Chapter - V

6. Summary and Conclusions

The intrinsic polymers composites are one of the important class of semiconducting materials for industries revolutions. In last few decades, researchers have shown that conjugated polymer composites exhibit conductivities varying from semi-conducting to metallic regime due to the delocalization of \( \pi \) – electron in benzene ring of the conducting polymer back bone. The physical properties like magnetic, electrical and thermal can be tuned by adding small amount to organic or inorganic materials.

The important out come of the present work is summarized as follows:

- We reported that the synthesis of polyaniline and its composites i.e. polyaniline – \( \text{ZnFe}_2\text{O}_4 \) composites and PANI / \( \text{NiFe}_2\text{O}_4 \) of various weight percentages prepared by oxidation polymerization technique using oxidant.
- To prepare these composites different surfactants are used which avoids the agglomeration and form individual grain with smooth interface as a results increment in the conductivity is observed. Also the synthesis conduction in presence of surfactant leads two dimensional nucleation growth to form cave like structure which helps in conduction mechanism of these composites.
- PANI/\( \text{ZnFe}_2\text{O}_4 \) nanocomposites were prepared by an interfacial polymerization method with different weight percentage of \( \text{ZnFe}_2\text{O}_4 \) (10, 30 & 50 wt %).
Five different polyaniline - NiFe$_2$O$_4$ composites with different weight percentage of nickel ferrite (5, 10, 15, 20 and 25) in polyaniline have been synthesized by chemical oxidation method.

Through various characterization techniques like XRD, FTIR and SEM were employed on these composites, it is noticed that;

- The X-ray diffraction (XRD) pattern shows the amorphous nature of polyaniline. It is found that the crystal structure of the metal oxide remains same even after blending with polymer matrix.
- XRD pattern of ZnFe$_2$O$_4$ nanoparticles. The peaks at 2θ values of 18.3, 29.99, 35.40, 36.90, 43.01, 53.86, 57.01 and 62.42 which corresponds to (111), (220), (311), (222), (400), (422), (511) and (440) crystal planes of cubic ZnFe$_2$O$_4$ with spinel structure.
- The pure polyaniline shows a broad peak at 2θ = 26.4° which is a characteristic amorphous peak of pure PANI synthesized by chemical oxidative polymerization.
- The average crystalline size of the ZnFe$_2$O$_4$ nanoparticles was determined by Scherrer’s formula and found to be 32 nm. The XRD patterns of the PANI/ZnFe$_2$O$_4$ (10 & 30 wt %) nanocomposites.
- The XRD patterns exhibit both the characteristic peaks of ZnFe$_2$O$_4$ and the broad diffraction peaks of PANI. These results confirm the formation of PANI/ZnFe$_2$O$_4$ nanocomposites.
- XRD pattern of nickel ferrite (NF) shows all the peaks corresponds to spinel ferrite phase matches well. The average crystallite size of the NiFe$_2$O$_4$ was found to be 14 nm.
- XRD pattern of PANI/NiFe$_2$O$_4$ composites shows diffraction peaks as superposition of those of polyaniline and nickel ferrite nanoparticles, indicating the formation of PANI/NiFe$_2$O$_4$ nanocomposites.
- It is observed that ZnFe$_2$O$_4$ and NiFe$_2$O$_4$ have retained its structure even though it is dispersed in PANI after polymerization reaction.
- The characteristic peaks of PANI occur at 1564 and 1468 cm$^{-1}$ are attributed the characteristic C=C stretching of the quinoid and benzenoid rings, the peaks at 1301 and 1244 cm$^{-1}$ are
assigned to C-N stretching of the benzenoid ring, the peak at 1137 cm\(^{-1}\) which is considered to be the measure of degree of electron delocalization and 808 cm\(^{-1}\) corresponds to the N-H out of plane bending in rocking mode.

FTIR spectra of ZnFe\(_2\)O\(_4\) nanoparticles. The main peaks 555 cm\(^{-1}\) is due to intrinsic stretching vibrations of the metal at the tetrahedral site and 464 cm\(^{-1}\) is due to octahedral-metal stretching vibrations.

FTIR spectra of PANI/ZnFe\(_2\)O\(_4\) (10, 30 & 50wt \%) nanocomposites respectively. The peaks of the composites shift to lower wave numbers. This indicates that there is some interaction between ZnFe\(_2\)O\(_4\) nanoparticles and PANI backbone.

The transmittance bands \(\nu_1\) and \(\nu_2\) around 611.12 cm\(^{-1}\) and 465.90 cm\(^{-1}\) in NiFe\(_2\)O\(_4\) are attributed to the stretching vibration of tetrahedral and octahedral group complexes of ferrites, respectively.

The bands at 1578.39 and 1487.89 cm\(^{-1}\) in pure PANI are the characteristics bands of nitrogen quinoid and benzoid forms due to the conducting state of the polymer.

In PANI/NiFe\(_2\)O\(_4\) nanocomposites, there are characteristic bands of NiFe\(_2\)O\(_4\) located around 600 cm\(^{-1}\) and 400 cm\(^{-1}\), indicating the well wrapping of NiFe\(_2\)O\(_4\) nanoparticles with PANI in the PANI/NiFe\(_2\)O\(_4\) composites. The interaction of nickel ferrite with polyaniline is confirmed from IR spectra of the nanocomposites.

By careful observation of FTIR spectra, it was found that the peaks have been considerably shifted towards lower frequency side for all samples of PANI- ZnFe\(_2\)O\(_4\) nanocomposites and PANI- NiFe\(_2\)O\(_4\) composites. The above mentioned peaks at corresponding stretching frequencies confirm the formation of composites and also suggest a Van der waal’s kind of interaction between the polymeric chain and ferrite particles.

The SEM micrograph of the PANI indicates the big globular agglomerates with smooth surface. Scanning electron microscope (SEM) was employed to visualize the shape and size to confirm the nanocrystalline nature of the ZnFe2O4.
SEM image of PANI-ZnFe$_2$O$_4$ nanocomposites and found that the grains are well interconnected, which will improve the transport property.

Pure Nickel ferrite prepared by citrate method and it is observed that the particles are spherical in shape, well interconnected to each other. The average size of the particles is calculated by using liner intercept method and its size were found to be 800 nm.

The polyaniline image shows the opal tube like morphology with the size of 1 µm. It is noticed that the polyaniline grows on the surface of ferrite in unidirectional form small rod like structure.

Following conclusions are drawn from the studies made on various electrical properties in case of polyaniline and its composites.

- Both dc and ac conductivity was carried for polyaniline and its composites by two probe method using Keithley meter and LCR Q meter.
- DC conductivity study shows that charge carries are polarons and bipolorans. The conductivity of polyaniline and its composites due to hopping of charge carriers and extended chain length of polymer.
- Further the three steps dc conductivity studies supports the one dimensional Variable Range Hopping (VRH) model proposed by Mott.
- It is observed that the conductivity of all weight percentages of PANI/ZnFe$_2$O$_4$ nanocomposites increases with increase in temperature. The three steps of conductivity were observed in these characteristics of semiconducting materials.
- 30 wt % of ZnFe$_2$O$_4$ doped PANI nanocomposites show high conductivity of 0.025 S/cm. This may be due to the decrease in distance between the entangled polymer chains and ZnFe$_2$O$_4$ nanoparticles, which combined with high activation energy of 2.91 eV, makes easy the hopping of the polarons from one site to another.
15 weight percentage of polyaniline – NiFe₂O₄ composite show high conductivity of 0.02 S/cm due to the elongation of polymer chain in framed network favorable of hooping polarons in long range orders.

Dielectric studies show that the conductivity of all three sets of composites is due to polarization processes. In all composites a multipule polarizations are observed and it is the characteristics of amorphous semiconducting materials.

In permittivity graph, it is observed that, in all these composites the dielectric constant is high at low frequencies and also the value is high for higher weight percentage of ZnFe₂O₄ and NiFe₂O₄ in polymer matrix.

Among all the composites, 30 wt. % showed a high conductivity of 0.08 S/cm, which is due to its low electrical resistance and low dielectric constant value. Above 30 wt. % loadings, all other compositions showed lower conductivity due to predominant dipole polarization which increases the value of dielectric constant.

15 wt. % composite shows a maximum conductivity of about 1.2 x 10⁻² S/cm due to low dielectric constant and impedance value of composite. The conductivity for this particular composite was improved due to excellent interaction between PANI and NiFe₂O₄ components.

The conductivity of all composites increases with increase in weight percentage of metal oxide as well as applied frequency due to the increase in the more free charges at higher frequency which reduce the grain resistance and bulk resistance of the composites.

High values of permittivity at lower frequency range are due to maximum accumulated charge carriers at the interface of grain boundaries. The strong frequency dispersion of permittivity is observed in the low frequency region followed by a nearly frequency independent behaviour above 10³ Hz.

Both ε' and ε'' exhibit strong dispersion towards low frequency side which is mainly due to accumulation of charge carriers at the interface between the sample and the electrodes resulting in space charge polarization along with non-negligible ionic conductivity.

The interaction between PANI chains and surface of ZnFe₂O₄ restricts the motion of dipoles which leads to decrease of ε' at higher frequencies. Among all composites it is observed that 30
wt% of PANI – ZnFe$_2$O$_4$ composite show low relative permittivity value of 5000 compared to other composites. Therefore these materials can be used as low dielectric materials, capacitor and other electronic applications.

- 15 wt. % of NiFe$_2$O$_4$ in PANI. It has been observed that the values of $\varepsilon'$ increases with the level of doping of NiFe$_2$O$_4$ in PANI in the lower frequency side and gradually decreases with increase in frequency and almost remains independent of the frequency beyond $10^3$ Hz.

- Three different processes occur is observed in the multiphase composite system: association of charge carriers, dielectric dispersion because of different dipole rotation and the presence of both dielectric dispersion as well as charge carriers union within measured frequency range.

### 6.1. Possible Applications

- On the basis of results of DC and AC conductivity properties, so obtained in polyaniline – ZnFe$_2$O$_4$ composites and they can be used as humidity and LPG gas sensors as surface has more porosity.

- Polyaniline – NiFe$_2$O$_4$ composites can be used in electrode in microbe identification, low k- dielectric materials, microwave absorbing materials and also in the fabrication of capacitors in high electric circuits, inorganic nanoparticle stabilization, Photoluminescence, Photonic application, EMI packaging, Li-ion batteries and actuator.

### 6.3. Scope of future work

We believe that this work could also help in future studies devoted to conducting substituted polyaniline. The improvement of the processability of substituted polyaniline with enhancing the conductivity and stability to prepare their nanocomposites will be topic for future investigations. This processable form of ortho chloropolyaniline and its organic doped polymers could be widely applicable to coatings, to making thin films, preparation of clay composites and solution blending with
other commodity polymers. Still much research work is necessary to understand the chemistry of the
structure of monomer, morphology of polymer to relate with the properties to get good solubility,
better conductivity and thermal stability. We believe that conducting nanocomposite polymers and
materials will play important roles in intelligent materials science in the near future.