



# Synthesis and Characterisation of Polyaniline-Polyvinyl Alcohol-NiO Nanocomposite Film

## KEYWORDS

IPN, PANI-PVA- NiO; composite film, XRD, SEM, IR.

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**ABSTRACT** The composites of interpenetrating polymer network (IPN) with oxide materials integrate the synthetic composites technology. The present work reports the synthesis and characterization of sequentially prepared interpenetrating polymer network (IPN) of polyaniline-polyvinyl alcohol-NiO nanocomposite film (PANI-PVA--NiO). This was prepared by the in situ polymerization of aniline in the PVA matrix using ammonium persulphate (APS) as an oxidizing agent. The thin film of the nano composite was obtained on 4x4 glass plate. The structure of as prepared composite was characterized by X-ray diffraction (XRD) tool, bonding by Fourier transform infrared spectroscopy (FTIR) tool, particle morphology of the said composite by scanning electron microscope (SEM). The ultraviolet absorption study was carried out for the uniformly formed interpenetrating polymer network of PANI-PVA-NiO composite.

**1. Introduction**

Combination of two Polymers network with crystalline materials constitutes Interpenetrating Polymer Networks (IPNs) composites [1]. New properties of IPNs viz. their very high mechanical strength, significant thermal stability, thermo sensitivity, limited solubility, volume phase transition etc. have attracted substantial interest and continue to be of interest in both fundamental and applied R & D investigations [2]. They have been utilized in wide spread commercial applications [3]. The first commercial application of the acrylic-isocyanate IPN has been in containers for the telecommunication equipments [4]. IPNs are considered promising in novel material development [5]. IPNs capability of forming tough but flexible materials enables its utilization for vibration and noise damping, natural products and renewable resources, ion exchange, formation of insoluble coatings, tough and impact resistant materials etc [6] and biomedical applications such as fabrication of artificial organs, controlled delivery of drug, solvent and other reactive species [7]. From a synthetic point of view, IPNs come in two varieties (i) a sequential IPN in which one network is swollen and another network is polymerized in the presence of it, and (ii) simultaneous IPN, in which both of the network precursors are synthesized at the same time by independent, non-interfering routes [8].

Conducting polymers have been the subject of continuous research and development due to their budding applications in various technological areas. Among the conducting polymers polyaniline (PANI) is one of the most promising conducting polymers due to its exotic properties, environmental stability, simple doping/ dedoping chemistry, price and ease of synthesis by different routes [9, 10]. Recently, conducting polymer-metal oxide nanoparticles composites have been considered as a new class of materials due to their improved properties such as solvent resistance, thermal stability, mechanical properties and decreased flammability when compared with those of pure conducting polymer and metal oxide [11-12]. Metal oxide nanoparticles dispersed polymer composites have been widely studied, since they exhibit interesting properties with many applications such as quantum electronic devices, sensors, capacitors, magnetic recording materials, smart windows, toners in photocopying, conducting paints, and rechargeable batteries [13-16]. Poly (vinyl alcohol) (PVA) being a biodegradable synthetic polymer, acquires special attention because of its high transpar-

ency, lustre, very good flexibility, anti-electrostatic properties, chemical resistance and wide commercial availability. Hence, the synthesis and characterization of PANI-PVA composites, blends, and IPNs were reported by earlier workers [17-18].

The present work reports the preparation and characterization of Nickel oxide nanoparticles dispersed PANI-PVA IPN composite film through sequential polymerization method. The composite has been thoroughly studied using different characterizations like spectral and morphological aspects.

**2. Experimental****2.1. Materials and methods**

All the chemicals and reagents used were of analytical grade. Aniline, benzene, hydrochloric acid and methanol supplied by SD Fine Chemicals Ltd. were used for the study. Polyvinyl alcohol (PVA) (Mol.Wt.125000) and ammonium persulphate (APS) were used from Qualigens Fine Chemicals. Water, benzene, methanol and aniline were double distilled before use as solvents and monomer in the work of the study. In situ polymerisation method was used for the preparation of the IPN composite.

**2.2. Synthesis of PANI-PVA IPN Composite**

2 % of aniline dissolved in 5ml of organic solvent ( $C_6H_6$ ) is polymerized in the 10 % aqueous solution of PVA by using aqueous acidic (HCl) solution of ammonium persulphate (APS) as an oxidizing agent, at room temperature. This resulted in the absorption of aniline monomer inside the cross linked PVA matrix forming an interpenetrating network (IPN). Aniline: APS ratio was maintained as 1: 2.5. Within few minutes after the addition of APS the solution becomes dark green colour indicating the beginning of the polymerization of aniline. The solution is then kept overnight so as to complete the polymerization process. The film of the nanocomposite was prepared by spreading measured amount of solution on 4x4 glass plates, and dried in air. Then the film was washed with 1:1 methanol/HCl mixture and was dried in vacuum at 50°C for 18 hours.

**2.3. Synthesis of PANI-PVA- NiO IPN Composite**

2 % of aniline dissolved in 5ml of organic solvent ( $C_6H_6$ ) is polymerized in the 10 % aqueous solution of PVA in the presence of known weight of NiO by using aqueous acidic (HCl) solution of ammonium persulphate (APS) as an oxidiz-

ing agent, at room temperature. This resulted in the absorption of aniline monomer and NiO nanoparticles inside the cross linked PVA matrix forming an interpenetrating network (IPN). Aniline: APS ratio was maintained as 1: 2.5. Within few minutes after the addition of APS the solution becomes dark green colour indicating beginning of the polymerization of aniline. The solution is then kept overnight so as to complete the polymerization process. The film of the nanocomposite was prepared by spreading measured amount of solution on 4x4 glass plates, and dried in air. Then the film was washed with 1:1 methanol/HCl mixture and was dried in vacuum at 50°C for 18 hours.

#### 2.4. Characterizations

The Fourier transform infrared (FTIR) spectra of the thin films of PANI-PVA-NiO IPN were recorded on a Nicolet iS5 model (Thermo fisher Scientific, USA) with Diamond ATR spectrometer in the range 4000-500  $\text{cm}^{-1}$ . The powder X-ray diffraction (XRD) patterns of the sample were recorded on Ultima IV X-ray diffractometer using Cu K radiation (1.54  $\text{\AA}$ ) at 40 kV and 30 mA. The scanning electron microscope images of thin films were taken on a Leica Instrument (Model No. 440) operating at 20 kV. The UV-Visible absorption spectrophotometric characterization of PANI-PVA-NiO IPN composite film was carried out over the wave length range of 200-1000 nm using double beam UV-Visible spectrophotometer-UV5704SS (Electronics Corporation of India Limited).

### 3. Results and discussion

#### 3.1. FTIR spectra

Figure 1 shows the FTIR spectra of PANI-PVA-NiO IPN composite film. The observation of some peaks below 1000  $\text{cm}^{-1}$  are observed due to the presence of dispersed nickel oxide material. The very strong broad band at 3296  $\text{cm}^{-1}$  is attributed to O – H stretching vibrations of PVA due to the strong hydrogen bonding of intramolecular and intermolecular type [19]. The peak at 2900  $\text{cm}^{-1}$  is due to the stretching vibrations of the methylene (– CH<sub>2</sub> –) group. The high frequency stretching vibration bands around 1600 and 1400  $\text{cm}^{-1}$  are due to the presence of the quinoid and the benzenoid ring of PANI respectively [20]. The intense peak around 1300  $\text{cm}^{-1}$  in the spectrum corresponds to the C–N stretching vibrations of a secondary aromatic amine [24]. A very strong and sharp peak around 1100  $\text{cm}^{-1}$  has been assigned to the B – NH<sup>+</sup> = Q vibration, indicating that the PANI is conductive and is in the form of emeraldine salt [22]. The intense peak around 1100  $\text{cm}^{-1}$  is due to C – O stretching vibrations of PVA component. While N-H stretching vibration band of PANI at 3000  $\text{cm}^{-1}$  overlaps with O – H stretching vibrations of PVA and hence cannot be separately assigned. The presence of bands at 1002, 689, 652, and 582  $\text{cm}^{-1}$ . The absorption bands below 1000  $\text{cm}^{-1}$  corresponds to the bending modes of Ni–O–H and metal–oxygen (Ni–O) vibrational modes of the dispersed metal oxide particles respectively. The intensity of the bands is reduced due to the presence of polymer components in the composite film. The results confirms the formation of PANI-PVA-NiO (IPN) composite film.

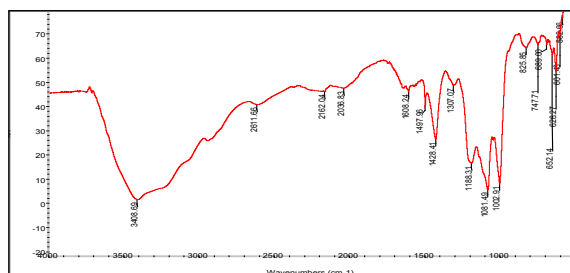


Figure 1: FTIR spectrum of as prepared PANI-PVA-NiO composite film

#### 3.2. X-ray diffraction (XRD) studies

Figure 2 shows XRD patterns of as prepared PANI-PVA-NiO nanocomposite film. The pattern is not showing any sharp peaks which indicates the masking PANI peak at  $2\theta = 25.3^\circ$ . However, after addition of NiO nanoparticles into the PANI-PVA network high intensity peaks were masked due to overwhelming amorphous nature of polymer components, thereby masking the sharp peaks due to the crystalline nature of NiO nanoparticles. This also confirms the uniform molecular level dispersion of NiO nanoparticles into polymer matrix, which is responsible for the decrease in crystallinity of NiO nanoparticles upon dispersion into the PANI-PVA network.

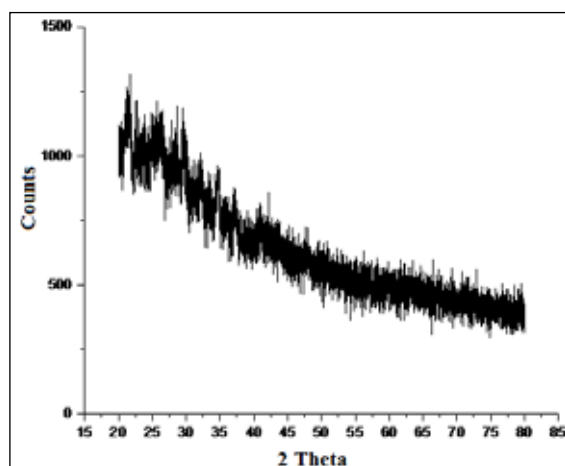


Figure 2: XRD Pattern of PANI-PVA-NiO

#### 3.3. Scanning Electron Microscopy (SEM)

SEM images of the PANI-PVA-NiO nanocomposite film at low and high resolution are shown in figure 3(a-b). The image show the amorphous film containing crystalline NiO particle. Due to masking of particles in the polymer matrix, the cluster of the close netting is observed. Particles with different shape in the polymer matrix is reduced the crystallinity of the composite is observed by the formation of amorphous sheet like structure is viewed. However at high resolution (Fig.3b) surface morphology of the film depicts that these particles due to strong inter-particle interaction are closely packed to form the clusters.

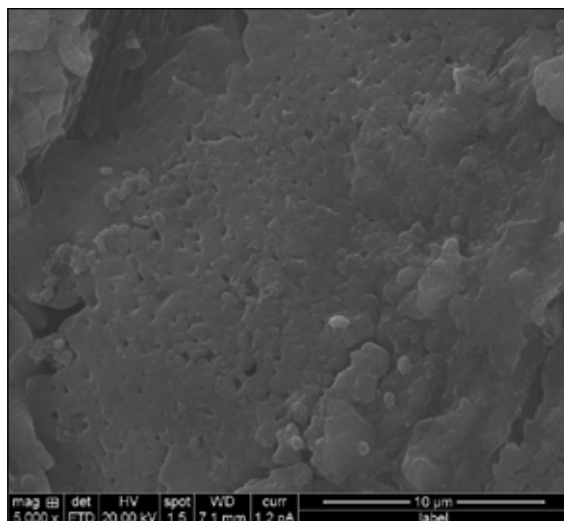


Figure 3(a): SEM image of PANI-PVA-NiO composite film

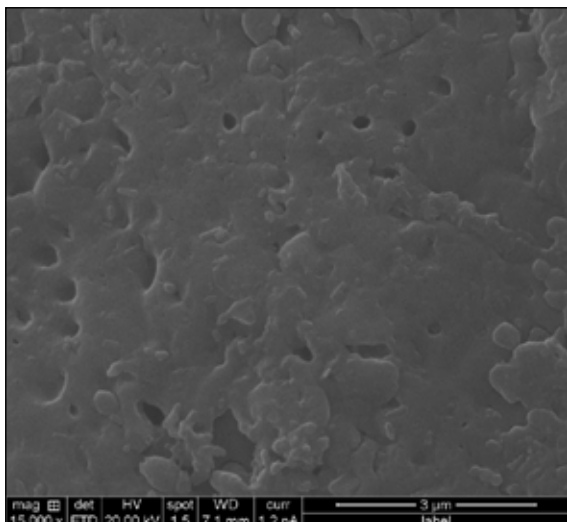


Figure 3(b): SEM image of PANI-PVA-NiO composite film

### Conclusions

The single step synthesis of PANI-PVA-NiO (IPN) nanocomposite was achieved successfully at room temperature by the in-situ polymerization of aniline in the PVA matrix in the presence of NiO nanoparticles. Surface morphology of the film depicts that the nickel oxide nanoparticles are uniformly dispersed in the polymer matrix which was supported by XRD studies. The FTIR spectra confirm the formation of PANI-PVA-NiO (IPN) nanocomposite. This method may be also adopted for the synthesis of some other IPNs.

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