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Review Article

**POLY VINYL ALCOHOL (PVA) DOPED WITH ZnO ITS FTIR
AND X-RAY DIFFRACTION STUDY**

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Abstract:

Polymer composites of ZnO nanoparticles doped polyvinyl alcohol (PVA) matrix have been prepared using solvent casting method. The microstructural properties of prepared films were studied using FTIR, XRD. In the doped PVA, many irregular shifts in the FTIR spectra have been observed and these shifts in bands can be understood on the basis of intra/intermolecular hydrogen bonding with the adjacent OH group of PVA.

Keywords: ZnO, polyvinyl alcohol, FTIR, XRD.***Address for Correspondence:***

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INTRODUCTION:

The doping of nanoscopic organic or inorganic materials into polymeric matrices represents a strategic route to improve the performance of material characteristics like structural, physical, chemical, optical, electrical, and mechanical properties. These nano composites are of new class of materials made with nanosized fillers like metals, metal oxides, and so forth. Thus metal-polymer composites can be obtained by in situ and ex situ techniques [1-5]. In the in situ methods, metal particles are generated inside a polymer matrix by decomposition (e.g., thermolysis, photolysis, radiolysis, etc.) or chemical reduction of a metallic precursor dissolved into the polymer. In the ex situ approach, nanoparticles are first produced by soft-chemistry routes and then dispersed into polymeric matrices [6-7]. For the synthesis of metal-polymer composites the ex situ techniques are frequently preferred because of the high quality of the film.

Materials required:

Over the past decades, transition metal oxides (TMOs) have been widely investigated for use in applications related to electronic, optical, and mechanical properties. Among these, TMOs, zinc oxide (ZnO), and tungsten oxide (WO_3) are promising materials for the various above mentioned applications [8]. When these TMOs are incorporated in polymers, it improves their electrical, mechanical, and optical properties due to their high interfacial interaction between organic moieties and inorganic nanoparticles. The basic idea of this research is preparation of different concentrations of both zinc oxide (ZnO) doped PVA composite films and improving the structural and mechanical property of the PVA composite. The preparation of the nanoparticles doped polymer composite film can be done by many methods, out of which solution casting is the simplest technique. 97 to 100 mol% hydrolyzed PVA compound (Mowiol 10-98 fully hydrolysed grade, Sigma Aldrich, Germany) was procured commercially as a basic polymeric material. The procured PVA has molecular weight g/mol, degree of polymerization, and bulk density of 0.4–0.6 g cm^{-3} . For the doping purpose two metal-oxide nanomaterials, zinc oxide (average size < 50 nm, g/mol), and tungsten oxide (average size < 100 nm, g/mol), were also procured. 6 g of PVA is dissolved completely in 100 mL of distilled water under constant stirring at 1000 rpm for one hour while the mixture is heated up to 90°C until the polymer completely dissolved and formed a clear viscous solution. The viscous solution was cooled down to room temperature and stirring was continued using mechanical stirrer at 180 rpm for 3 hrs to

ensure the homogeneity of the composition. The obtained PVA solution was divided into six equal parts and each part of viscous solution of prepared PVA was treated by adding mixed fillers PVA/ ZnO where, 1%, 5%, 7.5%, 10%, 14%, and 15% weight concentration and then it was mixed ultrasonically by using probe ultrasonicator for 20 minutes with pulse on time 10 s and off time 10 s. To prepare polymer film of treated polymer, the viscous solution was cast onto a Petri dish and left to dry in air for 3 days at room temperature. The films were peeled off from the casting glass plate and kept in vacuum desiccators for further study. The thickness of the prepared polymer composite film is measured by using dial thickness gauge (Mitutoyo, Japan). Three trails of thickness were measured at different places of each polymer film and average thickness of the film was calculated. Thin films of thickness ranging from 100 to 150 μm were obtained.

FTIR Analysis

The FTIR spectra of pure and ZnO nanoparticles doped PVA samples were obtained using KBr pelleting method. The FTIR spectrum shows a strong absorption broad band at 3624.55 cm^{-1} is assigned to O–H stretching vibration of hydroxyl groups of PVA. The band corresponding to C–H asymmetric stretching vibration occurs at 2996.84 and 2920.66 cm^{-1} whereas C–H symmetric stretching vibration at 2878.24, 2850.27, and 2821.35 cm^{-1} . The sharp band at 1151.29 cm^{-1} corresponds to C–O stretching of acetyl group present on the PVA backbone. Corresponding bending deformation and wagging of CH_2 vibrations are at 1479.13 cm^{-1} and C–H wagging at 1221.68 cm^{-1} [9-10]. In the case of PVA doped ZnO, PVA doped with WO_3 , and PVA doped with both ZnO the FTIR spectra show shifts in the corresponding bands with a change in intensities. The changes in the regularly arranged hydroxyl groups of the polyvinyl alcohol chain are capable of forming chemically more or less stable complex compounds associated with certain substances. This indicates the considerable interaction between PVA doped with ZnO. The new bands may be correlated to the defects induced by charge transfer reaction between the polymer chain and the dopant. These observations suggest that the interaction between ZnO with acetyl group dominates (as given in figure 1). The shift in bending of CH_2 vibrations, respectively, indicates the chemical interactions of Zn and W ions with PVA matrix. The shift in acetyl C–O stretching of PVA also supports the existence of chemical interaction. This modification may be understood by invoking to the intra/intermolecular hydrogen bonding and complex formation of the PVA molecules with ZnO as shown in figure 1. It

also modifies the wagging, bending, skeletal, and out of plane vibrations. Further, the vibrational peaks found in the range $800\text{--}600\text{ cm}^{-1}$ can be attributed to Zn–O which indicates the mixed dopants are complexed with the polymer matrix. Hence, it can be concluded that the OH group of the PVA interact with Zn and W forms a complex. Due to this interaction and complex formation, the frequencies corresponding to other vibrations in PVA such as --CH_2 , --CH group, and C–O groups will be affected.

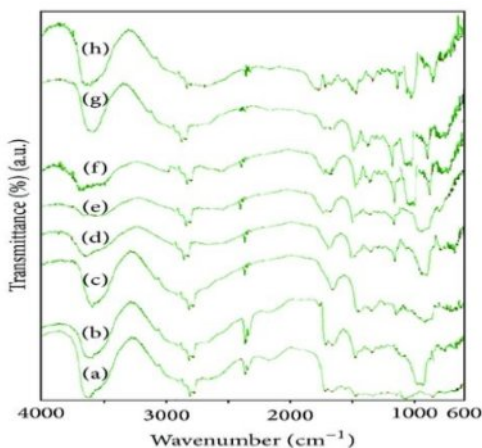


Fig1 FTIR study of ZnO doped of PVA at different concentrations

X-Ray diffraction Study:

The XRD studies in the range (to 120°) reveal that all the films under study show semi crystalline structure. There is a broad intense peak appearing at scattering angle corresponding to spacing of 4.57 \AA for PVA. The crystalline nature of PVA is due to the strong intermolecular interaction between PVA chains through intermolecular hydrogen bonding [11-13]. The crystalline peaks observed at, 34.39 , 36.93 , 48.49 , 57.66 , 64.23 , 67.67 , and 69.35 degrees correspond to the hexagonal phase of zinc oxide (ICSD Collection Code: 154490; JCPDS code: 36-1451, 89-7102, and 65-3411) and peaks at, 24.4 , 26.5 , 33.2 , 34.39 , 36.22 , 47.50 , 55.6 , 62.3 , and 66.9 degrees correspond to tungsten oxide (ICSD Collection Code: 836; JCPDS code: 05-0363 and 33-1387). The peaks at, 23.8 , 37.8 , 49.75 , 55.44 , and 62.51 degrees (ICSD Collection Code: 153197) do not belong to PVA crystalline spectra but it may arise from scattering atomic planes of some crystalline patterns of the PVA-ZnO complex. The intensity of the diffraction peak and also the size of the crystals in PVA are determined by the number of PVA chain packed together. After complexation with dopants, the intensity of the PVA diffraction peaks is further decreased. This may be due to the interaction between PVA and mixed dopants, which leads to

decrease in the intermolecular interaction between PVA chains. The diffraction pattern confirms the presence of ZnO in the film. The change in intensity of sharp peaks for different values of can be attributed to the change in the content of the mixed dopants when added to the PVA matrix [14-16]. The particle size of ZnO embedded in polymer matrix obtained for different dopants is in the same range of procured nanoparticles for doping with polymer matrixes shown in figure 2.

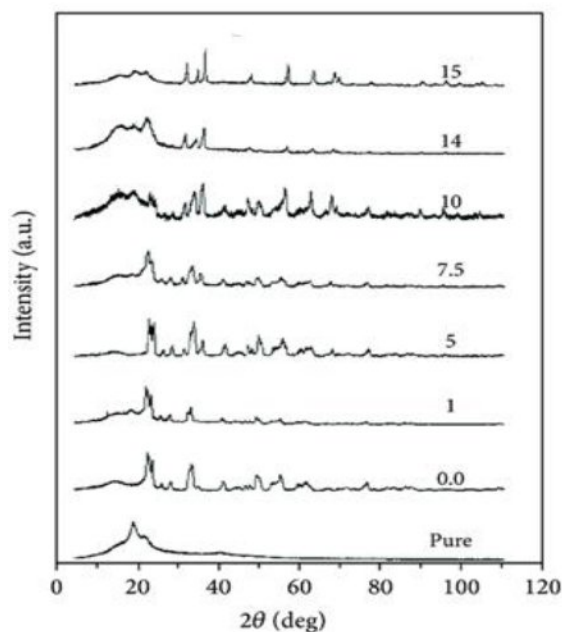


Fig 2 XRD Study of ZnO doped of PVA at different concentrations

CONCLUSION:

We have studied the effect of ZnO nanoparticles on the semi crystalline polymer PVA matrix allowed us to draw the following conclusions. (i) The FTIR study shows that the Zn ions of the dopant interacts with the OH groups of PVA and form a complex via intra/intermolecular hydrogen bonding. (ii) The XRD results show that, due to the interaction of dopant and hence the complex formation, the structural repositioning takes place, which changes the crystallinity.

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