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Optical, Electrical and Thermal Properties of SnO₂ Nanoparticles doped Poly Vinyl Alcohol-Poly Vinyl Pyrrolidone Blend Polymer Electrolyte

B Guruswamy¹, V. Ravindrachary¹*, C. Shruthi¹, Shreedatta Hegde¹, Rohan N. Sagar¹, S. D. Praveen²

¹Department of Physics, Mangalore University, Mangalagangotri - 574 199, Mangalore, Karnataka, India, ²Department of Physics K V G College of Engineering, Kurunjibhag, Sullia - 574 327, Dakshina Kannada, India.

ABSTRACT

Semiconductor SnO_2 nanoparticles were synthesized using standard route and the effect of these nanoparticle doping on structural, optical, electrical, and thermal properties of the poly vinyl alcohol-poly vinyl pyrrolidone (PVA-PVP) polymer blend has been investigated using various techniques. Pure and PVA-PVP/SnO₂ nanocomposites films were prepared using solution casting technique. The Fourier transform infrared study shows that the SnO_2 nanoparticle interacts with the OH group of PVA and carboxylic group of PVP and forms the complex within the blend matrix. The optical study shows that the absorption in the ultraviolet region and transparence in the visible region. From electrical conductivity measurements, it is clear that doping and hence the complex formation enhances the conductivity of the composite. The thermogravimetric analysis results reflect that the doping also affects the thermal properties of the composite. The scanning electron microscope images show that the nanoparticles embedded within the polymer blend matrix are of spherical in shape and the surface morphology of the composite films (roughness) increases with addition of SnO_2 nanoparticles. Hence, this study shows that SnO_2 nanoparticle doping forms the complex and the presence of these complexes affects the optical, thermal, electrical, and structural properties of the blend composite.

Key words: Poly vinyl alcohol-poly vinyl pyrrolidone/SnO2, Fourier transform infrared, Ultraviolet-visible, Thermogravimetric analysis, Scanning electron microscope, Conductivity.

1. INTRODUCTION

It is known that the desire property of a polymer for a particular application can be obtained by blending and doping. Here the polymer blending is considered to be the one of the important and modern way of developing new polymeric materials with a wide variety of physical and chemical properties. The advantage of polymer blending is that the properties of a final product can be tailored suitably for specific application as these blend properties are mainly depends on the characteristics of the parent homopolymers and the composition. Doping a polymer is another way of tailoring the physical and chemical properties of the polymer for specific applications. Here the change in the property of the polymer due to doping mainly depends on the type of the polymer, chemical nature and size of the dopant and the way the in which the dopant interacts with the host polymer. Hence, the nanoparticles doped polymers are attracted much attention due to the various applications including of sensor properties. Here the combination of inorganic nanoparticles and an organic polymer provides a simple route to stable and processable composite materials, which integrating the promising properties of both components [1-4]. Poly vinyl pyrrolidone (PVP) is an amorphous polymeric material which is hygroscopic in nature, and it attains complex formation ability, exquisite environmental stability, easy processability, modest electrical conductivity, and more charge transport mechanism, these chemical structures induce extreme changes in electronic properties.

Poly vinyl alcohol (PVA) is one of the superior polymeric materials with semi-crystalline nature with properties such as water-soluble, synthetic

and biocompatible non-toxic, odorless, film formation ability, and adhesive nature which are very much essential for various applications in biomedical field. When PVA/PVP blend is formed, the interactions between the carbonyl group of PVP and the hydroxyl group of PVA takes place through the intermolecular hydrogen bonding as a result new structure is to be formed.

When such blend is doped with suitable metal oxide nanoparticles that forms a polymer composite whose microstructure and other macroscopic properties are altogether different from parent one. SnO_2 nanoparticles embedded within the polymer blend composite films. The properties of the film further enhance the conductivity and also become optically transparent thin films. These films are useful in the field of electronic devices such as liquid crystal displays, photovoltaic devices including high energy electrochemical devices such as batteries, and fuel cells but the foremost advantage is found to be its sensor application [4-7]. Keeping in view the above applications, the present work aims to

*Corresponding author: *E-mail: vravi2000@yahoo.com*

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Received: 13th November 2017; **Revised:** 19th December 2017; **Accepted:** 07th January 2018 prepare SnO_2 nanoparticles and dope these into PVA-PVP blends to obtain suitable films for prospective optical, electrical, and thermal applications.

2. EXPERIMENTAL

The PVA was obtained in powder form from M/s. S. D. fine-Chem. Ltd, Mumbai. PVP, SnCl₂ 2H₂O from M/s. Loba Chemie Pvt. Ltd. Mumbai. SnO₂ nanoparticles were synthesized through a chemical precipitation method using SnCl₂2H₂O. The pure and SnO₂ doped PVA-PVP composite films were prepared by solution casting method [1,3,7]. The Fourier transform infrared (FTIR) spectra of pure and composite polymer films were recorded using IR-Prestige 21 FTIR spectrophotometer in the wave number range 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹. The optical absorption spectra of pure and doped PVA-PVP composite films were recorded using ultraviolet-visible (UV-Vis) Shimadzu UV1800 Spectrophotometer. Universal TA (SDT Q600) TG/DTA instrument is used to study the thermal properties of the films from 30°C to 600°C at a heating rate of 10°C/min under nitrogen atmosphere. The electrical conductivity study was carried out using KEITHLEY-236 source measure Unit and morphology study using FESEM with Carl Zeiss instrument.

3. RESULTS AND DISCUSSION

3.1. FTIR Studies

The observed FTIR spectra of pure and SnO_2 doped PVA-PVP blends are shown in Figure 1. From the figure, it is clear that for pure PVA/PVP polymer blend the O–H stretching vibration band is observed around 3445 cm⁻¹. The weak bands at 2922 and 2851 cm⁻¹ are corresponded to asymmetric and symmetric stretching vibration of C–H, respectively, and the band at 1742 cm⁻¹ corresponding to C=O stretching. The band at 1652 cm⁻¹ is attributed to stretching vibration of C=C (aromatic) of PVP and the bands corresponding to C–H bending and C–O stretching vibrations are observed at 1470 and 1085 cm⁻¹, respectively [2,3,7]. For the composite films these bands are shifted from 3445, 2922, 2851, 1742, 1652, and 1740 cm⁻¹ to 3341, 2939, 2830, 1733, and 1636 cm⁻¹, respectively, and the new bands are observed at 530 and 674 cm⁻¹. These new bands are attributed to stretching vibrations of Sn-O and O-Sn-O.

The blending of PVA and PVP results in the formation of four different types of polymer-polymer interaction such as Vander Waals, hydrophobic, electrostatic, and hydrogen bonding. In the present case, the hydrogen bonding interaction between the carbonyl group of PVP chain and a hydroxyl group of PVA chain is expected within the blend matrix. Apart from the above interaction when SnO₂ nanoparticles are embedded within such a matrix, the nanoparticles interact with the carbonyl and OH groups leads to the complex formation within the blend, which modifies the chemical structure and hence modifies the physical and chemical properties. The complex formation occurs in a cooperative way, leading to compact structures which are reflected in the form of change in the intensities in some IR bands and new band arises on doping.

3.2. Optical Studies (UV-Vis Absorption)

The optical studies were carried out for pure blend, and composite films and the observed spectra are given in Figure 2. From the figure, the observed peak at 240 nm for pure blend and is due to the presence of carbonyl group and OH group interaction, which can be assigned to localized $n-\pi^*$ transitions. For the SnO₂ doped composite film, from the figure it is clear that the absorption peak intensity increases along with a peak position shift toward the lower wavelength with increase in SnO₂ concentration For the composite films, along with absorption



Figure 1: Fourier transform infrared spectra of pure blend and poly vinyl alcohol-poly vinyl pyrrolidone/SnO₂ nanocomposites.



Figure 2: Ultraviolet-visible spectra of pure poly vinyl alcoholpoly vinyl pyrrolidone (PVA/PVP) blend and PVA-PVP/SnO₂ nanocomposites.

band at 240 nm for pristine blend a new band at 283 nm is observed for doped films and is due to the presence of circulating tumor cells (CTC). The formation of CTC is the result of hydrogen bonding interaction between the carbonyl group of PVP and the hydroxyl group of PVA and SnO₂. To understand this further other optical parameters are calculated using Tauc's plot [1,2] the results are given in Table 1.

From the table, it is clear that the optical energy band gap decreases and activation increases with increase in doping level.

3.3. Thermogravimetric analysis (TGA)

TGA is carried out for pure PVA/PVP blend and PVA/PVP/SnO $_2$ composite to understand the thermal properties and the results are shown in Figure 3.

For pure PVA/PVP blend, TGA curve exhibits three steps of weight loss at different temperatures. First weight loss occurs within 70–150°C and is related to the evaporation of solvent which is absorbed during the doping process. The second weight loss was observed between 225°C and 320°C and third weight loss is observed between the temperature range of 375 and 475°C are attributed to the degradation of the polymer chains [2,3]. For composite, TGA curve also exhibits three steps of weight loss similar to the pure blend but with small variation

Table 1: Optical absorption parameters of pure blend and PVA/PVP/SnO₂composites.

Doping (wt%)	$\lambda_{\mathrm{ma} \times 1}$ (nm)	$\lambda_{\mathrm{ma}\times 2}$ (nm)	$E_{\rm g}({\rm eV})$	$E_{\rm a}({\rm eV})$
Pure blend	233	288	4.75	0.21
2	232	284	4.74	0.29
4	231	282	4.73	0.32
6	230	278	4.72	0.38
8	230	274	4.72	0.38
10	225	272	4.67	0.46

PVA-PVP: Poly vinyl alcohol-poly vinyl pyrrolidone

in the temperature range. Here the first weight loss occurs within the temperature range of 50–125°C and it is slightly less compared to the pure blend. The second weight loss is shifted to 250–320°C and third weight loss to 400–500°C, respectively, for doped composite. Apart from the shift in the weight loss steps, it is to be noticed for composite the weight loss is not going to be zero even after 500. This feature indicates that PVA/PVP/SnO₂ composite films are not degrades chemically with temperature.

Here for the composite films the residual weight increases with increase in doping concentration even after 500°C. This shows the thermal stability of the composite was found to increase with increasing doping concentration, which is reflected in the form of a decrease in percentage weight loss. This increase in thermal stability of the blend on doping is mainly due to the change in chemical behavior of the blend due to the presence of CTC within the composite on SnO₂ doping.

3.4. DC conductivity

The DC conductivity measurements were carried out for pure PVA-PVP blend and PVA-PVP/SnO₂ nanocomposite films. The variations of the measured DC conductivity of pure blend and PVA-PVP/SnO₂ nanocomposite films at room temperature are shown in Figure 4. It is observed that the conductivity increases with increasing doping concentration and these results are understood on the basis of modified interpolator hopping model [5,7].

According to this model, DC conductivity arises due to the hopping of charge carriers between the polarons and/or bipolarons. The conduction carried through the phonon-assisted hopping of charge carriers between the localized sites which are created in the form of CTC on doping. When the concentration of doping increases the delocalization of these charge carriers within the polymer matrix increases may lead to an increase in structural defects. Here it is clear that the conductivity of the composite films arises due to the hoping of charge carriers takes place through inter/intramolecular chain, whereas hopping distance decreases with increase in doping level.

3.5. Morphological Studies

The surface morphological study of SnO_2 doped PVA-PVP blend composite films was carried out for pure SnO_2 , Pure blend, 2 wt% and 10wt% of PVA-PVP/SnO₂ films and the results are shown in Figure 5. From Figure 5a it is observed that pure SnO_2 nanoparticles are spherical in shape and it consists of agglomerated particles and from Figure 5b pure blend PVA-PVP, the image shows smooth surface. When SnO_2 nanoparticles are embedded into the polymer blend matrix, the fig shows the surface of the films varies with increasing doping concentration [2,3]. For 2 wt% composite films Figure 5c, the roughness of the film increases compared to pure blend. This roughness further increase in 10 wt% composite films



Figure 3: Thermogravimetric analysis thermograms of pure poly vinyl alcohol-poly vinyl pyrrolidone (PVA/PVP) blend and PVA/PVP/ SnO2composites.



Figure 4: Variation of DC conductivity with SnO2 wt%



Figure 5: Field emission scanning electron microscopy micrographs of pure SnO₂, pure poly vinyl alcohol-poly vinyl pyrrolidone (PVA-PVP) blend, 2 wt%, 10 wt% PVA-PVP/SnO2

Figure 5d compared to 2 wt% films. The results show crystalline surface of composite films and roughness may help to enhance the conductivity which is reflected from conductivity study.

4. CONCLUSION

 SnO_2 nanoparticles were synthesized using standard method, and the effect of SnO_2 nanoparticle doping on structural, optical, electrical, and thermal properties of the PVA-PVP polymer blend was studied. From these studies, it is evident that the doped SnO_2 nanoparticle has an immense effect on the optical, thermal, electrical, and structural properties of the blend composite.

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Prof. V. Ravindrachary has completed his M.Sc (Physics) and Ph.D in University of Mysore. At present, he is working as a professor of Physics in Department of Physice, Mangalore University. His research areas are Polymer Microstructural studies using Positron Annihilation Spectroscopy, Growth and characterization of NLO crystals. Guided few Ph.D. students and M.Phil. student. More than 200 research papers have been published in reputed journals and presented in conferences. Completed research project funded by UGC and DAE-BRNS