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Synthesis and characterization of γ-Fe_2O_3 functionalized polyaniline - PVA nanocomposite film

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- **Novelty and Highlights:**

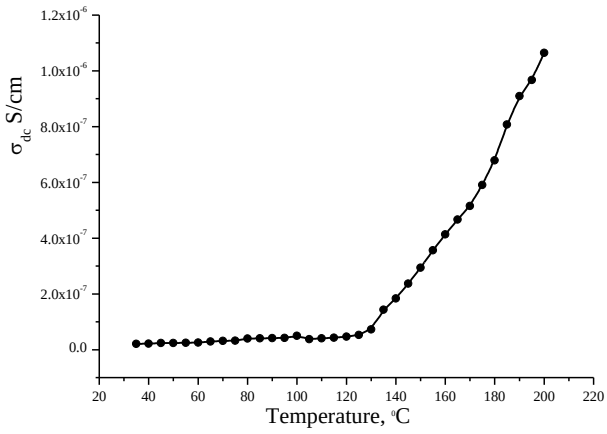
1 – The γ-Fe_2O_3 dispersed functionalized polyaniline -PVA nanocomposites (FPNC) film, is a stable interpenetrating polymer network (IPN)

2 – The molecular structure of the dopants used affects the electrical properties of the conducting polymers

3 – The combination of two polymer network with crystalline materials constitutes interpenetrating polymer networks (IPN) increases its mechanical strength.

- **Graphical Abstract:**

The DC conductivity of the FPNC film at room temperature increases the conductivity value comparable more than the other pure polyaniline. The conductivity of our sample is increased with rise in the temperature due to the addition ferrite γ-Fe_2O_3 nanoparticles.



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Synthesis and characterization of γ-Fe_2O_3 functionalized polyaniline - PVA nanocomposite film

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Abstract

Polymer nanocomposites have been studied change in their physical and chemical behaviour when doped with nanoparticles. They are used in electrical, optical, electrochemical devises, sensors and other biomedical applications. γ-Fe_2O_3 nanoparticles dispersed polyaniline - Polyvinyl alcohol (PVA) nanocomposites have increased attention due to its applications for making capacitors and sensors. In the present work we synthesized γ-Fe_2O_3 dispersed functionalized polyaniline -PVA nanocomposites (FPNC) film, an interpenetrating polymer network (IPN) through in situ doping polymerization in the presence of HCl as a dopant. The synthesized FPNC film were characterized, employing powder XRD through X-ray diffractometer, molecular structure through FT-IR spectroscopy, thermal (TGA/DSC) study by thermal analyzer, surface morphology is studied using SEM and DC conductivity measured employing four probe Keithely high precision multimeter. All the characterizations confirmed the obtained FPNC film is a stable interpenetrating polymer network. The synthesized film FPNC envisioned for capacitors and sensors.

Keywords: *Polyaniline, Polyvinyl alcohol, γ-Fe_2O_3, nanocomposite.*

Introduction

The unique behaviours of conducting polymer nanocomposites with inorganic nanoparticles have been used for various electrical and electronic devices [1]. Conducting polymers in the form of molecular wires have received more attention in the field of nanotechnology due to its similarity in metal like conductivity [2]. Multi functionality of nano structured conducting polymer is very essential in nanotechnological applications. The electromagnetic functionality of nanostructured conducting polymer has increased attention due to its optical, electromagnetic interference shielding, and making the electro-chromic devices [3-4]. It is reported the molecular structure of the dopant used affects the electrical properties of the conducting polymers. Conductivity of PANI nanotubes doped with inorganic acids (e.g. HCl, H_2SO_4, H_3PO_4 and HBF_4) could be achieved as high as 10^{-1}- 10^{o} S Cm^{-1}[5-6]. The general approach to tailor the surface property of the particles for many applications can be achieved by fictionalizations [7]. The combination of two polymer network with crystalline materials constitute interpenetrating polymer networks (IPN) composites and its high mechanical strength significant thermal stability limited solubility attracted substantial interests in fundamental and applied research [8]. From the synthetic point of view the IPN can be in two varieties first a sequential IPN in which one network is swollen and another one is polymerized in the presence of it, whereas second is a simultaneous IPN in which both of the network precursors are synthesized at the same time through independent and non-interfering routes [9]. In views of the above said applications the aims of this work to synthesize γ-Fe_2O_3 dispersed polyaniline PVA nanocomposite (FPNC) film an interpenetrating polymer network (IPN) through in situ doping polymerization method and have been thoroughly studied employing characterization techniques.

Experimental

Synthesis of γ-Fe_2O_3 dispersed functionalized polyaniline-PVA nanocomposite (FPNC) film.

γ-Fe_2O_3 nanoparticles were synthesized by combustion method as reported earlier [10]. Aniline, ammonium persulphate (APS), benzene, hydrochloric acid (HCl), polyvinyl alcohol (PVA) and methanol was commercially procured from SD fine chemicals Ltd. In situ doping polymerization method is adopted for the synthesis in the presence of HCl as dopant, solvent were double distilled before use. The synthesis process as follows. 2% of aniline monomer dissolved in 5 ml of benzene is polymerized in the 10% aqueous solution of PVA in the presence of known weight of γ-Fe_2O_3 nanoparticles by using aqueous acidic HCl solution as dopant and ammonium persulphate as an oxidizing agent at room temperature. This resulted in the

absorption of aniline monomer and γ-Fe_2O_3 nanoparticles within the crossed linked PVA matrix forming an interpenetrating polymer network (IPN) within a few minutes after the addition of APS the solution becomes dark green colour indicating the beginning of polymerization. The solution is then kept for overnight for complete polymerization. The FPNC film was prepared by casting method by spreading the final solution on the glass substrate and dried in air, then the film was washed with methanol and dried. Further the film was thoroughly studied employing characterization technique using powder XRD, spectroscopy, thermal, morphology, and electrical conductivity.

Characterization techniques

XRD pattern obtained with Regaku Ultima IV X-ray diffractrometer using Cu k radiation (= 1.5405 A^o) at 20 kV. The FTIR Studies was undertaken employing Thermo Fisher ATR Nicolet model using diamond (iS5) in the range 4000-400cm^{-1}.Thermal Studies were carried out employing Linseis STA PT1600 Thermal Analyser under nitrogen atmosphere with a heating rate of 10^oC/minute at a flow rate of 100 ml/min and temperature up to 600^o C. The Scanning Electron Microscopy (SEM) images of the sample were obtained on a Leica 440 Cambridge steroscan operated at 20 kV. The D.C. conductivity measurement was carried out employing four probe method using a Keithely high precision multimeter. The1 sq.cm film with thickness of 0.4 micron was used for the measurement.

Results and discussion

Powder X-ray diffraction (XRD) studies. Figure 1 shows the powder XRD pattern of γ-Fe_2O_3 dispersed functionalized polyaniline -PVA nanocomposites (FPNC) film. The pattern showing semi sharp peak at 2Θ = 33.5^o due to the crystalline nature of γ-Fe_2O_3 which conforms the uniform molecular level distribution of γ-Fe_2O_3. The masking of many peaks due to the amorphous nature of interpenetrating polymer network on the surface of γ-Fe_2O_3 decreased in the crystallinity confirms the functionalization of γ-Fe_2O_3 nanoparticles with IPN.

FTIR studies. The FTIR spectrum of FPNC film is shown in figure 2 indicates the spectrum's major peaks are associated with polyaniline. The band observed at 3247cm^{-1} due to the O-H strong stretching of the PVA. The high frequency bands 1509cm^{-1} and 1416cm^{-1} are due to the presence of benzenoid ring and quinoid ring respectively. A peak 1026cm^{-1} due to the B – NH^+ = Q vibration indicating the PANI conductive [11]. The peak at 876 cm^{-1} is due to $\upsilon_{\text{-C-H}}$ bending. The bands 574cm^{-1} to 527cm^{-1} were due to γ-Fe_2O_3 ferrite [12]. The instrumental limitation did not allow the more peaks to be clearly shown. The peaks position of FPNC film clearly indicates the formation of IPN. This observation also collaborates from SEM image.

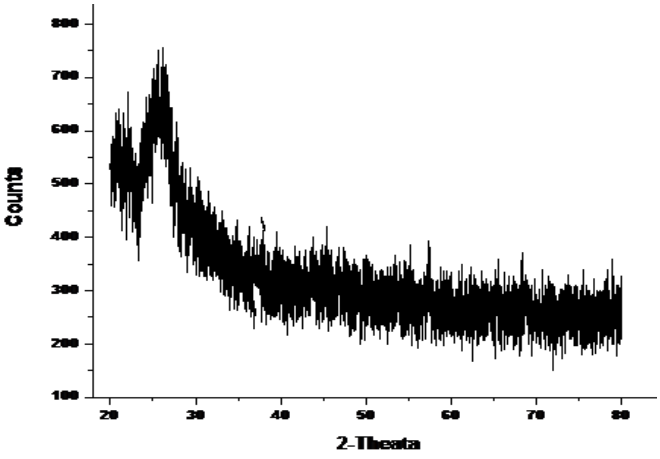

Figure 1 Shows the XRD pattern of FPNC film

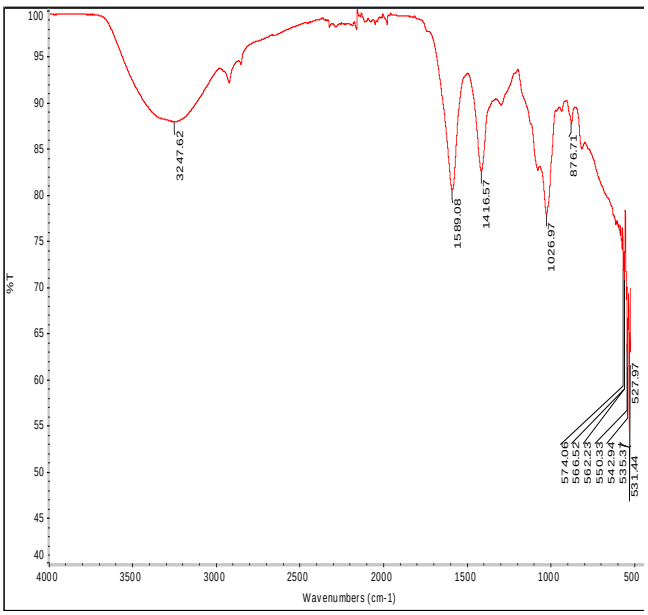

Figure 2 Shows the FTIR spectrum of FPNC film

Thermal analysis studies. In thermal studies thermo gravimetric analysis (TGA) and differential scanning calorimetric (DSC) of FPNC film were undertaken. Figure 3 a, b shows TGA and DSC traces respectively. The TGA trace shows a two-step mass loss. The first mass loss of 9% was observed from 60^o C to 111^o C due to O-H molecules present in the PVA. The second mass loss of 69 % occurs in the range of 289^o C to 600^o C decomposition of polyaniline-PVA binding leaving behind a residual of γ-Fe_2O_3. The figure 3b) shows two endothermic peaks with multi shoulders from 60^{o}C to 489^{o}C slow decomposition of polyaniline PVA due to IPN. The DSC traces shown in figure 3b collaborates to TGA traces shown in figure 3a.

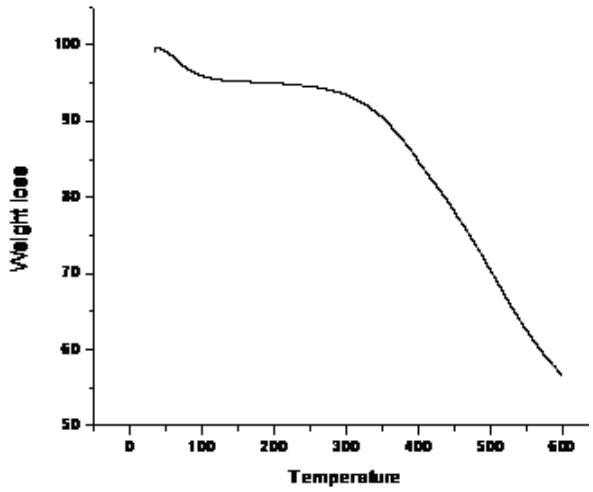

Figure 3 a. shows TGA of FPNC film.

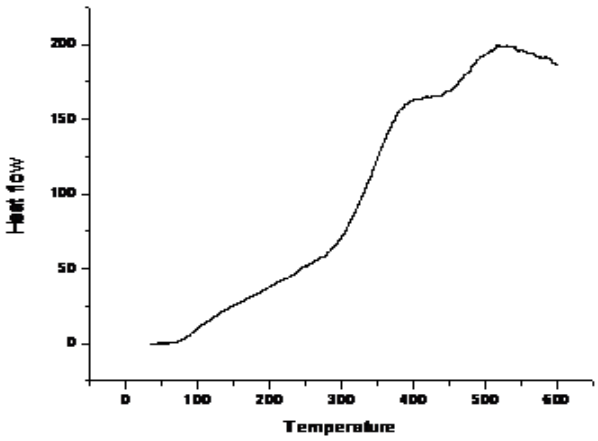

Figure 3b shows DSC of FPNC film.

Scanning Electron Microscopy (SEM). The figure 4 shows the SEM images of FPNC film form a uniform distribution of γ-Fe_2O_3 nanoparticles as clusters of flakes within the polymer matrix. However some smooth surface solid block observed it may be due to much closed packing of γ-Fe_2O_3 nanoparticles in the polyaniline PVA IPN. The SEM image suggests the closer association of unique chemical homogeneity of the film.

Electrical conductivity. Figure 4 shows the DC conductivity of the FPNC film. The room temperature conductivity value is in the order of 2.0 x10^{-7} S/cm. comparable more than the other pure polyaniline film from the literatures. The conductivity of our sample is increased with rise in the temperature due to the addition ferrate nature of γ-Fe_2O_3 nanoparticles in the IPN matrix.

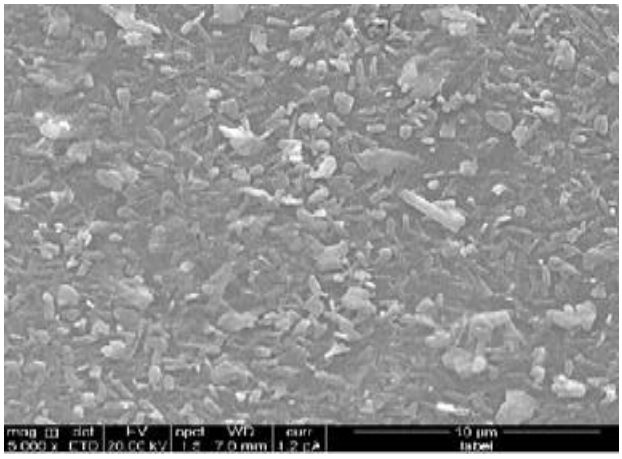

Figure 3 shows SEM image of FPNC film

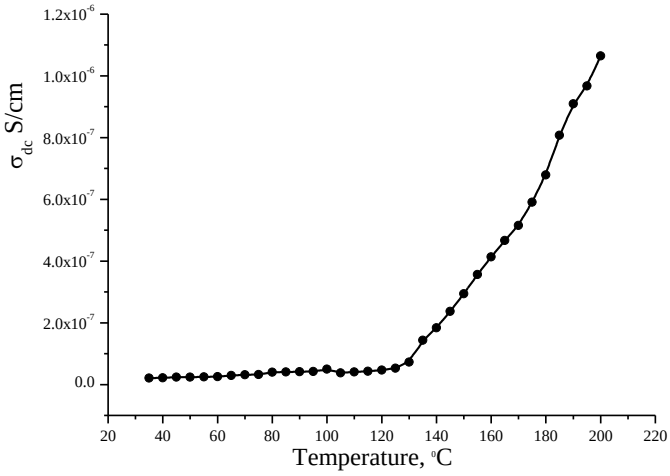

Figure 4 shows the DC conductivity measurement of FPNC film.

Conclusions

We have obtained the stable FPNC film an interpenetrating polymer network (IPN). The powder XRD pattern showed the semi crystalline peaks γ-Fe_2O_3 and confirms the functionalization within the polymer matrix. The FTIR spectroscopy showed several vibration bands at various wave numbers, several bands disappeared in the IR spectra due to IPN formation of polyaniline and PVA it also collaborates with SEM image which observed smooth surface due to chemical homogeneity and uniform distribution of γ-Fe_2O_3 nanoparticles within the polymer matrix. The increases in thermal (TGA/DSC) stability of FPNC film are also confirm the IPN formation. The change in the conductivity of film indicates a change in doping state of polymer due to incorporation of γ-Fe_2O_3 nanoparticles in the polymer matrix. The obtained film envisioned for making capacitors and sensors.

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