Synthesis, Characterization and Studies on Polyaniline/Nanocomposites Thin Films

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Abstract: Nanocomposites of Polyaniline/Copper oxide were prepared by in-situ polymerization method. These composites were characterized by employing Scanning Electron Microscope (SEM), Transmission Electron microscopy (TEM), Thermal study by (TGA). The dc conductivity of prepared composites was measured as a function of temperature which shows the strong interaction between Pani and copper oxide particles and exhibits semiconducting behavior. The prepared composites show better Electrical & Thermal properties which may be useful for Potential applications.

Keywords: PANI, Nanocomposites, TEM, SEM, conductivity, Sensitivity

1. Introduction

Traditionally polymers were seen as good electrical insulators and most of their applications had relied on their insulating properties [1]. However, until three decades ago researchers showed that certain class of polymers exhibits semiconducting properties. Early studies showed that polyaniline exhibit signs of conductivity. This discovery was followed by the work of Shirakawa and co-workers in 1977 who reported the first synthesis of doped polyacetylene which was formed accidentally [2]. This incident took place when one of the co-workers mistakenly added excessive amount of catalyst in the reaction vessel for the polymerisation of acetylene. This resulted in the formation of a silver film instead of the expected black powder[4].Conjugated polymers, most notably polypyrrole (PPY), polythiophene (PT), polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT), and poly(p-phenylene vinylene) (PPV) have been synthesized, in free-standing film and bulky powder forms, using electrochemical or chemical polymerization methods [3]. PPY and PANi can be formed chemically or electrochemically through oxidative polymerization of pyrrole and aniline monomers, the final form of PPY and PANi are those of a long conjugated backbone. Owing to its features of good electrical conductivity and environmental steadiness, PPy has been reckoned as one of the most important conducting polymers. However, its low mechanical strength, fragility and poor processability restrict PPy to limited uses. Preparation of composites with inorganic components is a feasible process to overcome these limitations [4-7].
2. Experimental

2.1. Chemical Synthesis of Polyaniline

The synthesis was based on mixing aqueous solution of aniline hydrochloride and ammonium per sulphate at room temperature, followed by the separation of PANI hydrochloride precipitate by filtration and drying. Aniline hydrochloride (equimolar volume of aniline and hydrochloride acid) was dissolved in distilled water in a volumetric flask to 100 ml of solution. Ammonium per sulphate (0.25M) was dissolved in water and also to 100ml of solution. Both solutions were kept for 1 hour at room temperature, then mixed in a beaker, stirred with a mechanical stirrer, and left at rest to polymerize. Next day, the PANI precipitate was collected on a filter, washed with 0.2 M HCL, and similarly with acetone. Polyaniline hydrochloride powder was dried in air and then in vacuum at 60°C for 24 hours. Polyaniline prepared under these reaction and processing conditions are further referred to as “standard” samples.

2.2. Synthesis of PANI/Copper Oxide nanocomposites

Synthesis of the PANI-copper oxide composites was carried out by in-situ polymerization method. Aniline (0.1 M) was mixed in 1 M HCl and stirred for 15 min to form aniline hydrochloride. copper oxide particles were added in the mass fraction to the above solution with vigorous stirring in order to keep the copper oxide homogeneously suspended in the solution. To this solution, 0.1 M of ammonium persulphate, which acts as an oxidizer was slowly added drop-wise with continuous stirring at 5°C for 4 h to completely polymerize. The precipitate was filtered, washed with deionized water, Acetone, and finally dried in an oven for 24 h to achieve a constant mass. In these way, PANI–copper oxide composites containing various weight percentage of Copper oxide (10 %, 20 %, 30 %, 40 %, and 50 %) in PANI were synthesized.

2.3. Preparation of copper oxide nanocomposite film

Polyvinyl alcohol (PVA) with molecular weight Approx. 1, 25,000 was obtained commercially with AR grade, and Polyaniline/ Copper oxide was synthesized by In-situ polymerization method. Powdered PVA of about 2.5 g was dissolved in 50ml of double distilled water by stirring. The solution was then warmed up to 333 K and thoroughly stirred, using a magnetic stirrer, for about 1h until the polymer became completely soluble.

A thick film of the sample was prepared by solution casting method in the following manner. The synthesized Polyaniline/ Copper oxide nanocomposites powder was dissolved in PVA solution and this was sonicated for 15-20 min. The sonicated solution was stirred for 1/2 hour, and then the paste of PVA/Polyaniline/ Copper oxide nanocomposites was formed. Then known volume of viscous PVA/Polyaniline/ Copper oxide nanocomposites solution was poured onto a leveled clean glass plate and left to dry at room temperature for about 48 h. The dried films were peeled off from the glass plate and cut into suitable pieces for characterization and applications.

3. Characterization

The morphology of the composites in the form of powder was investigated using scanning electron microscope (SEM) Model-EVO-18 (Special Edison, Zeiss, Germany). Differential scanning calorimetry (DSC) was investigated by Instrument: DSC Q20 V24.10 Build 122. DC conductivity of these nanocomposites are studied by using Keithley 6514 electrometer.

4 Results and Discussion

4.1 Thermal studies

Figure 4.1 shows the DSC graph of Pani/Copper oxide composites. The DSC graph shows two weight losses as seen in fig 3, the first weight loss corresponds the evaporation of water molecules from the prepared composites. The second weight loss is due to the decomposition of organic moiety.
4.2 Scanning Electron Microscopy

Figure 4.2 (a) shows the SEM micrographs of the copper oxide particles these are spherical in shape. Figure 4.2 (b) shows that Scanning Electronic Micrograph (SEM) image of 50wt% of Pani/Copper oxide 50wt% composite. The particles are highly agglomerated granular in shape and amorphous nature is found. The grains are well interconnected with each other.

4.3 Transmission Electron Microscopy

Figure 4.3 TEM micrographs of the copper oxide
Figure 4.3 shows the TEM image of copper oxide nanoparticles. The nanoparticles are in spherical shape was clearly visible and impurity phase was not detected. The shape of the particles is spherical and the average diameter is 50 nm which was evenly distributed in polymer matrix.

4.4 DC Conductivity

Electrical conduction in these Polymers is dominant by polarons and bipolarons. At low doping levels, the chain is ionized and produces a radical cation (Polaron) which does not contribute significantly to the conductivity, however at higher doping levels the polarons can combine or ionize to form spinless dications (Bipolarons) which extend over few rings. As the strength of applied field increases the number of such polarons and bipolarons increases which means an increase in current. Doping results in the alternation of the aromatic configuration to the higher energy quinoid configuration and confines the charge localized along the Chain, which means increase in conductivity. We observed that the temperature dependence for each polymer behaves in the usual activated manner indicating semiconducting property. This suggests that the conductivity increase with temperature is due to the increase of efficiency of charge transfer. It is also proposed that the thermal curling affects the chain alignment of the polymer, which leads to the increase of conjugation length and which in turn brings about the increase in conductivity. Also, there will be molecular rearrangement on heating, which make the molecules favorable for electron delocalization. Figure 4.4 shows the Dc conductivity of copper oxide nanoparticles.

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![Figure 4.4 DC conductivity](image-url)

**Figure 4.4 DC conductivity**

5. Conclusion

In the present article, we report on the preparation of composites of conducting Pani/Copper Oxide nanocomposites and thin films by using in-situ chemical polymerization route & solution casting method. The conductivity and thermal behavior of these composites were studied. The effects of Copper Oxide concentration on conductivity properties were investigated. The linear variation in the Dc conductivity parameters indicates the prospects of these thin films composite as an efficient conducting material.

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