CHAPTER-VI

SUMMARY AND CONCLUSIONS

6.0 Summary and Conclusions

The advent of conducting polymers represents one of the important industrial revolutions of the current century. For more than a decade now, researchers have shown that certain class of polymers which are conjugated (those possess extended $\pi$ – conjugation along their polymer backbone) exhibit conductivities varying from semi-conducting to metallic regime. An important fundamental property, i.e., electrical conductivity distinguishes polymers from metals. Polymers possessing high electrical conductivity are also referred as synthetic metals or conducting polymers offer lot of advantages over the metals. These newly developed materials will not only replace metals in many areas, but also infiltrated our day-to-day life with a wide range of products extending from most common consumer goods like batteries to highly specialized applications in space and aeronautics.

Among conducting polymers, polyaniline family has attracted much attention of scientists world-wide because of their ease of synthesis, unique conduction mechanism, high environmental stability in the presence of oxygen and water, low cost, light weight and good sensing capability. They also exhibit highly reversible redox behavior, which is very important for many applications.

Extensive literature review suggests that the considerable efforts have been made by researchers all over the world in improving the conductivity of polyaniline by various doping techniques, but little is known about the dielectric properties of conducting polymers associated with conduction mechanism. It has also been noted
Summary and Conclusions....

through literature survey that the studies on dielectric and sensing properties of polyaniline composites is scarce.

To suggest any material to be used as a potential candidate for technological applications, it is essential for researchers to undertake basic studies governing electrical and sensing properties of such materials. Hence through this work author has made an attempt to tailor the electric and sensing properties of polyaniline by selecting appropriate materials as composites with polyaniline.

The important outcome of the present work is summarized as follows:

1) In this present study, the author has synthesized successfully the conducting polymer, Polyaniline and its composites i.e. PANI / ZnFe$_2$O$_4$, PANI / NiZnO$_3$ and PANI / CuO in 10, 20, 30, 40 and 50 weight percentages.

2) Through various characterization techniques employed on these composites, it is noticed that;

2.1) X-ray diffraction pattern of polyaniline shows the presence of amorphous nature in polyaniline and a well ordered crystallinity in polyaniline composites. The chain separation are calculated using the relation $R = 5/8(\lambda/\sin \theta)$. The various values obtained are tabulated:

<table>
<thead>
<tr>
<th>Dopant (Primary /Secondary)</th>
<th>$2\theta$</th>
<th>Inter Chain separation ($A^0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>25.40</td>
<td>2.24</td>
</tr>
<tr>
<td>ZnFe$_2$O$_4$</td>
<td>34.34</td>
<td>1.706</td>
</tr>
<tr>
<td>NiZnO$_3$</td>
<td>28.66</td>
<td>2.007</td>
</tr>
<tr>
<td>CuO</td>
<td>25.25</td>
<td>2.207</td>
</tr>
</tbody>
</table>
Summary and Conclusions....

It is found that as the diffracting angle increases the inter chain separation decreases.

2.2) IR spectra confirms the homogeneous mixing of ZnFe$_2$O$_4$, NiZnO$_3$ and CuO in polyaniline, formation of new composites whose properties does not resembles either polyaniline or the individual materials used for preparation of composites. The characteristic stretching frequencies are shifted towards higher frequency side which indicates the homogeneous distribution of ZnFe$_2$O$_4$, NiZnO$_3$ and CuO particles in the polymeric chain. Further it confirms the Vander walls force of attraction between ZnFe$_2$O$_4$, NiZnO$_3$ and CuO with polymeric chain.

The FTIR spectra of pure PANI gives important characteristic peaks at 1566 cm$^{-1}$ corresponds to C = C stretching vibration of quinoid ring, 1548 cm$^{-1}$ for C=N bond stretching, 1494 cm$^{-1}$ corresponds to stretching vibration of benzenoid ring, 1406 cm$^{-1}$ is the characteristic vibration mode of C - H bonding of aromatic nuclei, 1302 cm$^{-1}$ assigned to the stretching of C-N bonds of aromatic amines, 1140 cm$^{-1}$ an strong band which considered to be the measure of degree of electron delocalization, 796 cm$^{-1}$ corresponding to the N-H out of plane bending in rocking mode respectively.

The FTIR spectra of polyaniline/ZnFe$_2$O$_4$ composites at different percentages shows the absorption peaks at 3441 is correspond for N-H stretching vibration, 1581 cm$^{-1}$ is corresponds to C = C stretching vibration of quiniod ring, 1481 cm$^{-1}$ is corresponds to stretching vibration of benzenoid ring, 1300 cm$^{-1}$ is for the stretching of C-N bonds of aromatic amines, 240 cm$^{-1}$ for the C-N stretching of benzenoid ring, 1140 to 1145 cm$^{-1}$ is correspond to C-H in plane of aromatic rings is found to be an
Summary and Conclusions....

strong band which considered to be measure of the degree of electron delocalization, and other bands like 802 cm$^{-1}$, 738 cm$^{-1}$, and 686 cm$^{-1}$ are due to the out of plan blending of C-H bond in aromatic ring, respectively. The samples show characteristic absorptions bands of Zinc ferrite, the absorptions bands at 507 cm$^{-1}$ is due to the intrinsic vibration of Zn$^{+2}$ which is present in tetrahedral positions and around 415 cm$^{-1}$ is corresponds to the vibration of octahedral group of Fe$^{+3}$O$^{2-}$, which confirm the formation of the polyaniline / Zinc ferrite composites.

The FTIR spectra of PANI/NiZnO$_3$ composites shows the absorption peaks around 3441-3443 cm$^{-1}$ is correspond for N-H stretching vibration, 1548 - 1581 cm$^{-1}$ is corresponds to C = C stretching vibration of quiniod ring, 1408 - 1487 cm$^{-1}$ is corresponds to stretching vibration of benzenoid ring, 1300 - 1305 cm$^{-1}$ is for the stretching of C-N bonds of aromatic amines, 1240 -1298 cm$^{-1}$ for the C-N stretching of benzenoid ring, 1140 - 1145 cm$^{-1}$ is correspond to C-H in plane of aromatic rings is found to be an strong band which considered to be measure of the degree of electron delocalization, and other bands like 802 cm$^{-1}$, 738 cm$^{-1}$, and 686 cm$^{-1}$ are due to the out of plan blending of C-H bond in aromatic ring, respectively. The samples show characteristic absorptions bands of Zinc ferrite, the absorptions bands at 422 - 507 cm$^{-1}$ is due to the intrinsic vibration of Ni$^{+2}$ which is present in tetrahedral position and around 422cm$^{-1}$is vibration of octahedral group of Zinc which confirms the formation of PANI/NiZnO$_3$ composites.

The important peaks of PANI/CuO composites of different weight percentages are found to be in between 1572-1552 cm$^{-1}$ is due to the C = C stretching vibration of quinoid ring, 1460 -1481 cm$^{-1}$ corresponds to stretching vibration of benzenoid ring, 1246-1304 cm$^{-1}$ is assigned for stretching of C-N bonds of aromatic
Summary and Conclusions:

amines, 1118-1143 cm\(^{-1}\) is due to a strong band which considered to be the measure of degree of electron delocalization and 501-599 cm\(^{-1}\) is due to the stretching vibration of M-O in composites. The important characteristic peaks of the prepared composites obtained are tabulated;

<table>
<thead>
<tr>
<th>Sample</th>
<th>Frequency (cm(^{-1}))</th>
<th>Important band due to</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI</td>
<td>1548, 1492, 1406, 1140</td>
<td>C = C stretching (Quinoid ring), C = N stretching (Benzonoid ring), C – H bonding of aromatic nuclei &amp; degree of electron delocalization.</td>
</tr>
<tr>
<td>PANI/ZnFe(_2)O(_4)</td>
<td>1581, 1481, 1300, 1140 to 1145</td>
<td>C = C stretching (Quinoid ring), C = N stretching (Benzonoid ring), C – H bonding of aromatic nuclei &amp; degree of electron delocalization.</td>
</tr>
<tr>
<td>PANI/NiZnO(_3)</td>
<td>1556, 1487, 1302, 1140</td>
<td>C = C stretching (Quinoid ring), C = N stretching (Benzonoid ring), C – H bonding of aromatic nuclei &amp; degree of electron delocalization.</td>
</tr>
<tr>
<td>PANI/CuO</td>
<td>1566, 1548, 1406, 1140</td>
<td>C = C stretching (Quinoid ring), C = N stretching (Benzonoid ring), C – H bonding of aromatic nuclei &amp; degree of electron delocalization.</td>
</tr>
</tbody>
</table>

2.3) Morphology of composites materials one of the important factor which helps in charge transportations and influence to other applications like humidity sensing, microwave absorptions, organic photovoltaic device etc. SEM micrographs show the presence of micro crystallinity in polyaniline and transformation from a highly granular structure to different patterns of ZnFe\(_2\)O\(_4\), NiZnO\(_3\) and CuO in polyaniline.

- The Scanning Electron Micrograph of PANI/ZnFe\(_2\)O\(_4\) composites were highly clustered, spherical in shape and have interlinked to each other which decreases the inter-granular distance. The decrease in the inter-granular distance between the grains helps the charge transfer mechanism from one
Summary and Conclusions....

grain to another grain. The crystallinity of the ZnFe$_2$O$_4$ decreases with the addition of PANI in it. It is clearly observed that ferrites were homogeneously distributed throughout polyaniline matrix.

- It is clearly observed that the above 30 wt % ferrites particles are not well bonded with the polyaniline due to increasing in the percolation limit to the ratio of filler concentration of the matrix.

- Scanning electron micrograph of PANI/NiZnO$_3$ composites were highly agglomerated, irregular in shape and non porous in nature.

- The grains are well interconnected with each other which indicate that they have enough binding energy to combine with neighbor grains or molecules.

- The SEM image of PANI/CuO composites shows that the grains are highly agglomerated, irregular in shape but they are well interconnected each others.

- Some of the grains are irregular in structure, some of them are elongate and some are spherical in shape.

- The average grain size increase with increase in weight percentages of metal oxide in polyaniline.

- From the SEM images, it can be conclude that the gradual increase in granular size and change in morphology helps the transportation of charge particles through the carbon back-bone of polymer chains.

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

3.1) The DC conductivity of various metal oxides like ZnFe$_2$O$_4$, NiZnO$_3$ and CuO doped polyaniline indicate that there was a strong influence in the conductivity with increase weight percentages. The conductivity of all composites increases with
increase in temperature. The increase in the conductivity is observed up to 30 wt % after that its conductivity decrease and hence this 30 wt% may be the critical dopant concentration which significantly affects the electrical properties of composites. Further the dc conductivity studies supports the one dimensional Variable Range Hopping (VRH) model proposed by Mott.

- Dc conductivity of polyaniline is $3 \times 10^{-3}$ S/cm
- The dc conductivity of PANI/ZnFe$_2$O$_4$ composite of 30 wt% show high conductivity of $4 \times 10^{-2}$ S/cm.
- The dc conductivity of PANI/ NiZnO$_3$ composite of 20 wt% show high conductivity of $8.9 \times 10^{-3}$ S/cm.
- The dc conductivity of PANI/ composite of 50 wt% show high conductivity of $8.5 \times 10^{-3}$ S/cm.

3.2) Ac conductivities studies carried over polyaniline and its composites show the presence of polaron as charge carriers and confirm the extended chain length of polyaniline. All the composites show three steps conductivity which are the important characteristic of amorphous semiconductor materials properties.

3.3) The dielectric constant and dielectric loss response as a function of frequency shows Debye – type relaxation mechanism in polyaniline and in polyaniline composites. Even though ZnFe$_2$O$_4$, NiZnO$_3$ and CuO are added up to 50 wt% in polyaniline, the behavior of dielectric loss with respect to frequency follows same trend as that of pure polyaniline.

3.4) At higher frequencies these composites exhibit low dielectric loss, which suggests that these composites are lossless materials beyond 1 MHz frequencies.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Highest AC conductivity</th>
<th>Highest Dielectric constant</th>
<th>Dielectric loss at Low frequency</th>
<th>Dielectric loss at High frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI</td>
<td>$1.3 \times 10^{-3}$ S/cm</td>
<td>$5.5 \times 10^{4}$</td>
<td>10</td>
<td>0.1</td>
</tr>
<tr>
<td>PANI / ZnFe$_2$O$_4$</td>
<td>40 wt % 1.40 x $10^{-3}$ S/cm</td>
<td>20wt% 5.0 x $10^{5}$</td>
<td>10</td>
<td>1.0</td>
</tr>
<tr>
<td>PANI / NiZnO$_3$</td>
<td>40 wt % 6.45 x $10^{-3}$ S/cm</td>
<td>40 wt% 6.53 x $10^{5}$</td>
<td>10</td>
<td>0.7</td>
</tr>
<tr>
<td>PANI / CuO</td>
<td>40 wt % 6 x $10^{-3}$ S/cm</td>
<td>40 wt% 3.3 x $10^{6}$</td>
<td>10</td>
<td>1.5</td>
</tr>
</tbody>
</table>

4.0) Conclusions from Studies on Humidity sensing:

4.1) The exponential behavior of ZnFe$_2$O$_4$, NiZnO$_3$ and CuO in polyaniline to the broad range of concentration of humidity proves to be promising materials as humidity sensors.

4.2) Because of the electrical conductivity of polyaniline with ZnFe$_2$O$_4$, NiZnO$_3$ and CuO these composites may find extensive technological applications which are to be explored in near future.

4.3) Polyaniline – ZnFe$_2$O$_4$, Polyaniline – NiZnO$_3$ and polyaniline- CuO composites are preferred for applications involving electrical properties and can be used as humidity sensors and high dielectric materials.

6.1 Applications

On the basis of results of electrical and sensing properties,

a) Polyaniline – ZnFe$_2$O$_4$ composites, can be used in the fabrication of capacitors in high electrical circuits and humidity sensors.

b) Polyaniline – NiZnO$_3$ composites can be used as humidity sensors.
Summary and Conclusions....

c) The high electrical conductivity of polyaniline and high dielectric constant of Polyaniline-CuO composites can be utilized to sense the volatile gases.

6.2 Challenges in sensor study

a) The search and selection of proper materials, as well as improved and novel recognition mechanisms necessary for instant identification of a target component and the mechanism to create the signal will be obtained from the sensor.

b) The development of new materials for use as matrices to effectively immobilize receptor molecules to obtain stable and reproducible sensor function.

c) The development of solid-state versions of pH and ion-selective sensors.

d) Novel sensor substrates and internal electrodes for new planar fabrication designs to facilitate the use of advanced fabrication for automated sensor manufacturing, with the help of printing or semiconductor technologies for miniaturized sensor arrays, and improvements in signal processing technologies and instrumentation.

6.3 Scope of future work

The author has studied the bulk samples of these composites in the present study and is interested to undertake studies on these composites in the form of nanomaterials. As a continuation of this work author also wishes to execute sensor studies on formaldehyde, ammonia and hydrogen sulfide gases in these composites in near future.