Synthesis and ac conductivity studies of polyaniline-Co3O4 composites prepared by ex situ polymerization technique

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Abstract- This work describes the development of polyaniline-Co_3O_4 composites by ex situ polymerization technique. The composites with varying Co_3O_4concentration were subjected to morphology and structural using scanning electron microscopy and X-ray diffraction. The room temperature conductivity and dielectric studies were conducted as a function of frequency. The conductivity of the composites tends to increase with increase in the frequency indicating hopping of charge carriers as a dominant mechanism. The variation of dielectric constant of all composites with respect to the frequency was analysed at room temperature. The dielectric constant was found to increase with the increase in Co_3O_4concentration and was found to highest for composite with 45% Co_3O_4. The thermogravimetric analysis carried out to study the thermal stability showed that the composite with highest Co_3O_4concentration displayed better stability.

Keywords: PANI-Co_3O_4, Scanning electron microscopy, X-ray diffraction.

I.INTRODUCTION

In the past few years, conducting polymers have received a lot of attention due to their attractive electronic, magnetic and optical properties. This is mainly because the mechanical and physical properties of these polymers can tuned by doping or protonation or by varying the synthesis techniques. Most of these conducting polymers have found applications in the area of microelectronic devices, microwave absorption and shielding [1, 2]. Among all conducing polymers, polyaniline has been explored due to its easy synthesis technique, light weight, high electrical conductivity, simple doping and de-doping chemistry and environmental stability. In particular due to its high electrical conductivity there have been lot of studies on ac/dc conductivity of emeraldine salt polyaniline and emeraldine base polyaniline [3]. Polyaniline is obtained by either electrochemical or chemical ways but the most widely used technique is electrochemical polymerization technique. In the recent days the chemical oxidative methods such as in situ polymerization, solution blending and enzymatic polymerization have been explored a lot for synthesis of polyaniline [4].However polyaniline alone has certain drawback such as poor process ability and insolubility which limits its commercial applications. In order to attain desired properties like good mechanical strength and enhanced electrical conductivity it is necessary to have good synthesis technique along with appropriate filler material. In line with this there have been many attempts to improve the properties by incorporating the metal and metal oxide particles in to the polyaniline [5, 6].

There has been interest in developing materials with high dielectric constant with low dielectric loss and excellent temperature stability. So for this many metal and metal oxides are studied with various polymer materials keeping good conducting properties in mind. In the recent years the inorganic particles such as Co_3O_4, Fe_2O_3 and Fe_3O_4 are used to a long polyaniline to produce composites with enhanced physical properties. Out of mentioned inorganic particles, Co_3O_4 exhibits interesting magnetic properties. It exhibits anti-ferromagnetism in bulk crystalline form while super para-magnetic properties in nano-size form. Apart from this, it has superior stability, high activity, low cost and environmental friendly transition metal oxide. Many attempts have been made to tap the exciting properties by introducing Co_3O_4 in the polyaniline to synthesize novel composites. Shambharkar and Umare [7] studied the electrical conductivity and electrochemical performance of polyaniline/Co_3O_4 nano-composite. The nanocomposite with different molar ratio of aniline to Co_3O_4 was prepared by chemical oxidative in situ technique. The electron microscopy studied showed that the Co_3O_4 particles were present in spherical shape in PANI matrix. The room temperature electrical conductivities of nanocomposites were found to decrease with the increase in Co_3O_4 content. Further electrochemical studies showed that the Zn-Co_3O_4 with PANI has greater discharge life time when compared to that of PANI alone. In another work, Wang et al [8] studied the electro catalytic and electrochemical behaviour of Co_3O_4/PANI/reduced graphene nano-composite. The nano-composite displayed good electrocatalytic behaviour for oxidation in N-acetyl cysteine. The electrochemical behaviour displayed high sensitivity, selectivity and stability which is promising for qualities for enzymatic sensor.In another work Lin et al [9] studied the electrochemical performance of graphene/polyaniline/Co_3O_4 ternary hybrid aero gels by in situ polymerization and hydrothermal treatment. The 3D macro porous network structure of hybrid aerogels possesses large specific capacitance and good cyclic stability. The reason behind the good electrochemical performance was attributed to synergistic effects of PANI, Co_3O_4 and graphene and there 3D porous structure. In addition to this no capacitance loss after 3500 cycles shows the excellent cyclic stability. This type of material with such porous structure has potential applications in the field of super capacitors as electrode material.

Here in present work we report the synthesis of PANI-Co_3O_4 composites by ex situ polymerization technique. The composites were characterized using X-ray diffraction and scanning electron microscope techniques. The ac conductivity of composites with varying Co3O4 content was studied to understand the conductivity of the composites.

II.EXPERIMENTATION

Synthesis

Synthesis of the PANI–Co_3O_4composites was carried out by polymerization *ex situ*. Aniline (0.2 M) was dissolved in 1 M HCl and stirred for 2 hrs to form aniline hydrochloride. Nickel oxide was added in the mass fraction to the above solution with vigorous stirring in order to keep the Co_3O_4 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 a hot air oven for 24 hrs to achieve a constant mass. In this way, PANI–Co_3O_4 composites containing various mass fractions of Co_3O_4 (5%, 15%, 25%, 35% and 45%) in PANI were synthesized.

Characterization

The powder morphology of synthesized PANI/Co_3O_4 composites was analysed using scanning electron microscopy (SEM, JSM-6360LV, Japan). The X-ray diffraction analysis was carried out using Philips XPERT diffractometer using Cu Kα radiation (λ = 1.54 A˚). The AC conductivity and dielectric properties of all the composites with different Co_3O_4 content was studied in the frequency range of 0.2 to 10 MHz using LCR-Q meter (Wayne Kerr, 4300) analyser. Thermo gravimetric analysis was also performed in nitrogen atmosphere having heating rate at 2 ºC /min for the temperature range of room temperature to 1000ºC using Thermal Analyzer STA PT 1600 (Linseis make, Germany).

III.RESULTS AND DISCUSSION

Characterization: SEM and X-ray diffraction

The scanning electron micrographs (SEM) depicting particle morphology of PANI/Co_3O_4 composites is shown in Fig 1 (a) to (e). Almost all composites with varying Co_3O_4concentration showed aggregated globular powder particle structure. The aggregated powder particles had irregular morphology and with the increase in Co_3O_4 content (5% to 45%) the surface morphology was found to be changing. The dispersion of $Co_3O_4$was found to be uniform throughout the PANI matrix but was showed some agglomeration when the concentration was increased from 5% to 45%. The Co_3O_4 particles where found to be surrounding the PANI matrix and each aggregated particles interlinked with each other. This interlinking between particles will be advantageous for charge transfer mechanism. The change in morphology of particles is usually favourable for charge transfer in the PANI/Co_3O_4composite. Fig 2 shows the X-ray diffraction patterns taken for all composites with varying Co_3O_4concentration. The diffraction peaks observed at 2θ values of 26° corresponds to (0 2 0) crystal plane of the polyaniline. For composite with 5% and 15% the Co_3O_4 weren't properly seen in the X-ray diffraction pattern due to their small content in the composites. For composites with higher concentration of Co_3O_4 that is about 25% to 45% the strong peaks of Co_3O_4 were observed. The sharp diffraction patterns seen at the 31.90°, 36.10°, 38.20°, 44°, 48.20° and 65.10° corresponds to (2 2 0), (3 3 1), (2 2 2), (4 0 0), (3 3 1) and (4 4 0) crystal planes of Co_3O_4. This identified crystal planes are in line with that of cubic Co_3O_4 as mentioned in JCPDS 43-1003. The obtained results matches with that of X-ray diffraction patterns obtained for $Co_3O_4$by Wang et al [8] in their work on Co_3O_4/polyaniline composites.

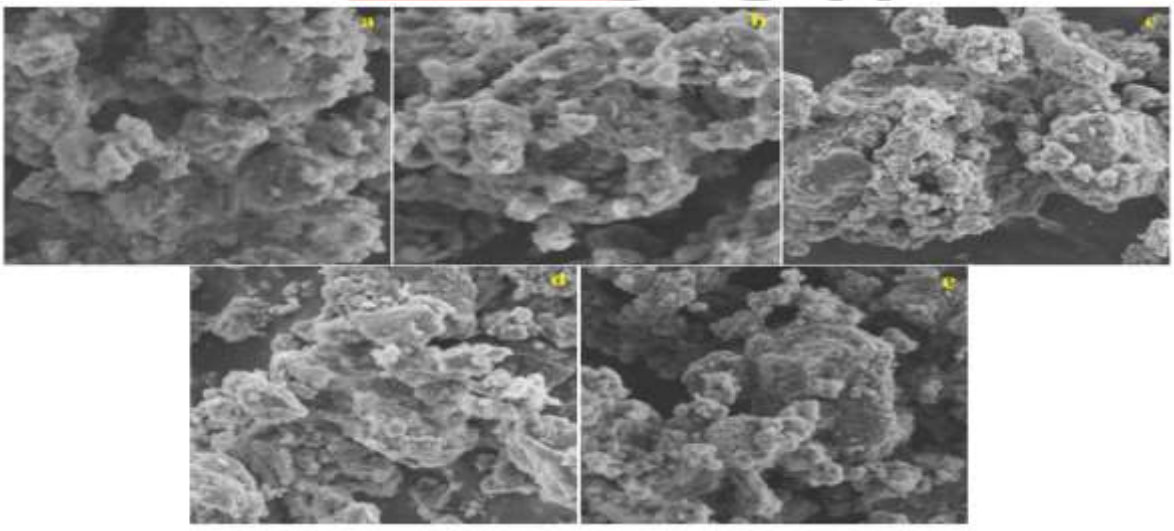

Fig. 1 SEM micrographs of PANI/Co_3O_4 composites with different Co_3O_4 content: (a) 5, (b) 15, (c) 25, (d) 35 and (e) 45 wt%.

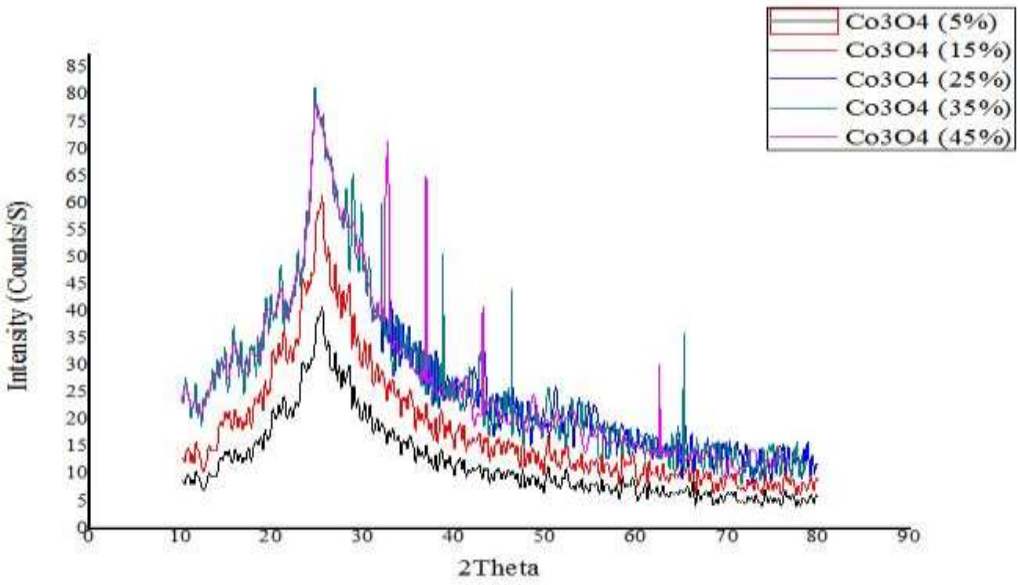

Fig. 2 X-ray diffraction patterns of PANI/Co_3O_4 composites with different Co_3O_4 content.

AC conductivity studies

The variation of ac conductivity with respect to that of frequency for all composites is shown in Fig 3. It can be seen that at higher frequencies the conductivity has highest values when compared to that of lowest frequencies. The conductivity tends to increase with increase in frequency which indicates increased hopping frequency of the charge carriers. Further the increase in conductivity can also be attributed to the formation of interfacial p-n hetero-junction barrier between PANI and Co_3O_4. The formation of bond between the two constituent materials helps the PANI chains to grow at larger lengths. At higher frequencies the charge carriers get sufficient energy to hop between the desired sites. The influence of external electric field is such that the charge carriers at hop at greater distance indicating increase in hopping length which in turn increases the conductivity. The highest conductivity was observed for composites with highest Co_3O_4 concentration of 45%. Overall at highest frequencies particularly in the composites with higher concentration of Co_3O_4 the transport is dominated by hopping mechanism [10].

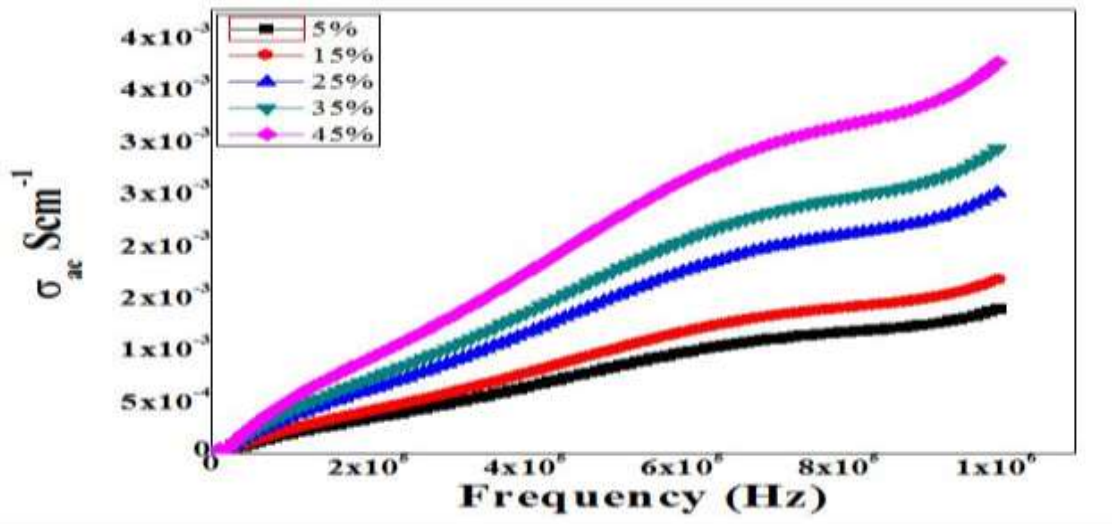

Fig. 3 AC conductivity of PANI/Co_3O_4 composites at different frequencies.

Dielectric behaviour

The dielectric behaviour (ε') as a function of frequency for PANI/Co_3O_4 composites with varying Co_3O_4 content is shown in figure 4. It can be observed that inclusion of Co_3O_4 metal oxides in PANI matrix has led to increase in the dielectric constant of the composites. The dielectric constant tends to increase in the composites with the increase in the concentration of the Co_3O_4. The highest dielectric constant was obtained for composites with 45% of Co_3O_4 concentration. It is well known that charges get accumulated at the interfaces, so in present case the charges or dipoles are expected to get accumulated at the PANI and Co_3O_4 interfaces due to their dielectric constants which can cause interfacial polarization. So due to strong polarization in PANI/Co_3O_4 composites due to the presence of charges will tend to improve the dielectric constant. Here it is interesting to note that the dielectric constant has almost same value up to 5×10^5 Hz frequency and thereafter tends to increase with the increase in the frequency. With the increase in frequency the accumulation of electrons particularly at grain boundaries is found to increase which will result in the increase in dielectric constant at higher frequencies.

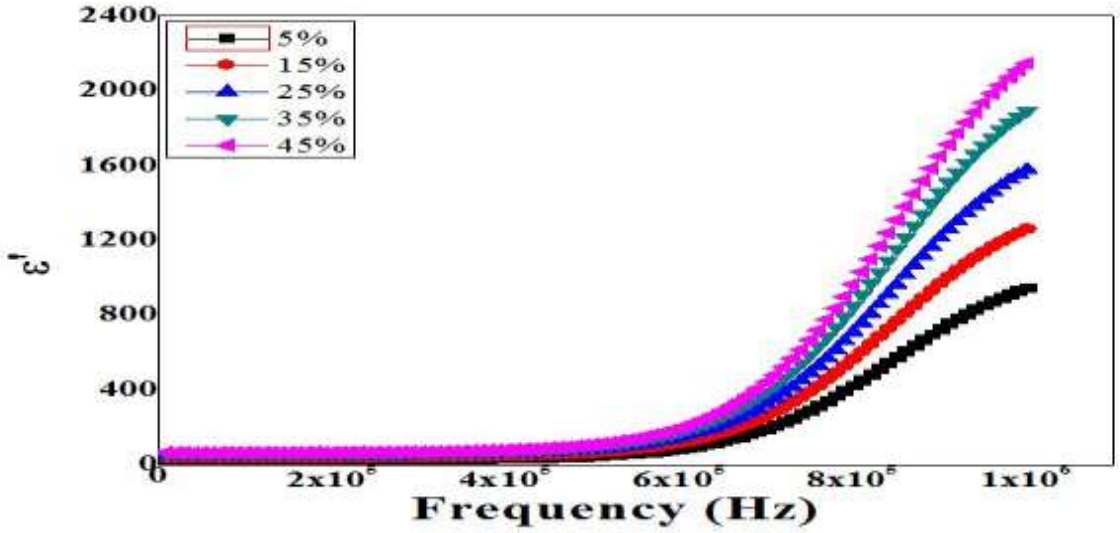

Figure 4: Variation of ε' for PANI/Co_3O_4 composites as a function of frequency for different Co_3O_4 content.

Thermal analysis

The thermograms of composites with different concentration of Co_3O_4 are shown in figure 5 (a) – (e). The thermograms were obtained in the temperature range of 30 to 1000°C. It is observed that the weight loss in the composites comprises of two stages of decomposition. The first stage of decomposition for 5% Co_3O_4 commences at 80°C with a weight loss of close to 14% suggesting weight loss due to vaporisation of moisture. While for 45% Co_3O_4composite the decomposition begins at 80°C but the weight loss when compared to that of 5% is just 3%. The second stage of decomposition begins at 210°C for all composites and ends around 800°C. At this stage this indicates the thermal degradation of polyaniline chains. It is found that with the increase in Co_3O_4 concentration in composite the thermal stability is found to increase which is attributed inclusion of more quantity of inorganic content. Further the thermal stability improvement is attributed to interaction between $Co_3O_4$and polyaniline. Out of all composites the one with highest Co_3O_4 concentration of 45% is found to be more stable than that of other composites.

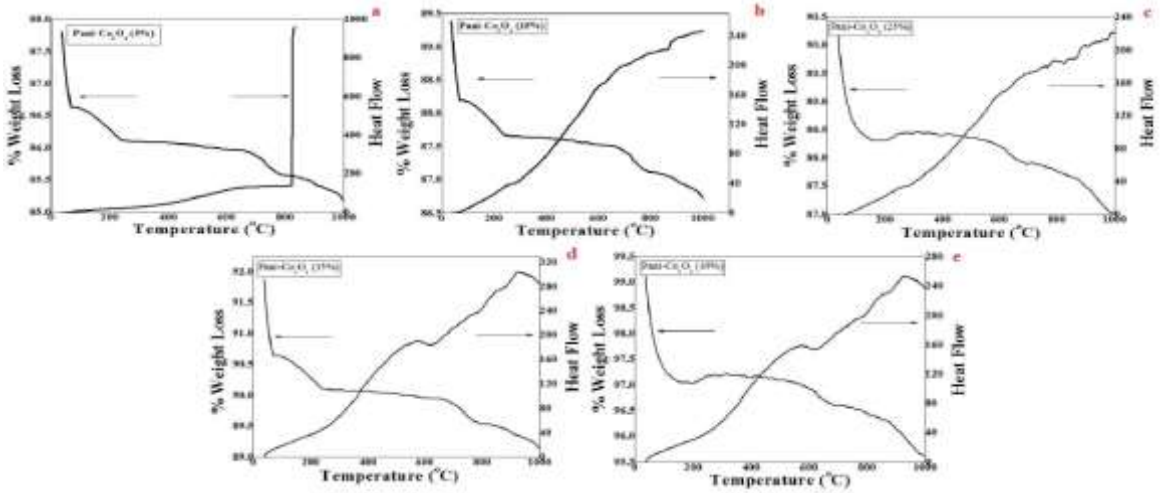

Fig. 5 Thermograms of PANI/Co_3O_4 composites: (a) 5, (b) 15, (c) 25, (d) 35 and (e) 45 wt% Co_3O_4 content.

IV. ACKNOWLEDGEMENT

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V. CONCLUSIONS

The following conclusions were drawn from the current study,

- PANI/Co_3O_4 composites with varying Co_3O_4 content from 5% to 45% have been successfully synthesized by ex situ polymerization technique.
- The composites showed higher conductivity values at higher frequencies due to hopping of charge carriers.
- Out of all, the composite with highest Co_3O_4 content of 45% was found to possess highest AC conductivity indicating charge transport as dominant mechanism.

- The composites with 35% and 45% Co_3O_4 contentdisplayed better thermal stability when compared to that of other composites.

VI.REFERENCES

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