DC CONDUCTIVITY STUDIES ON POLYANILINE-WO_3 COMPOSITES SYNTHESIZED BY IN- SITU POLYMERIZATION TECHNIQUE

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Abstract : This work is focused on the development on polyaniline-WO_3 composites with varying tungsten oxide concentration by in situ polymerization technique. The structural and microstructural characterization was conducted using X-ray diffraction and scanning electron microscope. The DC conductivity of all the composites were measured over the temperature range of 30 - 200°C while the thermal stability was measured over the temperature range of 30 - 1000°C. All the composites showed increase in conductivity values with the increase in WO_3 content where the composite with 45% WO_3 content showed highest value of 0.12 S/cm while the lowest conductivity of 0.06 S/cm was found in 5% WO_3 content composite. The composites with WO_3 content more than 15% displayed better thermal stability when compared to that of 5 and 15% WO_3.

Keywords: Polyaniline-WO_3, Scanning electron microscopy, X-ray diffraction.

1. INTRODUCTION

Day by day the need for miniaturization and performance of electronic components is growing at faster pace. In this regard the embedded components have been developed have received a great deal of attention as they offer various advantages like improved electrical properties, functionality, improved design flexibility, inclusion of more number of components and reduced cost. For this purpose there has been intense research going on to develop polymer composites with high conductivity and high dielectric properties. Apart from having good properties the polymer composites should have easy to synthesize and low manufacturing costs [1, 2]. In this regards the polymers such as polyanilline and polypyrrole has been explored greatly due to outstanding properties. In particular the polyaniline has been studied most due to its ease of processing, simple doping/depoing chemistry, high conductivity and good environmental stability. Polyaniline is generally found in three oxidation states which are namely emeraldine, leucoemeraldine and pernigraniline. Out of these three the emeraldine is most attractive owing to its tunable states. The polyaniline can be synthesized by various routes such as in situ polymerization, dispersion technique, enzymatic polymerization or by solution blending [3].The organic electronics whose attributes like light weight, flexible and thin are based on polyaniline. These are applied in display, solar and sensor applications which is mainly because of polyaniline which helps composite or other material help in achieving semiconducting or conductive properties [4, 5].

It is well known that the polyaniline based composites with their unique electrical properties are prime candidate material for electronic applications; many studies have been carried out to study the conductivity by both analytical and experimental methods. Cristovan et al [6] studied the DC conductivity of polyaniline/poly(acrylonitrile-butadiene-styrene) blends prepared by solution blending route. The electrical conductivity of blends was studied in the temperature range of 80 - 320 K using a two probe method. It was observed that with the increase in temperature and amount of doped polyaniline in the blends the DC conductivity was found to increase. A good interaction between ABS and polyaniline and an increase of density of states with polyaniline resulted in obtaining desired electrical properties. In another work Sobha and Narayanankutty [7] studied thermal stability of conductivity of functionalised multiwalled carbon nanotubes/polyaniline composites prepared by dynamic interfacial and single phase polymerization technique. The DC conductivity of composites was measured in the temperature range of 30 to 150°C at an interval of 30 minutes for up to 200 minutes. It was found that the electrical conductivity of composites prepared by interfacial polymerization technique were ten times more than that of composites prepared by single phase polymerization technique. Along with this the thermal stability of the composites through interfacial polymerization showed better thermal stability in electrical conductivity during cyclic and isothermal aging when compared to that of single phase polymerization. In their study Dutta et al [8] reported DC and AC conductivity of polyaniline/polyvinyl alcohol blends in the frequency range of 1 kHz to 5 MHz. The DC conductivity of the blends was measured in the temperature range of 80 - 300 K using standard four probe method. The DC conductivity

was found to increase with increase in polyaniline volume fractions at room temperature. However with the decrease in temperature showed decrease in conductivity for all compositions indicating semiconducting behaviour.

On the other hand inorganic metal oxide like tungsten oxide (WO_3) has been successfully utilized in many applications like solar cells, gas sensors and electrochromic devices due to its chemical stability, wide band-gap and good adhesion to substrate materials. In this regards many studies have been reported on inclusion of WO_3 in polymer matrices because of their interesting properties [9, 10]. Amaechi et al [11] studied the temperature dependence resistivity of polyaniline/*n*-WO_3 composites by oxidative polymerization technique. The electrical resistivity of the composites measured in the temperature range of 300-700 K by 2 point probe method displayed the semiconductor behaviour. In another work Kumar and Yadav [12] reported the sensing studies of polyaniline/WO_3 composites prepared by chemical polymerization method. The electron microscopy images showed that the WO_3 were dispersed randomly throughout the polyaniline matrix. The composites at all WO_3concentrations showed good sensing ability where the percentage of relative humidity varied from 10 to 85%. So overall keeping these interesting properties of polyaniline and WO_3 in mind we report here the development of polyaniline/WO_3 composites by in situ polymerization technique and study its conductivity with varying WO_3 concentration.

2. EXPERIMENTATION

2.1. Synthesis

Synthesis of the PANI–tungsten oxide (WO_3) composites was carried out by polymerization in situ. Aniline (0.2 M) was dissolved in 1 M HCl and stirred for 2 hrs to form aniline hydrochloride. Iron oxide was added in the mass fraction to the above solution with vigorous stirring in order to keep the WO_3 homogeneously suspended in the solution. To this mixture, 0.2 M of ammonium persulphate, which acts as an oxidant was slowly added drop-wise with continuous stirring at room temperature for 8 hrs to completely polymerize the monomer aniline. The precipitate was filtered, washed with demonized water, and finally dried in an oven for 24 hrs to achieve a constant mass. In this way, PANI–WO_3 composites containing various mass fractions of WO_3 (5%, 15%, 25%, 35% and 45%) in PANI were synthesized.

2.2. Characterization

The morphology and the structures of as synthesized PANI–WO_3 composites were studied using Philips XL-30 ESEM scanning electron microscopy (SEM). X-ray diffraction (XRD) patterns of the powders were taken using Rigaku-Ultima IV, Japan diffractometer with Cu Kα radiation (λ = 1.54 A˚). The DC conductivity of all the composites with varying WO_3 concentration with respect to the temperature were measured by standard four probe method. The thermal behaviour of the polymer samples was examined by simultaneous differential scanning callorimetry (DSC) and thermo gravimetric analysis (TGA) up to 1000ºC using Thermal Analyzer STA PT 1600 (Linseis make, Germany) in nitrogen atmosphere at heating rate at 2 ºC /min.

3. RESULTS AND DISCUSSION

3.1. Characterization: SEM and X-ray diffraction

Figure 1 a - e shows the SEM micrographs of morphology of PANI/WO_3 composites with varying WO_3 content from 5% to 45%. Several irregularly shaped aggregations were seen which are mainly composed of polyaniline and WO_3 particles unlike in another work where the authors [13] have observed spherical aggregations of polyaniline and TiO_2 particles. So in present case the polyaniline was found to be covering the WO_3 particles and had very rough surfaces with irregular shaped aggregations. The observation of SEM micrographs of all the composites with different WO_3 concentration clearly tells that the WO_3 particles are embedded in the polyaniline matrix. Here the size of these aggregations increased with the increase in the WO_3 concentration from 5% to 45%. The WO_3 had strong effect on morphology of polyaniline because one can see that there is transformation from fibrous to particles of polyaniline.

Figure 2 shows the X-ray diffraction pattern of all composites with the varying WO_3 concentration. Almost all sharp and large peaks show the presence of WO_3 particles in the polyaniline-WO_3 composite. The intense sharp peaks seen at 2θ = 23°, 24.1°, 33°, 50° and 56° indicates the presence of WO_3 particles which are having both monoclinic and orthorhombic phase. All the peaks seen at these 2θ angles were in line with the JCPDS No. 00-024-0747 and also 01-071-0131 which corresponds to monoclinic and orthorhombic phase of WO_3. However due to overlapping of peaks of polyaniline with that of WO_3 particles is the reason why we are unable to see any peaks corresponding to polyaniline. Here the sharp diffractions peak of all composites indicates strong intensity of crystalline structure of the composites.

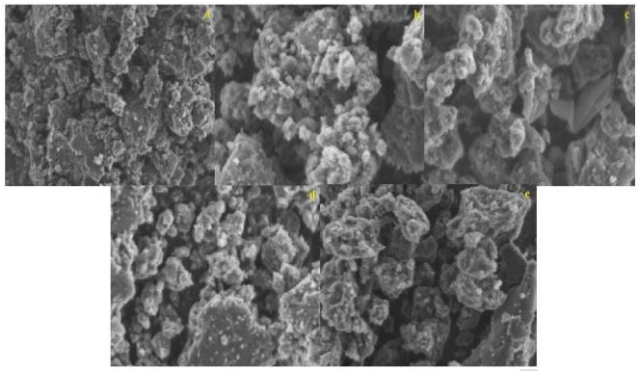

Figure 1: SEM micrographs of PANI/WO_3 composites with different WO_3 content: (a)5 (b) 15 (c) 25 (d) 35 and (e) 45 wt%.

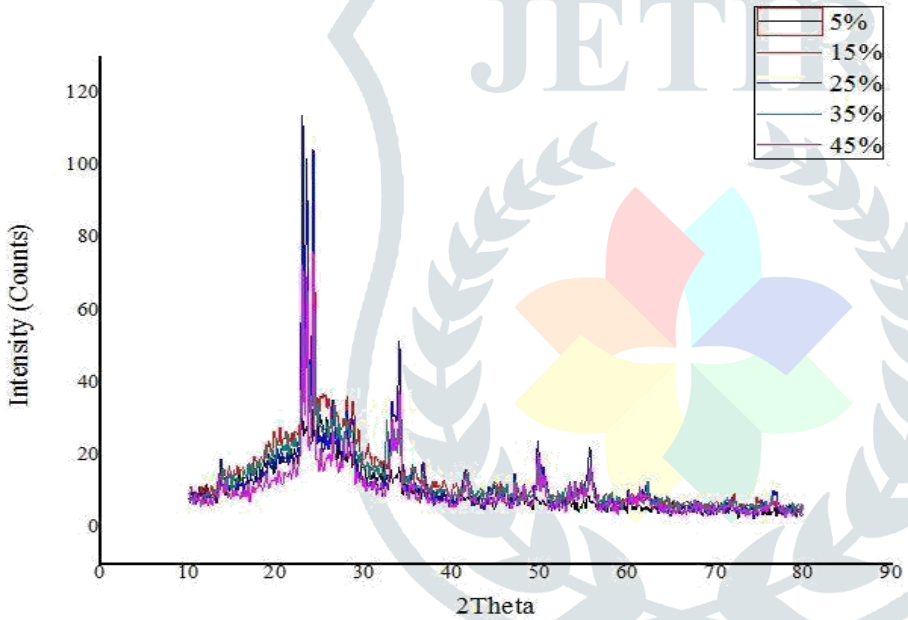

Figure 2: X-ray diffraction patterns of PANI/WO_3 composites with different WO_3 content.

3.2. DC conductivity studies

Figure 3 shows the conductivity of poyaniline-WO_3 composites with varying WO_3 content from 5% to 45%. Here the conductivity was measured using a four point probe method in the temperature range of 30 - 200°C. It can be seen that with the increase in concentration of WO_3, the conductivity is found to increase. Among all composites, the one with 45% WO_3 content was found to have highest conductivity of close to 0.12 S/cm while least conductivity value of 0.06 S/cm was noted in composites with 5% WO_3 content. The increase in conductivity is generally attributed to extended chain length of polyaniline which help in hopping of charge carriers. But unusual behaviour in conductivity was observed when the temperature was varied from 30 to 200°C. It was seen that there were two temperature ranges were the conductivity was found to increase with the increase in temperature and these were 70 to 110°C and 160 to 200°C. So the highest conductivity was seen at 200°C for all composites with different WO_3 concentration. As said earlier with the increase in WO_3 content and increase in temperature the efficiency of charge transfer between the polyaniline and WO_3 increases.

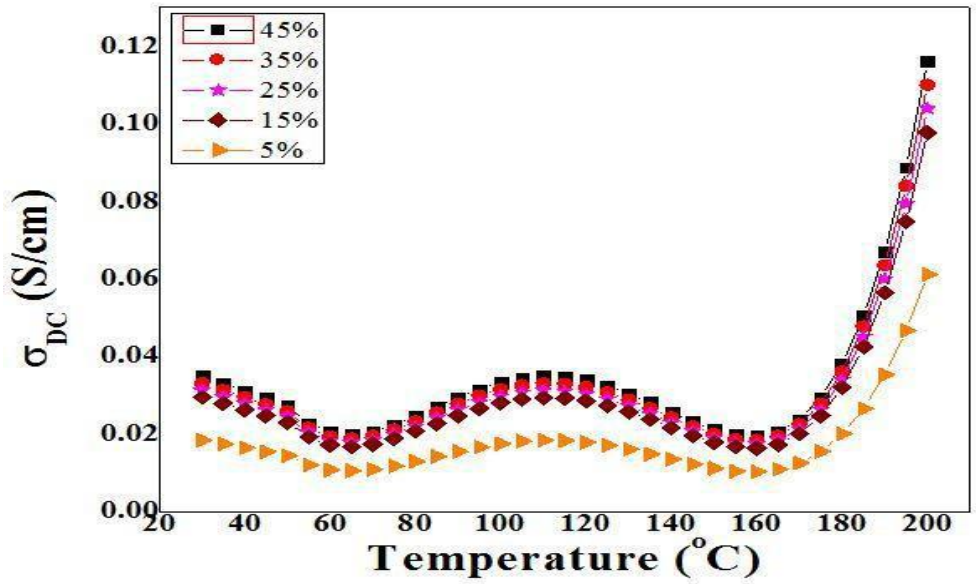

Figure 3: DC conductivity of PANI/WO_3composites at different temperatures.

4. THERMAL ANALYSIS

Thermal stability of the synthesized PANI/WO_3 composites were obtained from thermogravimetric analysis and shown in Figure 4 a-e. The thermograms for all the composites were obtained from 30 to 1000°C. Out of all composites, the one with 15% WO_3 content displayed interesting behaviour over a temperature range of 30 - 950 °C with close to 3% weight loss. There is an abrupt degradation of polymer chains at a temperature range of 950 and it continues up to 1000°C. However the mass loss of this composite for a temperature range of 30 to 950°C is just over 3% which could be due to loss of water molecules entrapped in the polymer matrix. Further from 950 - 1000°C the weight loss of about 5% was observed which could be due to partial leaching of WO_3 from polyaniline matrix. It can be observed from the thermograms that all the composites with above 15% WO_3 concentration the thermal stability were found to be almost same. These three composites showed a weight loss of about 3% over the temperature range of 30 to 1000°C displaying better thermal stability.

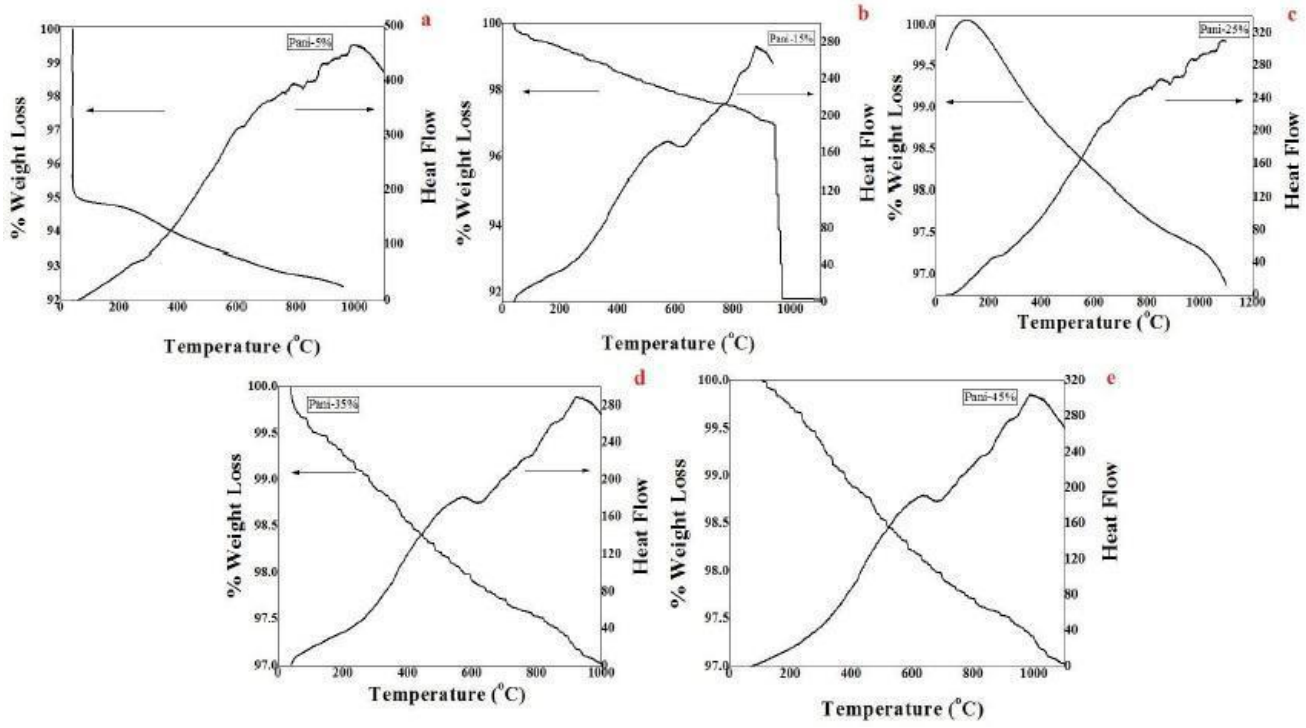

Figure 4: Thermograms of PANI/WO_3 composites: (a) 5, (b) 15, (c) 25, (d) 35 and (e) 45 wt% WO_3 content.

5. CONCLUSIONS

The conclusions drawn from the present work are as follows,

1.PANI/WO_3 composites with varying WO_3 content from 5% to 45% have been successfully synthesized by in situ polymerization technique.

2.The composites showed higher conductivity values above temperature of 160°C due to improvement in charge transfer efficiency at higher temperatures.

3.Out of all, the composite with highest WO_3 content of 45% was found to possess highest DC conductivity of 0.12 S/cm at
higher temperature of 200°C.

4.The composites with WO_3 content more than 15% displayed better thermal stability when compared to that of other composites.

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