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Structural and Spectroscopic Properties of Zno/Pva Nanocomposites

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Abstract: ***Zinc oxide–Polyvinyl alcohol (ZnO/PVA) nanocomposites doped with varying concentrations of nano ZnO were prepared by solution casting method. Zinc oxide nanoparticles were synthesized by simple chemical route. Structural, Optical and Spectroscopic properties of the prepared nanocomposites were studied by using Ultra Violet Visible Spectrophotometer (UV-Vis), X-ray diffraction (XRD), Fourier Transform Infra Red Spectrophotometer (FTIR) and SEM techniques. XRD and FTIR are used to determine the effect of the synthetic conditions and resulting processing on the material structure. XRD reveals the presence of nano ZnO with hexagonal wurtzite phase in the polymer matrix. The peaks in FTIR spectra of the prepared films show the interaction between nano ZnO and the PVA polymer. SEM shows homogenous dispersion of zinc oxide nanoparticles in the polyvinyl alcohol matrix. The optical properties of ZnO/PVA nanocomposites have been investigated.***

Keywords: ***ZnO nanoparticles, ,Polyvinyl Alcohol (PVA), nanocomposite , XRD, Optical properties.***

I. INTRODUCTION

In the past years, considerable research efforts have been devoted to the design, preparation and characterization of nanocomposite materials due to their potential applications in various fields [1]. Nanocomposites based on the reinforcement of polymers with nanoparticles has found wide interest because of their capacity to unite the advantages of both polymers and filler constituents. Polymers are able to protect the novel size dependent properties of nanomaterials with proper required control of filler particles. ZnO is promising semiconductor (direct wide band-gap ~3.37 eV) with good piezoelectric properties, high chemical stability, a high exciton binding energy (60meV) and bio-compatibility [2].Well dispersed ZnO nanoparticles with very fine sizes are promising in many applications such as solar cells, devices, varistors, light emitting diodes, gas sensors, biosensors, degradation of pollutants and random lasers etc. [3,4]. ZnO based polymeric nanocomposites have created a large interest due to their prospective uses in various fields. ZnO nanoparticles incorporated into the polyvinyl alcohol can alter or improve the morphological, structural and optical properties [5, 6]. The present study involves the polymer nanocomposites of zinc oxide with polyvinyl alcohol for its structural and spectroscopic properties. Polyvinyl alcohol (PVA) was selected due to its low cost, high transparency, aqueous solubility and its attractive film forming physical properties [7].Besides it can readily mix with inorganic filler components. It is widely used in pharmaceutical and biomedical applications [7, 8]. Here, ZnO nanoparticles were prepared by using simple chemical route. ZnO/PVA nanocomposites doped with varying concentrations of zinc oxide nanoparticles were characterized by various characterization techniques to determine the surface morphology, the chemical composition in these films.

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II. EXPERIMENTAL

ZnO nanoparticles were synthesized by the simple chemical route using zinc chloride and sodium hydroxide (NaOH) as precursors. ZnO nanoparticles about ~3-5 nm sizes were synthesized by dissolving 20 ml of zinc chloride (0.1M) ,100 ml of sodium hydroxide (0.1 M NaOH) and thioglycerol (0.1 M TG) (all in methanol) [9]. The precipitate was washed in methanol. After washing the precipitate was dried at room temperapture to obtain ZnO nanoparticles in white powder form. The synthesized ZnO-TG NPs were dried in an oven, suspended in water and then used for treatment. For fabrication of zinc oxide- Polyvinyl alcohol (-[C-C(OH)n,PVA) nanocomposites a known weight of polyvinyl alcohol was dissolved in de-ionized water and stirred at 80^0C for one hr to obtain a clear viscous solution. Presynthesized zinc oxide nanoparticles were added rapidly to this solution with continuous stirring. The mixture was then heated at 40^0C to ensure complete dissolution and again sonicated for 30 minutes. ZnO nanoparticles with different concentrations were used to form 1:1, 2:1 and 5:1 ZnO/PVA nanocomposite films. Finally the films were cast from solution on silicon substrates and then dried under vacuum at 40^0 C to obtain the dry composite films for more than 5-7 days prior to tests. For reference, neat PVA film was prepared. The substrates were cleaned and oxidized in solution containing 70 vol. % concentrated H_2SO_4 and 30 vol. % H_2O_2 and washed abundantly with de-ionized water, acetone and iso-propanol afterwards. The freshly prepared ZnO nanoparticles and ZnO-PVA nanocomposites were thoroughly characterized.

III. RESULTS AND DISCUSSIONS

The size and morphology of the ZnO nanoparticles were investigated using TEM. It shows the presence of spherical monodispersed particles and the lattice of ZnO is clearly seen. Particles with ~3 to 5 nm size can be seen [9]. Figure 1 shows the optical transmittance spectra of ZnO/PVA nanocomposites.

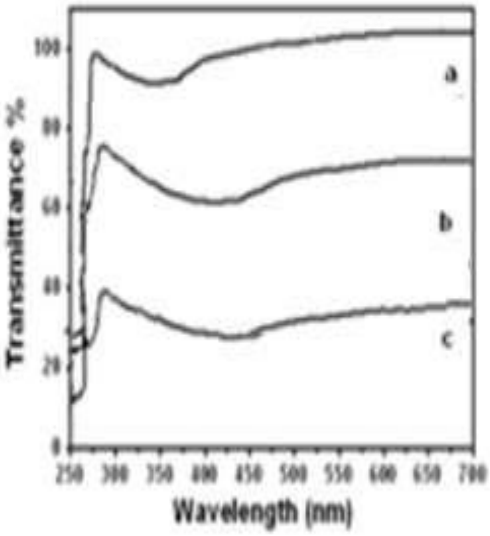

Fig.1. Transmittance spectra of ZnO/PVA nanocomposite films with different concentrations of ZnO nanoparticles (a) 1:1 (b) 2:1 (c) 5:1

It is clear from this figure ; the ZnO/PVA nanocomposite film having ratio 1:1 exhibited an intense absorption and centered at ~ 350 nm, feature of the nano ZnO film . Spectra show red shifting of λonset as the nano ZnO concentration increases, i.e. Larger aggregates containing more ZnO content were formed in the samples. The spectral redshifting of PEO/ZnO films has also been reported by Xiong et al [10].The absorbance in the UV region is developed with the accumulation of zinc oxide nanoparticals because of high-energy gap. This finding agrees with the SEM observation in the nanocomposite films. The nanocomposite film sample having ratio 1:1 shows better transmission of visible light as compared to higher concentrations. Higher ZnO concentration in the solutions will promote aggregation to affect UV absorption and scatter visible light. i.e. due to the presence of nano ZnO the optical properties of the polymer gets modified.Figure 2 shows the XRD patterns of the polyvinyl alcohol (PVA) film cast from its aqueous solution, Pure ZnO film and ZnO/PVA nanocomposite films with different nanoparticle loadings. The observed diffraction peaks corresponding to the (100), (102), (101), (102), (110), (103), (112) planes are present. XRD images confirmed the presence of nano ZnO with hexagonal wurtzite phase in the polymer matrix having lattice constants of a=3.248Å and c = 5.199 Å. The obtained peak values in the patterns were compared and found to be consistent with the literature values given in JCPDS card no. 36-1451. The average particle size (D) can be calculated from the half-peak width using the Scherrer equation [11] is ~ 3.5 nm for ZnO nanoparticles, and the crystal size varies from ~4.5 nm to 4.8 nm for ZnO-PVA nanocomposites as the nano ZnO content increased in the composites. It was observed that the peak positions and their relative intensities changed slightly with changing the concentration of nano ZnO. Also, it is clear from the figure that the peak at 2θ ~ 19.8^0 matching to d spacing of 4.5511Å, and reflection plane (101), reflection plane of PVA & another small peak at 2θ ~29.36^0consistent with earlier studies [12],a more peak at ~40.6^0indicated the presence of the typical semi-crystalline structure of PVA [13].

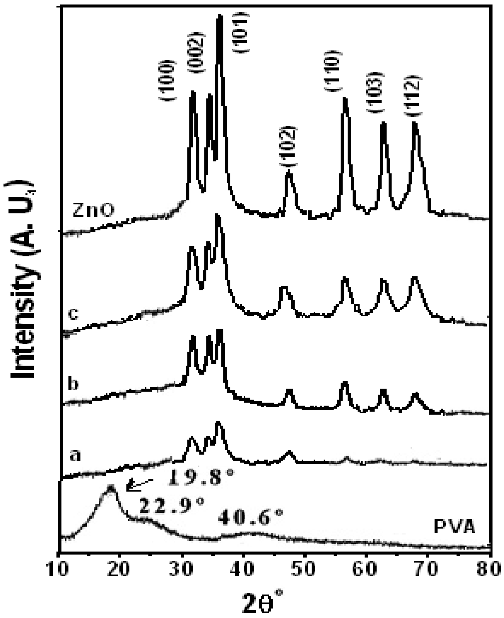

Fig. 2. XRD spectra of ZnO nanoparticles, Polyvinyl alcohol and ZnO/PVA nanocomposite films with different concentrations of ZnO nanoparticles (a) 1:1 (b) 2:1 (c) 5:1

The crystalline peak of polyvinyl alcohol disappeared, in all nanocomposite samples with different nano ZnO loadings. It indicates that the crystallinity of polyvinyl alcohol in all samples was considerably influenced by the presence of zinc oxide nanoparticles. The peak intensities in the nanocomposite samples increased with increase in nano ZnO content. i.e. the original structure of the zinc oxide nanoparticles remains unchanged in the polymer matrix. The morphological investigation of all the nanocomposite samples was made with SEM technique. Figure 3 presents the SEM images of the ZnO-PVA nanocomposites implies on Si substrate.

The morphology of the ZnO/PVA (1:1) [Figure 3(a)] nanocomposite sample was more homogeneous than those of the other samples with high nano ZnO concentration. SEM images show well homogenous dispersion of nano ZnO filler in the polymer matrix. The original structure of nano ZnO was conserved in the PVA marix, as confirmed by XRD results but as nano ZnO concentration increases agglomeration of particles of sizes ~ 20-50 nm was observed in [Figure 3 (b) and (c)] samples. The images also revealed the presence of few smaller particles with an average size < 10 nm. The agglomeration of particles may arises due to the high surface energy of the nano-size crystals. It looks that small particles aggregated to form larger ones. The chemical modifications in the nanocomposite samples are investigated by the FTIR studies. The FTIR spectra of ZnO nanoparticals pure Polyvinyl alcohol and ZnO/PVA nanocomposite films are shown in Figure 4.

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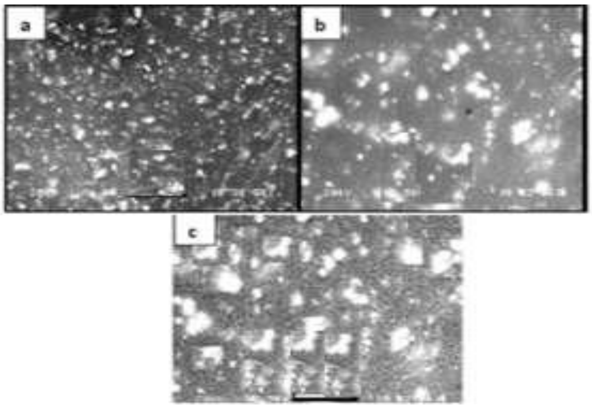

Fig.3. SEM images of ZnO/PVA nanocomposite films with different concentrations of ZnO nanoparticles (a) 1:1 (b) 2:1 (c) 5:1

In general the IR absorption bands of PVA are all quite broad and overlapped in the 600-1600 cm^{-1} region. In the spectra of pure PVA and ZnO/ PVA nanocomposites, the broad strong absorption band at ~ 3000- 3600 cm^{-1} is assigned to the stretching vibration of hydroxyl group (OH) [14].The FTIR spectrum of PVA shows the bands at about~2940, 1317, 1088, 940 and 845 cm^{-1} were attributed to the asymmetric -CH_2 stretching, C-O and CH_2 rocking vibration, C-C stretching vibration groups of PVA, respectively [15,16].

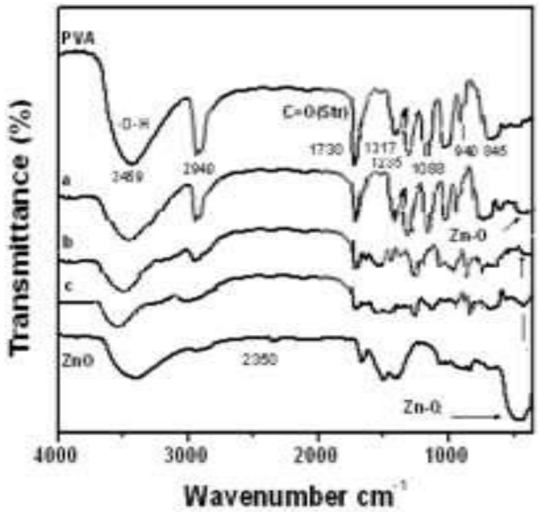

Fig. 4. FTIR spectra of ZnO nanoparticles, PVA and

ZnO/PVA nanocomposite films with different concentrations of ZnO nanoparticles(a) 1:1 (b) 2:1 (c) 5:1

As ZnO content in all nanocomposite samples increases the hydroxyl peak shifted from 3459 to 3515 cm^{-1}, which is due to the strengthening of hydrogen bonds present in ZnO and PVA matrix. Also, the C= O (str), band at ~1730 $c^{m-1,}$ in PVA shifted to higher wave number in ZnO/PVA nanocomposites of all the samples. The shifting of –CH_2 band at ~2940 cm_{-1} to ~2942, 2945 and 2950 cm^{-1} in the nanocomposites proved an interaction between zinc oxide and PVA matrix. The new absorption bands at ~464cm $^{-1}$ indicated the presence to Zn-O [17]. The above analysis indicated clearly the bonding nature between ZnO nanoparticles and the PVA matrix.

III. CONCLUSIONS

In the present work, zinc oxide nanoparticles were synthesized by simple chemical route. The ZnO/PVA nanocomposite flms were successfully prepared by solution casting method in different proportions and analyzed by various characterization techniques. XRD and FT-IR analyses demonstrate a strong interaction between zinc oxide nanoparticles and PVA matrix. XRD reveals the presence of nano ZnO with hexagonal wurtzite phase and PVA exhibited a typical semi-crystalline structure. The morphological investigation of all the nanocomposite samples was made with SEM technique. FT-IR spectra analyses confirmed the incorporation of ZnO nanoparticles in polyvinyl alcohol matrix. The changes in the optical properties due to the presence of nano ZnO was examined by UV-visible transmission spectra. The electrical, mechanical and barrier properties of such nanocomposites may be examined to find its aptness in various optoelectronic and electronic devices.

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