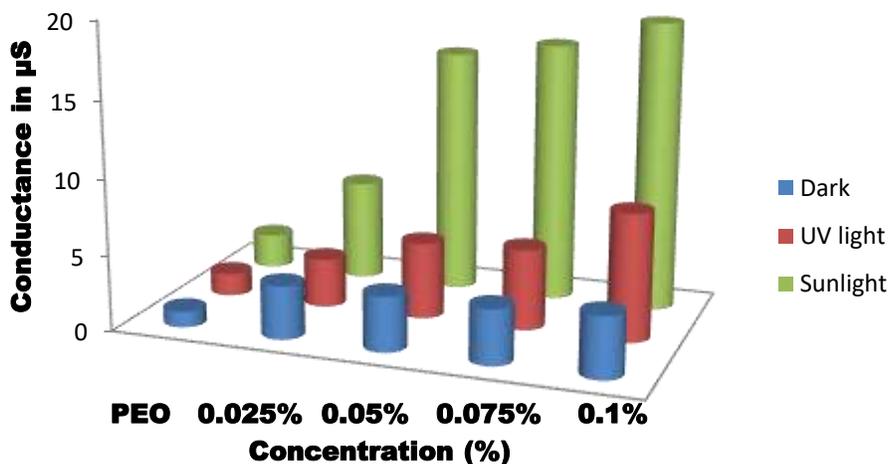
**Fig.4: FE-SEM images of (a) undoped PEO film and PEO film doped with (b) 0.025%, (c) 0.05%, (d) 0.075 % and (e) 0.1% CuO/ZnO/SnO nanoparticles.**

**Photo-voltaic activity:**

The photo-voltaic property of PEO films undoped and doped with different amounts of CuO/ZnO/SnO nanoparticles were studied by measuring the conductance and potential using conductometer and potentiometer at dark, sunlight and UV light [20]. The experimental results were tabulated in table 1 and graphically represented by fig.5 and fig.6. These results suggest that as concentration of dopant PEO:CuO/ZnO/SnO nanoparticles is increased, the conductance and potential also increased. The photo-voltaic property of PEO:CuO/ZnO/SnO nanocomposite films is enhanced to an appreciable extent in presence of sunlight than the UV light and dark conditions. Table 1 indicates PEO:CuO/ZnO/SnO (0.1%) polymer nanocomposite film shows higher conductivity and potential for sunlight compared to all other nanocomposite films. This confirms that PEO:CuO/ZnO/SnO (0.1%) film acts as a best capacitance material compared to remaining polymer nanocomposite films.

**Table 1: Conductivity and potential measurements of PEO and PEO:CuO/ZnO/SnO polymer nanocomposite films.**

Property	Polymer film	Dark	UV	Sunlight
Conductivity measurements in $\mu\text{S}$	PEO	1.05	1.5	2.3
	PEO:CuO/ZnO/SnO (0.025%)	3.52	3.23	6.68
	PEO:CuO/ZnO/SnO (0.05%)	3.62	5.03	16.2
	PEO:CuO/ZnO/SnO (0.075%)	3.63	5.32	17.2
	PEO:CuO/ZnO/SnO (0.1%)	4.02	8.39	19.2
Potential measurements in V	PEO	0.023	0.037	0.067
	PEO:CuO/ZnO/SnO (0.025%)	0.027	0.036	0.078
	PEO:CuO/ZnO/SnO (0.05%)	0.047	0.059	0.528
	PEO:CuO/ZnO/SnO (0.075%)	0.068	0.116	0.759
	PEO:CuO/ZnO/SnO (0.1%)	0.119	0.416	0.830

**Fig.5: Concentration V/s conductance graphs at different concentrations of PEO:CuO/ZnO/SnO films under different experimental conditions (Dark, sunlight and UV light).**

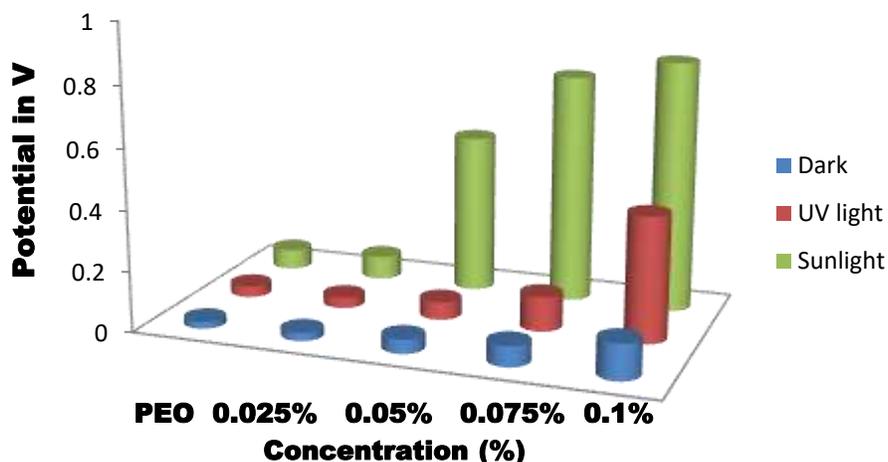


Fig. 6: Concentration V/s potential graphs at different concentrations of PEO:CuO/ZnO/SnO films under different experimental conditions (Dark, sunlight and UV light).

#### IV. CONCLUSION

PEO:CuO/ZnO/SnO polymer nanocomposite films were prepared from PEO aqueous solution and CuO/ZnO/SnO nanoparticles by solution casting method. The SEM images showed that the film surfaces had characteristic structures pertaining to different concentration of PEO:CuO/ZnO/SnO dopant. Incorporation of PEO:CuO/ZnO/SnO nanoparticles into PEO matrix induces the corresponding shift in the absorption bands which were observed by XRD and IR techniques. UV-Vis spectroscopy reveals the blue shift in the absorption edge indicating an increase in the bandgap energy upon nanoparticle doping. The conductivity and potential studies indicates an increase in conductance and potential of polymer films with increase in the amount of CuO/ZnO/SnO dopant.

#### ACKNOWLEDGEMENT

This research work is funded by UGC-BSR, New Delhi and DST-SERB and supported by University of Mysore, Mysuru. The authors greatly acknowledges UPE, CPEPA and DST Purse project, Vijnan Bhavan, University of Mysore for necessary instrumentation facilities.

#### CONFLICTS OF INTEREST

All the authors have declared that no Conflicts of interest exists.

#### REFERENCES

- [1] Gudrun, S., Matthew, M.M. 2003. Current Opinion in Colloid & Interface Science, 8(1): 103-108.
- [2] Supri, A.G., Siti Hajar, M.D., Hanif, M.P.M. 2016. Polymer Bulletin, 73: 2831-2841.
- [3] Zhong, Z., Wang, D., Cui, Y, Bockrath, M.W., and Leiber, C.M. 2003. Science, 302:1377-1379.
- [4] Hopkins, D.S., Pekkar, D., Goldbart, P.M., and Bezryadin, A. 2005. Science, 308:1762-1765.
- [5] Cl'emenson, S., L'eonard, D., Sage, D., David, L., and Espuche, E. 2008. Journal of Polymer Science A. 46: 2062-2071.

- [6] Temgire.,M.K., and Joshi,S.S. 2004. Radiation Physics and Chemistry. 71: 1039-1044.
- [7] Zheng, M., Gu, M., Jin, Y., and Jin,G. 2001. Materials Research Bulletin. 36: 853-859.
- [8] Stepanov, A.L., Abdullin, S.N. Petukhov,V.Y., Osin, Y.N., Khaibullin, R.I., Khaibullin, I.B. 2002. Philosophical Magazine B. 80: 23-28.
- [9] Yeum, Y.H., Deng,Y. 2005. Colloid and Polymer Science. 283: 1172-1179.
- [10] Beercroft, L.L., Ober,C.K. 1997. Chemistry of Materials. 9: 1302-1317.
- [11] Vijaya Kumar, R., Elgamiel, R., Diamant, Y., Gedanken, A., Norwig, J. 2001.Langmuir. 17: 1406-1410.
- [12] Saboormaleki, M., Barnes, A.R., Schlindwein,W.S. 2004. Abs.726, 205<sup>th</sup> Meeting, The electrochemical society, Inc.
- [13] Braun, H., Meyer, E. 2013. Int, J Mol Sci. 14(2): 3254.
- [14] Feldman,K., Hahner, G., Spencer,N.D., Harder, P., Grune, M. 1999. J.Am.Chem.Sco. 121: 10134.
- [15] Rakesh, Sowbhagya, Sannaiah Ananda, Netkal M.Made Gowda. 2015. International Research Journal of Pure and Applied Chemistry. 9(4): 1-13.
- [16] Gautam, A., Ram, S. 2010. Mater Chem Phys. 119: 266-271.
- [17] Hodge, R.M., Edward, G.H., Simon, G.P. 1996. Polymer. 37: 1371.
- [18] Selvasekarapandian, S., Baskaran, R., Kamishima, O., J.Kawamura, Hattori, T. 2006. Spectrochim.Acta Part A. 65: 1234.
- [19] Nicho, M.E., Hu, H. 2000. Solar Energy Mater.Solar Cells. 63: 423.
- [20] Raksha.K.R., and Sannaiah Ananda. 2014. Journal of Applicable Chemistry. 3(1): 397- 412.