Studies on synthesis, characterization and transport properties of PbO doped polyaniline composites

Nagajyoti and Sangshetty Kalayne

1Research scholar, Bheemanna Khnadre Institute of Technology, Bhalki, Bidar, Karnataka, India
2Associate Professor, Bheemanna Khnadre Institute of Technology, Bhalki, Bidar, Karnataka, India

ABSTRACT

Lead oxide doped polyaniline (PANI/PbO) composite were prepared by chemical oxidative method. A series of composites were prepared by incorporating the content of the PbO (5%, 10%, 15%, 20% and 25%). The PANI/PbO composites were characterized by different techniques such as XRD and SEM to describe the composite structure and morphological information. The results reveal the favorable interaction between the PANI and PbO. As a part of electrical conductivity, the AC and DC conductivity were studies out as function of measured frequency and temperature respectively. The AC conductivity and dielectric constant increases with increase in frequency and the conductivity increases as the content of PbO increased. The DC conductivity observed to be increasing with increase in temperature.

Keywords: PANI, PbO, AC, DC

1. Introduction

When the insulating properties of the polymer are made to good conducting polymers, they have less conductivity compared to metals. The discovery of the polymer led to increase to enhance the conductivity of the polymer by using different techniques and oxides. Electronic band structure is responsible for the change of electrical property in the CP’s. The conductivity of the material increases if the e’ of the lower band are excited to CB when it is small band gap which is compared to thermal excitation energies. In insulator the large band gap and the electrons are unable to excite to the CB due to insufficient thermal excitation [1-2].

Organic polymers behave as insulating due to the large band gap and free charge carriers does not support for conduction. By the process of redox, in organic polymers, the carriers can be generated with suitable doping agent [3-4].

PANI has wide range of application due to its flexible properties in different area. Such some applications are solar cell, LED, sensors, radiation absorbers and electromagnetic shields. It is possible to alter the properties of the PANI by the process of doping metal oxide or various types of particles with polyaniline. The conductivity results in the polyaniline composite due to the redox behavior [5]. There are many oxidation forms of the polyaniline, among these the most important form of polyaniline is green protonated emaraldine which can prepare by using chemical oxidative polymerization method. When the metal oxide or various types of particles are doped with polyaniline, the charge-transfer reaction takes place between polyaniline and doping agent. The bond length and angles changes when charges are removed from the polyaniline upon chemical doping. In the polyaniline main part is to minimize the residual presence in the polyaniline and along with to obtain yield [6-8].
Among all the conducting polymers, polyaniline has a unique and wide range electrical, dielectric properties and good stability. For the fabrication of technology devices, polyaniline is vital material and when polyaniline was doped with additives, it shows high conducting nature. MgO-Polyaniline is an organic conducting polymer that shows the behaviour of semiconductor or conductor. PANI has unique properties due to environmental stability, lightweight, easy synthesis route & it is possible to control the conductivity. Polyaniline (PANI) exist with one of three states of oxidation. Fully reduced “leucoemeraldine” base are the oxidation state of the polyaniline. These are colourless, poor conductor (even when doped with acids) and which are very reactive. Fully oxidised permigraniline base (C₆H₄N)n are another oxidation state of the polyaniline. They are blue/violet in colour, poor conductor and which is environmentally stable. Other usable state of oxidation of the PANI was partially oxidised emeraldine base/salt with green in colour for salt and blue in colour for base [9-12].

2. Materials and Method:

i. Preparation of Polyaniline

Solution 0.2M of aniline and 1 N of HCL solution was prepared and mixed using magnetic stirrer at room temperature for 2 hrs. The magnetic stirrer was used at constant RPM in order to complete the reaction. Further Solution 0.25M APS was incorporated drop wise into the above aniline and HCL mixer. This mixer was continuously stirred for 8 hrs. After the reaction, the precipitate formed was separated using filtering process and washed with deionised water. The obtained sample as further dried using oven.

ii. Preparation of PbO/PANI:

Aniline solution of 0.2M is mixed with 1N of solution of hydrochloric acid at room temperature. This mixer was stirred by magnetic stirrer for 2 hrs at constant RPM for the completion of the reaction. The solution of 0.25M ammonium persulfate was added drop wise into the mixer. PbO powder for different additive weight percentage (5%, 10%, 15% 20% & 25%) is dissolved in the mass fraction to the above solution with vigorous stirring in order to keep the PbO homogeneously suspended in the solution and stirring of final solution was continued for another 8 hours at RT. After the completion of the reaction, the precipitate was formed was filtered and separated using filtering process. Further washed with deionised water with acetone. The obtained final suspension was dried in an oven at 50°C for 24 hrs. The final product was grinded into powder.

3. X-ray diffraction:

A typical X-ray diffraction pattern of the undoped polyaniline (PANI) is shown in Figure-1. The broad diffraction peak was observed between diffracted angle 2θ ranges from 26°-30° which is characteristic peak polyaniline suggests the amorphous nature of the prepared PANI. The broad diffraction peak with d spacing d=3.29 corresponds to the reflection (200) due to parallel and perpendicular periodicity of the polymer (PANI) and no extra diffraction peaks are observed.

The average crystalline size of the PANI are estimated to be approximately 2.86nm (D) are calculated by using Debye - Scherrer formula,

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Where D is average crystalline size, λ is wavelength of the X-ray, K is crystallite shape factor a good approximation is 0.9, β is the full width at half the maximum (FWHM) of the X-ray diffraction peak and 2θ is the Bragg’s angle (deg.).

Figure 1: XRD pattern of Pure PANI
Figure 2: XRD pattern of PANI/PbO Composite
Figure 2 shows the XRD pattern of PANI/PbO composite (5%, 10%, 15%, 20% & 25%) and investigate the presence and effect of different weight percent of the PbO in the PANI matrix. The X-ray diffraction peaks at angle 2θ = 10.58, 21.1, 27.0, 27.99, 29.98, 33.47, 37.61, 44.89, 51.16 and 55.70 degree with d spacing d=8.35, 4.20, 3.20, 3.18, 2.97, 2.67, 2.38, 2.01, 1.78, 1.64 corresponds to the reflection planes (010), (110), (111), (020), (200), (210), (121), (220), (202) and (131) respectively (25%) pattern matches with PbO with a orthorhombic structure according to the standard diffraction data (JCPDS card 05-0561), (JCPDS No. 038-1477). The crystallite size was estimated to be around 8.29 nm for the full width half maximum peak (010). The average crystalline size of the PANI composite is estimated to be approximately 36.21 nm (D) is calculated by using Debye–Scherrer formula. Moreover the crystallite size of the undoped PANI is D=2.86 nm (25%) which is calculated using Debye–Scherrer equation. In the presence of the PbO, crystallite size of the composite increased from 2.86 of PANI to 36.21 nm of composite. It is also observed that, the intensity of the peaks is increasing from 1800 counts to approximately at around 4500 counts as doping concentration increased from 5% to 25%. This increase in the intensity of the XRD peak may suggest that, PbO oxide dispersed in the polyaniline matrix.

4. Scanning electron microscope:

Figure 3(a) is the SEM micrograph of the pure PANI and figure 3(b-f) is the SEM micrograph of the PANI/PbO composites. The SEM image of PANI shows uniform morphology with semi-crystalline like structure and has a substantial intra-granular distance between the grains. The SEM micrographs of the composites shows highly agglomerated and irregular arranged granular in shape under magnification 15000x. The grains are found to be well connected which suggests the higher binding energy between the grains. It is noticeable that the SEM micrograph of PANI/Ta2O5 composites presents different morphology as compared with the PANI particles.

Figure 3: SEM micrograph of a) PANI, b) PANI/PbO (5%), c) PANI/PbO (10%), d) PANI/PbO (15%), d) PANI/PbO (20%), e) PANI/PbO (25%) Composite

5. AC Conductivity:

Motion of delocalized electrons through conjugated system was responsible for the electrical conductivity in the conducting polymers. Also the process of hopping takes place between the nearest redox sites of the chain of the polymer. Figure 4 shows the electrical conductivity of the undoped polyaniline and PANI/PbO composite 5%, 10%, 15%, 20%, 25% as function of measured frequency. Almost the same trend in the variation of the conductivity of the PANI and its composites was observed. Initially the conductivity of the PANI and its composites was found to be almost constant up to 5logf and a drastic increase was observed after this
frequency. This behavior of the conductivity may due to the hopping conductivity of electrons increasing at relatively high frequency. The ac conductivity of Polyaniline exhibit two phases in the frequency range 50 Hz (1.75 logf) to 10^6 Hz (6.69 logf). In frequency range between 50 Hz (1.75 logf) to 10^5 Hz (5 logf), the conductivity values are almost constant. The conducive increase suddenly in the frequency range 10^5– 10^6 Hz (6.69 logf). However the increase seen in the conductivities of the composites except composite 5%. It can also been seen that the conductivity of the PANI/PbO composite increases with increase in the content of PbO in the PANI matrix may due the increase in effective dispersion of PbO particles [13].

<table>
<thead>
<tr>
<th>Sample</th>
<th>σ ac at 50Hz (S/cm)</th>
<th>σ ac at 10^6 Hz (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI</td>
<td>4.45x10^-3</td>
<td>4.13x10^-2</td>
</tr>
<tr>
<td>PANI/PbO-5%</td>
<td>4.45x10^-3</td>
<td>4.13x10^-2</td>
</tr>
<tr>
<td>PANI/PbO-10%</td>
<td>5.34x10^-3</td>
<td>4.96x10^-2</td>
</tr>
<tr>
<td>PANI/PbO-15%</td>
<td>6.94x10^-3</td>
<td>5.79x10^-2</td>
</tr>
<tr>
<td>PANI/PbO-20%</td>
<td>9.02x10^-3</td>
<td>4.39x10^-2</td>
</tr>
<tr>
<td>PANI/PbO-25%</td>
<td>1.26x10^-2</td>
<td>6.33x10^-2</td>
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6. DC Conductivity:

Figure-5 shows the dc conductivity of the pure polyaniline as a function of the temperature. The temperature dependence of conductivity of PANI was measured in the temperature range 40° C to 200° and it is found that there is increase in the conductivity of the PANI for the increase in temperature exhibiting semiconducting behavior and it is the characteristic property of materials. It is observed from figure that, conductivity of PANI showing in two phase i.e., the conductivity in the range 30° C - 150° C & 140° C - 200° C.

The first phase conductivity is almost constant may be due to inter-chain transport of charge carriers, i.e., hopping of charge carriers between the polymer chains and is usually observed at intermediate temperature. But, at high temperature region, (phase two) there is an sudden increase in the conductivity with increase in temperature due to intra-chain transport of charge carriers which can be described by the band conduction mechanism and is usually it is observed at high temperatures as reported by authors in their previous work [14-16]. Compared to the conductivity of the undoped polyaniline, the composite shows higher conductivity over measured temperature. Among all the PANI/PbO composite, the 25% additive percentage shows highest conductivity.
Figure-5: DC conductivity of PANI & PANI/PbO Composite

7. Dielectric constant:

The dielectric constant of polyaniline and PANI/PbO composite as a function of frequency (log f) was shown in Figure-6. The dielectric constant of the pure PANI was found to be maximum and followed by the composites sample. As the PbO doping percent increases in the polyaniline, the dielectric constant further increases when incorporating PbO particles. The dielectric constant of the PANI and PANI/PbO composite decreases with increase in measured frequency. The high dielectric constant was observed at lower frequency range and low dielectric values at higher frequency range. The higher dielectric constant at lower range frequency may attribute due to the PANI sample’s interfacial effects and also occurrence of periodic reversal of the electric field at higher frequency range. Further the decrease in the dielectric constant at higher range frequency may attribute to polarization due to decrease in the charge accumulation [17].

Figure-6: Dielectric constant of PANI & PANI/PbO Composite

8. Conclusion:

PANI/PbO composite with different doping percent are synthesized using chemical oxidative polymerization method. XRD characteristic peak polyaniline suggests the amorphous nature. XRD pattern of the PANI/PbO confirms the successful formation of composite with average crystalline size of the composite is estimated to be approximately 36.21 nm (D). The SEM image of PANI shows uniform morphology with semi-crystalline like structure and has a substantial intra-granular distance between the grains. Initially the AC conductivity of the PANI and its composites was found to be almost constant up to 5log f and a drastic increase was observed after this frequency. DC conductivity found that there is increase in the conductivity of the PANI for the increase in temperature exhibiting semiconducting behavior. Compared to the conductivity of the undoped polyaniline, the composite shows higher conductivity over measured temperature. As the PbO doping percent increases in the polyaniline, the dielectric constant further
increases when incorporating PbO particles. The dielectric constant of the PANI and PANI/PbO composite decreases with increase in measured frequency.

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9. References
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