

Study of Structural, Optical and Photoluminescence Properties of ZnO Doped PVA/PVP Nanocomposite

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Abstract: We report preparation and characterization of ZnO doped PVA/PVP Polymer nanocomposites using solvent casting technique. The FTIR and XRD studies confirm the formation of polymer nanocomposites through the interaction taking place between the nanoparticles and the polymer. The optical energy gap of the doped polymer decreases with an increase in doping concentration. The photoluminescence studies reveal that the intensity of the peak is maximum for a doping concentration of 8% ZnO. The optical and photoluminescence properties of PVA/PVP blend are enhanced due to doping. This makes ZnO doped PVA/PVP a prominent material for device applications.

INTRODUCTION

The blending of different polymers helps to tailor the properties of the constituent polymers. This is a technique used to enhance the physical properties of polymers. The properties of these polymer blends can be enhanced by the addition of suitable inorganic particles. Such polymer blend films find application in fuel cells, electro-chromic devices, batteries of higher specific energy [1]. Polyvinylpyrrolidone (PVP) is a very good polymer with excellent properties like high polarity, biodegradability, transparent, solubility in water, cohesive and adhesive properties, high compatibility, good dielectric constant and low toxicity. It is amorphous in nature. Poly Vinyl Alcohol (PVA) is a nontoxic, biodegradable, water-soluble polymer with good dielectric strength and good charge storage capacity. It has high tensile strength. The hydroxyl groups present in PVA is the source of hydrogen bonding which helps in the formation of networks in the polymer composite. When PVA and PVP are mixed hydrogen bonding is formed between the carbonyl group of PVP and hydroxyl group of PVA [2]. Blending of these polymers with transitional metal ions like zinc oxide nanoparticles is an area of interest due to its applications in optics, photonics, and electronics [3-4]. In the present work, an inexpensive solvent casting method is used to prepare PVA/PVP nanocomposite with various concentrations of ZnO nanoparticles. The study has been conducted to investigate the changes happening in structural, optical and photoluminescence properties of the polymer films upon doping.

EXPERIMENTAL DETAILS

Preparation of nanocomposite

Polyvinyl Alcohol (PVA-average molecular weight 89000-98000) and ZnO nanopowder (particle size < 50nm) were procured from Sigma Aldrich. Polyvinylpyrrolidone (PVP, molecular weight 1,300,000) was procured from Alfa Aeser. 3g each of PVA and PVP were taken in separate beakers and dissolved in 90 ml distilled water and continuously stirred for one hour using a magnetic stirrer at a temperature of 90^oC and 50^oC respectively until a clear solution was obtained. These two solutions were mixed and stirring continued for two hours at room temperature. This solution was divided into six equal parts. Zinc oxide nanoparticles in the wt percentages of 0, 2, 4, 8, 12 and 16 were added to these solutions and stirred continuously. Solutions consisting of nano dopants were kept in an

ultrasonicator for 10 minutes. These solutions were poured onto a petri dish and kept in an oven for one day at a temperature of 50°C. After drying the films were peeled from petri dish and placed in vacuum desiccators. The nanocomposite films of various concentrations of Zinc dioxide (ZnO) in PVA/PVP were prepared by incorporating a weight, W_d of the dopant (nanoparticles) in a weight W_p of the polymer. So, the percentage weight fraction (%) of the dopants was estimated by the following equation $x\% = \frac{W_d}{W_d + W_p} \times 100$.

CHARACTERIZATION

The UV Visible spectra of the prepared samples were recorded by using JASCO V630 UV visible spectrophotometer in the wavelength range 190–1100nm and FTIR studies were carried out with Shimadzu spectrophotometer in the wave number range 400– 4000 cm^{-1} . Bruker D8 Advance X-ray diffractometer was used to record X-ray diffraction spectra and photoluminescence studies were carried out using fluorescence Spectrophotometer F2700 with an excitation wavelength of 220nm.

RESULTS AND DISCUSSION

UV Visible Spectroscopy

UV/visible spectra of pure PVA/PVP and ZnO doped PVA/PVP is shown in Figure1. It indicates that in the wavelength region of 200-400nm, the absorption is high in the doped blends. Further, the absorption band edge shifts towards higher wavelength side with the addition of ZnO. The polar groups of the blend and Zn ions will form intra/intermolecular hydrogen bonding due to which there will be shifts in absorption bands. The absorption intensity decreases in the higher wavelength region. The absorption peak at around 220nm is due to semi-crystalline nature of the polymer and due to $n \rightarrow \pi^*$ transition [5-6].

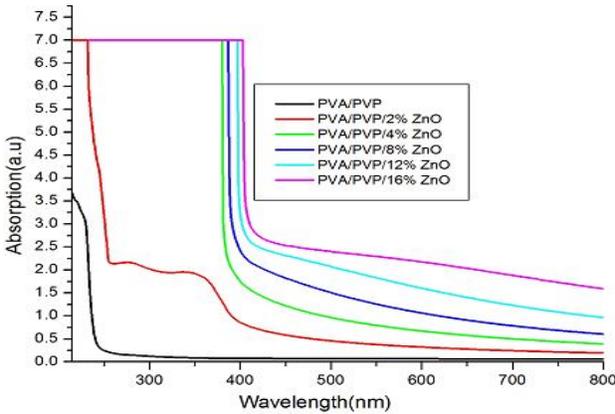


FIGURE 1: UV Visible spectra of pure PVA/PVP and ZnO doped PVA/PVP

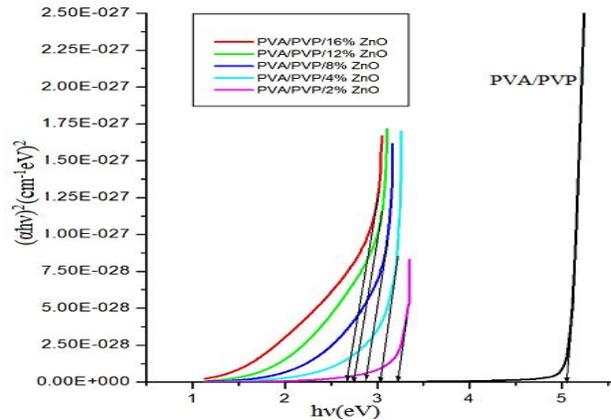


FIGURE 2: Optical energy gap of PVA/PVP and ZnO doped PVA/PVP

Optical Energy Gap

The shift in absorption edge in the UV Visible spectra of doped nanocomposites causes the change in energy band gap. The Absorption coefficient α is given by,

$$\alpha = \frac{2.303A}{d} \quad (1)$$

Where, A is the absorbance, d is the thickness of sample and α varies as a function of the photon energy. By transforming the UV Visible spectra into Tauc's plots and by using Mott and Devis frequency-dependent absorption coefficient the optical energy gap of the films can be calculated. [7-8]

$$\alpha(\nu) = \frac{\beta(h\nu - E_g)^r}{h\nu} \quad (2)$$

Where, β is a constant and r is an empirical index which may be equal to 1/2, 3/2, 2 or 3[9]. A plot of $(\alpha h\nu)^2$ vs $(h\nu)$ will provide us with direct band gap values as shown in Figure 2. The direct energy gap of PVA/PVP is 5.04 eV. The energy gaps of nanocomposites with ZnO Wt fractions of 2%, 4%, 8%, 12% and 16% reduces to 3.23eV, 3.04 eV, 2.90 eV, 2.74 eV, and 2.67 eV respectively. The decline in the energy gap values of the nanocomposite is due to the formation of charge transfer complexes and due to the availability of more number of metal ions with doping.

FTIR

The FTIR Spectra of various films is shown in Figure 3. The spectra indicates the presence of a strong broadband at around 3275 cm^{-1} referring to O-H stretching vibrations of PVA. There is a shift in the peaks towards the higher wavelength side upon an increase in doping concentration indicates stronger hydrogen bonding. There is a peak at 2931 cm^{-1} assigned to CH_2 asymmetric stretching vibrations. The peak at 1654 cm^{-1} refers to C=O stretching of PVP, peak at 1438 cm^{-1} is due to C=C Stretching and the peak at 1087 cm^{-1} is assigned to C-O stretch, C-H and O-H bending vibrations [10-11].

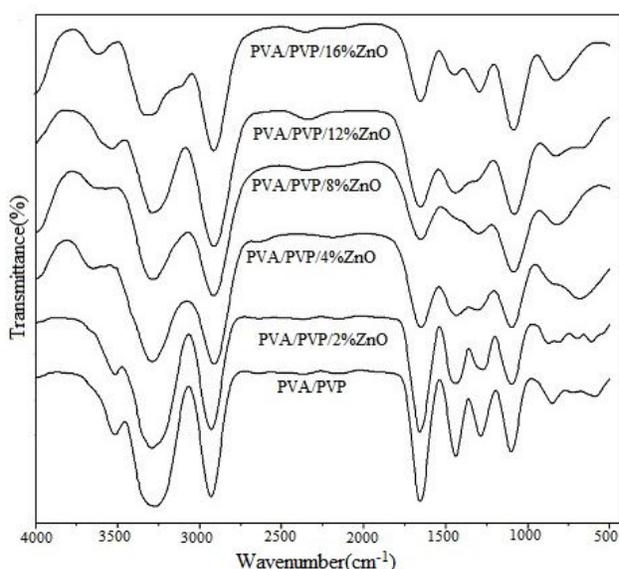


FIGURE 3: FTIR spectra of various films

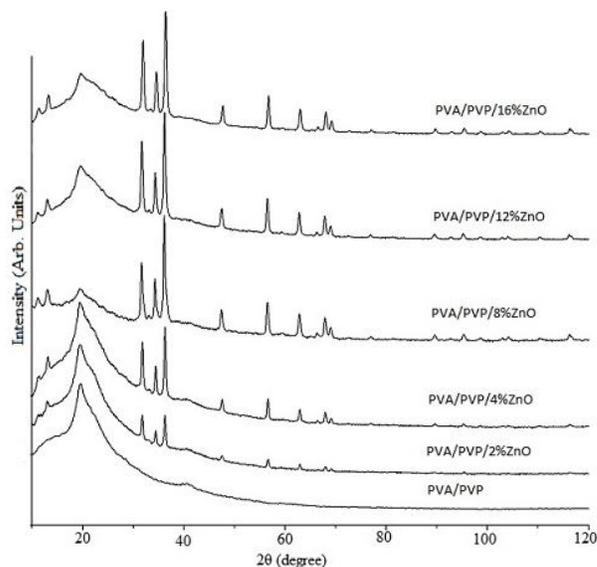


FIGURE 4: XRD spectra of various films

XRD STUDIES

The X-ray diffraction spectra of pure PVA/PVP and zinc oxide doped PVA/PVP is shown in Figure 4. For pure PVA/PVP film there is only one peak at $2\theta = 19.70$ which represents the semi-crystalline nature of PVA. This peak is observed for all the films. Fourteen peaks are observed for ZnO doped PVA/PVP nanocomposites at angles 31.94, 34.6, 36.4, 47.7, 56.76, 63.02, 66.54, 68.1, 72.77, 77.04, 89.72, 92.92, 95.42 and 98.72 which indicates the presence of ZnO nanoparticles in the composite. This is in agreement with the reported results [12]. The crystallite size of the nanocomposites is calculated using Debye-Scherrer formula. The average crystallite size is found to be 30.3nm. With the rise in doping concentration the intensity of the crystalline peaks increases which represents the increase in crystallinity of the samples.

PHOTOLUMINESCENCE STUDIES

Figure 5 shows the photoluminescence spectra of pure and ZnO doped PVA/PVP nanocomposites. The experiment was carried out using an excitation wavelength of 220nm. Three peaks were obtained in the spectra. The maximum intensity of the peak corresponds to a wavelength of 449nm. With an increase in doping concentration the intensity of the peaks found to be increased until the doping concentration reaches up to $x=8\text{wt}\%$ of PVA/PVP. Further addition of dopants leads to a reduction in the intensity of the peaks. This may happen due to clustering of nanoparticles at higher doping concentration which decreases the interfacial area within the polymer leading to quenching [13]. This indicates that the composites with 8% ZnO can be used for luminescence applications.

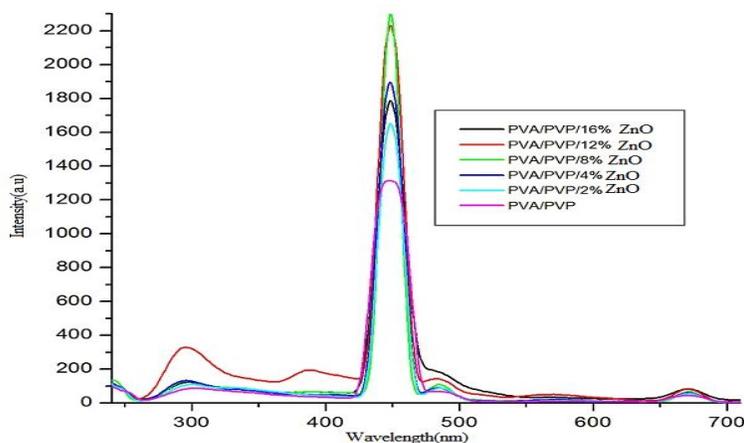


FIGURE 5: Photoluminescence spectra of PVA/PVP and ZnO doped PVA/PVP

CONCLUSION

The optical energy gap decreases with doping. The UV visible and FTIR Spectra indicate that there is a strong interaction between the dopant and the polymer matrix. XRD confirms the formation of the nanocomposite. The photoluminescence studies reveal that the nanocomposites exhibit luminescence properties in the visible region when excited with a wavelength of 220nm. Hence, due to doping the optical properties of polymer nanocomposites is enhanced. This indicates that ZnO doped PVA/PVP can be used for device applications.

REFERENCES

1. O.G. Abdullah, B.K. Aziz, D.M. Salh, Indian Journal of Applied Research, **3**, 477-480 (2013).
2. Cassu, S.; Felisberti, M. I. Polymer, **40**, 4845-4851(1990).
3. Jayakrishnan P, Ramesan, M.T. AIP Conf Proc **1620**, 165-172(2014).
4. A. Santhosh Kumar, K. K. Nagaraja and H. S. Nagaraja doi:10.1088/1757-899X/73/1/012077
5. M. A. El-Ahdal, International Journal of Polymeric Materials, **48**, 17-28 (2000)
6. K. A. M. Abd El-Kader and S. F. Abdel Hamied, J. of Applied Polymer Science, **86**, 1219 (2002)
7. N. F. Mott and E. A. Devis,(1979) Electronic Process in Non-Crystalline Materials, Oxford University Press, Oxford, UK, 2nd edition
8. J. Tauc,(1972) "Optical properties of solids," in Optical Properties of Solid, F. Abeles, Ed., p. 277, North-Holland, Amsterdam, The Netherlands
9. O.G. Abdullah, D.A. Tahir, S.S. Ahmad, H.T. Ahmad IOSR Journal of Applied Physics, **4** 52-57 (2013)
10. N. B. Rithin Kumar, Vincent Crasta, and B. M. Praveen, Hindawi Publishing Corporation Physics (2014) <http://dx.doi.org/10.1155/2014/742378>
11. R.F.Bhajantri, V.Ravindrachary, Boja Poojary, Ismayil, A Harisha, Vincent Crasta(2009)DOI10.1002/pen.21341
12. S.Mallakpour, M. Hatami Designed Monomers and Polymers **14** 461-473 (2011)
13. Basavarajeshwari Baraker, Blaise Lobo Canadian Journal of Physics **95** 738-747 (2016)