Synthesis and characterization of PEO:Sr/CuO polymer nanocomposite films and study of their optical, electrical and viscosity properties

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Abstract

PEO and PEO:Sr/CuO films have been prepared by the well known solution casting method. The structural studies of the polymer films are studied by X-Ray diffraction (XRD), Scanning electron microscope (SEM) and Fourier transform infrared (FT-IR) techniques. The optical property is studied by recording UV-visible spectroscopy. The structural properties of polymer films characterized by X-ray diffraction measurements confirm the semi-crystalline nature of PEO which contains crystalline and amorphous regions. The SEM of PEO:Sr/CuO films exhibit characteristic patterns on the film surface. Photo-voltaic activity of the films and viscosity measurements of PEO and PEO:Sr/CuO nanocomposite solutions are also studied.

Keywords: Polyethylene oxide, Sr/CuO nanoparticles, PEO:Sr/CuO films, photo-voltaic.

INTRODUCTION

Polymer nanocomposite materials attracted great interest over many years because of the enhanced properties exhibited by such material which includes optical, electrical, thermal, mechanical, magnetic and dielectric properties. Since the nanoparticles exhibit size related properties which significantly differ from bulk materials, it is more advantageous to use nanofillers as polymer additives instead of conventional additives. The nanoparticles are superior over traditional fillers owing to their high surface reactivity and large surface to volume ratio [1]. Polymer blending is most useful technique for designing materials with wide variety of properties and it is the most contemporary ways for the development and design of new polymeric

nanocomposite blend materials [2]. Polyethylene oxide (PEO) is a unique polymer soluble in both aqueous and organic solvents and it has polyether chain which can coordinate with alkali cations like Li^+ , Na^+ , Ca^+ , etc resulting in the formation of polyelectrolyte for supercapacitors, batteries and fuel cells [3-5]. Polyethylene oxide has linear structure offering number of most important physicochemical properties. Polyethylene oxide possesses interesting properties of biocompatibility, low toxicity, high melting point, low glass transition temperature and good structural integrity [6]. PEO segments have the high affinity to water molecules and this property is frequently used to modify hydrophobic molecules or macromolecules such as polythiophene to become water soluble. In self assembled monolayers of PEO entities it has been demonstrated that the molecular conformation in the ordered PEO phase either refers to a planar zigzag conformation or to a 7_2 helical conformation [7]. Recent experiments showed the importance of local interfacial water structures for protein adsorption on the surface grafted PEO thin films [8]. The high affinity between PEO segments and water molecules was observed in PEO micro droplets prepared from organic solvents such as chloroform and after the evaporation of the organic solvents the residual PEO phase immediately becomes hydrated. Water molecules immediately interact with PEO and keep the droplet in a liquefied state without crystallization or solidification owing to the high specific surface of the micro droplets [9]. The introduction of Sr/CuO nanoparticles 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.

EXPERIMENTAL

Materials and methods

Polyethylene oxide (molecular weight 5,000,000) supplied by Alfa aesar used as basic polymeric material. The copper metal wire from Alfa-Asear Pvt Ltd., platinum electrode from Elico Pvt Ltd., sodium bicarbonate and strontium chloride from Alfa-Asear was used. Sr-doped CuO nanoparticles prepared by the electrochemical method in our research laboratory had been used to prepare polymer nanocomposite films. Deionized water was used for all experiments. All chemicals were used as received without further purification.

Preparation of Sr-doped CuO nanoparticles by electrochemical procedure:

Nanoscale Sr-doped CuO nanoparticles are synthesized by the simple, cost-effective electrochemical method using SrCl_2 , copper electrode and platinum electrode in an aqueous system containing NaHCO_3 as conductive salt. An electrochemical process based on the electrolytic cell where the copper electrode was used as an anode and platinum electrode as a cathode with a lateral distance of 1cm. The electrolytic solution was optimized to 20 ml of 0.5% NaHCO_3 containing 0.05g SrCl_2 . A potential difference was applied between the electrodes using a DC source and current of 12mA and the synthesis was performed galvanostatically at room temperature without stirring for 3hrs. The electrochemical synthesis of Sr-doped CuO involves the

dissolution of copper electrode releasing Cu^{2+} ions which are electrochemically reacted with NaHCO_3 solution forming CuO followed by Strontium occupying the interstitial lattice of CuO resulting in the formation of Sr-doped CuO nanoparticles. The yield of nanoparticles obtained is 0.5-1g as synthesis is optimized to 20 ml of NaHCO_3 solution. The reaction can be repeated with the same experimental conditions to get the required amount of nanoparticles. The obtained nanoparticles are washed repeatedly with distilled water until sodium bicarbonate is completely removed, centrifuged and calcined at 500°C for 2 hrs for complete removal of sodium and hydroxide impurities and further used for the preparation of PEO:Sr/CuO polymer nanocomposite films.

Preparation of PEO:Sr/CuO polymer nanocomposite films:

Polymer nanocomposite films of PEO dispersed with different concentrations of Sr-doped CuO nanoparticles were prepared by solution casting method [10]. 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 Sr-doped CuO nanoparticles (0.025%, 0.05%, 0.075% and 0.1%) 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 techniques: The XRD diffractograms of PEO films undoped and doped with different concentrations of Sr-doped CuO nanoparticles were recorded using Rigaku Miniflex II desktop X-ray diffractometer equipped with Cu- $K\alpha$ radiation ($\lambda = 1.5406\text{\AA}$). Ultraviolet-visible absorption spectra were measured in the wavelength range of 200-800nm using JASCO UV-VIS spectrophotometer. The SEM images of the samples were recorded on ESEM Quanta - 200 FEI - Netherlands. FT- IR measurements were performed using JASCO, FT- IR in the spectral range of $4000 - 400\text{ cm}^{-1}$.

RESULTS AND DISCUSSION

X-ray Diffraction (XRD): The crystallographic interpretations are performed by X-ray diffractometer using Cu $k\alpha$ wavelength ($\lambda = 1.5406\text{\AA}$) in the scan range from 0° to 60° . Figure 1 represents the XRD pattern of pure PEO and PEO nanocomposite films doped with different concentrations of Sr/CuO nanoparticles (0.025%, 0.05%, 0.075 % and 0.1%). The diffraction pattern of pure PEO indicated by figure 1 (a) shows broad peak in between 2θ values equal to 15° and 25° . This indicating the semi-crystalline nature of PEO polymer which contains both crystalline and amorphous regions. The semi-crystalline nature is due to the presence of strong intramolecular hydrogen bonding in individual monomer unit of PEO and intermolecular hydrogen bonding between its different monomer units [11]. There is a decrease in the relative

intensity of broad peak which is corresponding to PEO after embedding the Sr/CuO nanoparticles into PEO matrix which is represented in figure 1 (b). As the concentration of the dopant nanoparticle in the polymer matrix increased, the peak height again increased and peak width decreased indicating the increase in crystallinity upon increase in nanoparticle doping percentage [12] represented by figure 1 (c) – figure 1 (e).

Figure 1: X-ray diffraction spectra of (a) undoped PEO film and PEO film doped with (b) 0.025% (c) 0.05%, (d) 0.075 % and (e) 0.1% Sr/CuO nanoparticles.

Fourier Transform Infrared analysis (FT-IR): Figure 2 represents the FT-IR spectra of pure PEO and PEO nanocomposite films doped with different concentrations of Sr/CuO 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 CH₂ of PEO. The doping of Sr/CuO nanoparticles into polymer films affects the height and the position of certain IR absorption peaks. The structural modifications can be identified by investigating the Sr/CuO 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 [13]. Further the variations in the intensity of the bands at 940 cm⁻¹, which characterized the syndiotactic structure of PEO, 1145 cm⁻¹, a u(CO) mode in the crystalline region of PEO, and 1469 cm⁻¹, which was assigned to the bending of CH₂ vibration, are related to the strong interaction between the dopant and the polymer. The new absorption bands at 428 cm⁻¹, may be correlated to defects induced by the charge transfer reaction between the dopant nanoparticle and the PEO polymer molecular chain [14].

Figure 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% Sr/CuO nanoparticles.

Ultraviolet-visible spectroscopy: The UV-visible spectra of the PEO: Sr/CuO

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

Figure 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% Sr/CuO nanoparticles.

Scanning Electron Microscopy: The morphology of the samples was studied by FE-SEM. SEM is used to investigate fully the effect of Sr/CuO nanoparticles on polymer content and to examine the dispersion of nanocomposites particles in the PEO polymer matrix. Figure 4 shows typical SEM images of PEO films undoped and doped with different concentrations of Sr/CuO nanoparticles. The SEM image figure 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 Sr/CuO nanoparticles in PEO blend films exhibits changes in the surface morphology of the system and exhibit characteristic patterns represented in figure 4(b) –figure 4(e). Sr/CuO microdomains are dispersed within PEO matrix in the blend film with relatively good interfacial adhesion between the two components.

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

Photo-voltaic activity: The photo-voltaic property of PEO films undoped and doped with different amounts of Sr/CuO nanoparticles were studied by measuring the conductance and potential using conductometer and potentiometer at dark, sunlight and UV light [15]. The experimental results were tabulated in table 1 and graphically represented by figure 5 and figure 6. These results suggest that as concentration of dopant nanoparticles is increased, the conductance and potential also increased. The conductivity of PEO:Sr/CuO nanocomposite films is enhanced to an appreciable extent in presence of UV light than the sunlight and dark conditions. The potential of

PEO:Sr/CuO nanocomposite films is enhanced to an appreciable extent for sunlight. Table 1 indicates PEO:Sr/CuO (0.1%) has higher potential for sunlight compared to all other polymer nanocomposite films. This shows that PEO:Sr/CuO (0.1%) nanocomposite film acts as a better capacitor compared to remaining polymer nanocomposite films.

Table 1: Conductivity and potential measurements for PEO and PEO:Sr/CuO films.

Property	Polymer film	Dark	Sunlight	UV
Conductivity in μS	PEO	1.0	1.5	2.3
	PEO:Sr/CuO (0.025%)	2.2	4.9	5.6
	PEO:Sr/CuO (0.05%)	4.3	16.5	17.6
	PEO:Sr/CuO (0.075%)	6.5	17.9	18.3
	PEO:Sr/CuO (0.1%)	8.6	18.5	19.6
Potential in V	PEO	0.023	0.067	0.037
	PEO:Sr/CuO (0.025%)	0.047	0.201	0.063
	PEO:Sr/CuO (0.05%)	0.052	0.279	0.096
	PEO:Sr/CuO (0.075%)	0.073	0.293	0.105
	PEO:Sr/CuO (0.1%)	0.086	0.417	0.131

Figure 5: Concentration V/s conductance graph at different concentrations of PEO:Sr/CuO under different experimental conditions (Dark, sunlight and UV).

Figure 6: Concentration V/S Potential graph at different concentrations of PEO:Sr/CuO under different experimental conditions (Dark, sunlight and UV).

Viscosity properties of PEO and PEO:Sr/CuO polymer nanocomposite solutions: Viscosity measurements of PEO:Sr/CuO polymer nanocomposite solution were performed by simple and inexpensive Ostwald method in which viscosity is measured by comparing the flow times of the two liquids of equal volumes using same viscometer. The experiment was carried out taking water as solvent at different concentrations of PEO:Sr/CuO. Different concentrations of polymeric samples were prepared by adding different concentration of Sr/CuO nanoparticles (0.002, 0.004, 0.006 g/dl) in PEO solution. Using the same viscometer, the flow times of pure PEO and PEO:Sr/CuO of different concentrations have been measured. For each concentration of polymer nanocomposite solution, the corresponding relative viscosity (η_r), specific viscosity (η_{sp}), reduced viscosity (η_{sp}/C), inherent viscosity ($\ln \eta_{sp}/C$) and intrinsic viscosity [η] are calculated. The double extrapolation plots of reduced viscosity and inherent viscosity against concentration gives the intrinsic viscosity [η].

Table 2: Viscosity data for PEO at 25 °C.(Flow time for water, $t_0 = 130$ sec)

Concentration of PEO (g/dl)	Flow time, t (sec)	Relative viscosity $\eta_r/t_0 = \eta_r$	Specific viscosity $\eta_r - 1 = \eta_{sp}$	Reduced viscosity η_{sp}/C (dl/g)	$\ln \eta_r$	Inherent viscosity $\ln \eta_r/C$ (dl/g)	Intrinsic viscosity $[\eta]$ (dl/g)
0.0008	142.0	1.0923	0.0923	115.38	0.0882	110.35	111.4
0.0012	148.3	1.1407	0.1407	117.30	0.1316	109.70	
0.0016	154.8	1.1907	0.1907	119.23	0.1745	109.08

Figure 7: Plot of reduced and inherent viscosity for PEO.

Table 3: Viscosity data for different concentrations of PEO with 0.004g/dl of Sr/CuO.

Concentration of PEO (g/dl)	Flow time, t (sec)	Relative viscosity $t/t_0=\eta_r$	Specific viscosity $\eta_r-1=\eta_{sp}$	Reduced viscosity η_{sp}/C (dl/g)	$\ln \eta_r$	Inherent viscosity $\ln \eta_r/C$ (dl/g)	Intrinsic viscosity $[\eta]$ (dl/g)
0.0008	150.3	1.1561	0.1561	195.19	0.1450	181.31	191.5
0.0012	160.8	1.2369	0.2369	197.41	0.2126	177.17	
0.0016	171.5	1.3192	0.3192	199.51	0.2770	173.14

Figure 8: Plot of reduced and inherent viscosity for different concentration of PEO with 0.004g/dl of Sr/CuO nanoparticles.**Table 4:** Viscosity data for different concentrations of PEO with 0.008 g/dl of Sr/CuO.

Concentration of PEO (dl/g)	Flow time, t (sec)	Relative viscosity $t/t_0=\eta_r$	Specific viscosity $\eta_r-1=\eta_{sp}$	Reduced viscosity η_{sp}/C (dl/g)	$\ln \eta_r$	Inherent viscosity $\ln \eta_r/C$ (dl/g)	Intrinsic viscosity $[\eta]$ (dl/g)
0.0008	152.91	1.1762	0.1762	220.28	0.1589	202.86	207.0
0.0012	165.2	1.2707	0.2707	225.58	0.2395	199.63	
0.0016	178.2	1.3707	0.3707	231.73	0.3153	197.07

Figure 9: Plot of reduced and inherent viscosity for different concentration of PEO with 0.008 g/dl of Sr/CuO nanoparticles.

Table 5: Viscosity data for different concentrations of PEO with 0.012g/dl of Sr/CuO.

Concentration of PEO (g/dl)	Flow time, t (sec)	Relative viscosity $t/t_0 = \eta_r$	Specific viscosity $\eta_r - 1 = \eta_{sp}$	Reduced viscosity η_{sp}/C (dl/g)	$\ln \eta_r$	Inherent viscosity $\ln \eta_r / C$ (dl/g)	Intrinsic viscosity $[\eta]$ (dl/g)
0.0008	157.09	1.2084	0.2084	260.57	0.1892	236.62	248.5
0.0012	171.49	1.3191	0.3191	265.96	0.2769	230.79	
0.0016	186.01	1.4309	0.4309	269.32	0.3583	223.93

Figure 10: Plot of reduced and inherent viscosity for different concentration of PEO with 0.012g/dl of Sr/CuO/ nanoparticles.

Figure 11: Plot of intrinsic viscosity $[\eta]$ for different concentrations of Sr/CuO nanoparticles.

The study of variation of the intrinsic viscosity $[\eta]$ against the concentration of Sr/CuO nanoparticles reveal that there is a gradual increase in the intrinsic viscosity of the polymer solution as the concentration of the Sr/CuO nanoparticles is increased. During the polymer dissolution, a slow penetration of the nanoparticles into the interstices of the polymer exists and forces them to swell which is also evident by the increase in intrinsic viscosity in polymer upon increase in % wt of doping. The process of swelling increases the volume of the PEO polymer matrix. The giant size and the increased volume of the polymer molecules as the concentration of Sr/CuO nanoparticles increases restrict its molecular mobility in the solution and increase inter molecular friction. The PEO:Sr/CuO polymer nanocomposite solution is therefore highly viscous.

CONCLUSION

PEO:Sr/CuO polymer nanocomposite films were prepared from PEO aqueous solution and Sr/CuO nanoparticles by solution casting method. The SEM images of PEO:Sr/CuO showed that the polymer nanocomposite film surfaces had characteristic structures pertaining to different concentration of Sr/CuO dopant nanoparticles. Incorporation of Sr/CuO 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 doping. The conductivity and potential measurement studies indicates an increase in conductance and potential with increase in the amount of Sr/CuO dopant nanoparticles. The viscosity studies revealed that there is a gradual increase in the intrinsic viscosity of the polymer solution as the concentration of the Sr/CuO nanoparticles is increased.

ACKNOWLEDGEMENTS

This research work is funded by SERB-DST, UGC-BSR New Delhi, India and supported by the University of Mysore. The authors greatly acknowledge UPE, CPEPA and DST Purse projects, Vijnana Bhavana, University of Mysore, Mysuru for necessary instrumentation facilities.

REFERENCES

- [1] Gudrun, S., Matthew, M.M., 2003, "Properties of polymer-nanoparticle composites", *Current Opinion in Colloid & Interface Science*, 8(1), pp. 103-108.
- [2] Supri, A.G., Siti Hajar, M.D., Hanif, M.P.M., 2016, "Effect of type of conductive fillers and poly(ethylene glycol) diglycidyl ether on the electrical conductivity and morphology properties of poly (vinyl chloride)/poly (ethylene oxide) conductive films", *Polymer Bulletin*, 73, pp.2831-2841.
- [3] Lan,T., Kaviratna, P.D., Pinnavaia, T.J., 1996, "Epoxy self-polymerization in smectite clays" *Journal of Physics and Chemistry of Solids*, 57, pp. 1005–1010.
- [4] Yang, X.Q., Lee, H.S., Hanson, L., McBreen, J., Okamoto, Y., 1995, "Development of a new plasticizer for poly(ethylene oxide)-based polymer electrolyte and the investigation of their ion-pair dissociation effect" , *Journal of Power Sources*, 54(2), pp.198–204.
- [5] Mishra, R., and Rao, K.J.,1998, "Electrical conductivity studies of poly(ethylene oxide)-poly(vinylalcohol) blends" , *Solid State Ionics*, 106, (1-2), pp.113–127.
- [6] Saboormaleki, M., Barnes, A.R., Schlindwein,W.S., 2004, Abs.726, 205th Meeting, The electrochemical society, Inc.
- [7] Dormidontova, E.E., 2002, "Role of competitive PEO-water and water hydrogen bonding in aqueous solution PEO behaviour", *Macromolecules*, 35 (3), pp. 987-1001.
- [8] Leung, B.Q., Yang, Z., Wu,S.S.H., Chou, K.C., 2012, "Role of interfacial water on protein adsorption at cross-linked polyethylene oxide interfaces", *Langmuir*, 28, pp.5724-5728.
- [9] Takahashi, Y., Sumita, I., Tadokoro, H., 1973, "Structural studies of polyethers. IX. planar zigzag modification of poly(ethylene oxide), *Journal of Polymer Science and Polymer Physics*, 11, pp.2113-2122.
- [10] Rakesh, Sowbhagya, Sannaiah Ananda, Netkal M.Made Gowda, 2015, "Optical, electrical, viscosity properties of poly (vinyl alcohol) films embedded with Cr₂O₃ nanoparticles synthesized by biological and electrochemical methods", *International Research Journal of Pure and Applied Chemistry*, 9(4), pp.1-13.
- [11] Gautam, A., Ram, S., 2010, "Preparation and thermomechanical properties of Ag-PVA nanocomposite films" ,*Materials Chemistry and Physics*, 119 (1-2), pp.266-271.

- [12] Hodge, R.M., Edward, G.H., Simon, G.P., 1996, "Water absorption and states of water in semicrystalline poly (vinyl alcohol) films", *Polymer*, 37, pp.1371-1376.
- [13] Selvasekarapandian, S., Baskaran, R., Kamishima, O., Kawamura, J., Hattori, T., 2006, " Laser Raman and FTIR studies on Li⁺ interaction in PVAc-LiClO₄ polymer electrolytes", *Spectrochimica Acta Part A*, 65, pp.1234-1240.
- [14] Nicho, M.E., Hu, H., 2000, "Fourier transform infrared spectroscopy studies of polypyrrole composite coatings", *Solar Energy Materials and Solar Cells*, 63, pp.423-435.
- [15] Hosaholalu Balakrishna Uma, Sannaiah Ananda, Siddaramaiah Basavarajaiah, 2019, "Synthesis and characterization of PVA/PEO/In₂S₃ polymer nanocomposite films and study of their optical, electrical and thermal properties", *Journal of Applicable Chemistry*, 8(3), pp.1123-1134.