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AC conductivity of Polyaniline/Mixed metal oxide (Pani/$NiCoFe_2O_3$) Composites

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Abstract

Intrusion of Mixed metal oxides with polymer enhances the properties and applications of polymer composites. Metal oxide composites (MOC) were prepared by microwave irradiation of different single metal oxides using a polyvinyl alcohol as a fuel. Nickle oxide (NiO), Cobalt (Co) and Ferrous oxide (Fe_2O_3) are used to form MOC. The conducting polymer (PANI/MOC) composites were synthesized by in-situ polymerization technique by mixing thoroughly grinded powder of MOC during the polymerization of aniline. The formation of mixed phases of the polymer together with the conducting emeraldine salt phase was confirmed by spectroscopic techniques like XRD, FTIR & SEM images indicated a systematic morphological variation of particles aggregated in the composite matrix as compared to the pure PANI. AC conductivity of these composites ware investigated in the frequency range 50 Hz to 5MHz. It is found that AC conductivity obeyed the variation of conductivity with wt% of MOC and could be related to conductivity relaxation phenomenon.

Keywords: Polyaniline, AC conductivity,

1. INTRODUCTION

Conducting polymers have become the foci of interest in materials science because of their unique electronic properties, which can be tailored via synthetic organic chemistry. The resulting PANI/MOC has specific electronic conduction ranging from insulating to semi conducting to highly conducting phase. The multiplicity of intra

and intermolecular vibrational modes in conjugated polymers are the key for the many exciting properties, leading to numerous technological applications, such as active electrode materials in energy storage [1]. Optoelectronic devices [2, 3], display devices [4, 5], corrosion inhibitors [6, 7], controller of electromagnetic radiations and electrostatic charge [8 - 11].The electrical transport in polymeric materials has become an area of increasing interest in research because of the fact that these materials have great potential for solid state devices [12, 13]. Conducting polymer composites with some suitable metal oxide compositions led to desirable properties [14-17]. These materials are especially important owing to their bridging role between the world of conducting polymers and that of nanoparticles. Understanding the effect of polymers/ MOC in enhancing the electrical conductivity is a long-standing problem and is of great importance due its potential application. The discovery of doping in conducting polymers has led to further dramatic increase in the conductivity of such conjugated polymers to values as high as 10^5 Scm-1. Among all conducting polymers, Polyaniline (PANI) achieved widespread importance because of its exceptional conduction mechanism and environment stability. The survey of literature reveals that the detailed conductivity studies on PANI/MOC are inadequate. In the present study, PANI and PANI/ MOC composite have been synthesized and the results on ac conductivity of these samples are reported.

2. EXPERIMENTAL

Chemicals used in our study are of analytical grade (AR). The monomer aniline was doubly distilled were used for synthesis of Polyaniline / $NiCoFe_2O_3$ MOC composites by single step in situ polymerization technique. 0.1M of aniline was dissolved in 1M of Hydrochloric acid to form aniline hydrochloride. Thoroughly grinded powder of $NiCoFe_2O_3$ is added in the weight percent of 10, 30 and 50 to the aniline hydrochloride solution with continuous stirring to keep $NiCoFe_2O_3$ suspended in the solution. To this reaction mixture, 0.1M of oxidizing agent ammonium persulphate [$(NH4)_2S_2O_8$] in 1M of Hydrochloric acid was added slowly with continuous stirring for 6 – 8 hrs at 0 – 5^0 C to polymerize. The precipitated powder was recovered, vacuum filtered and washed with deionized water. Finally, the resultant precipitate was dried in an oven for 24 hrs to achieve constant weight. In this way, three different PANI / $NiCoFe_2O_3$ MOC composites with different wt% (10, 30 and 50) in PANI have been synthesized [24-33]. The pellets of 10 mm diameter and thickness of 2 mm ware prepared by applying pressure of 10 Tons using Universal testing machine (model UTM-40). The pellets were coated with silver paste on either side of the surfaces and used for AC conductivity measurement in the frequency range 50 Hz to 5 MHz at room temperature using Hioki impedance analyzer, model 3532-50 (JAPAN) programmable LCR meter. The characterization studies are employed on all the synthesized PANI/MOC composites to confirm the presence of $NiCoFe_2O_3$ in PANI, three different samples of each composite varying in their weight percentage are investigated for their frequency dependent conductivity.

3. RESULTS AND DISCUSSIONS

Figure 1 shows the micrograph of pure PANI. The SEM micrograph of Polyaniline has clusters of spherical shaped particles with elongated chain.

Figure 2 and 3 shows the SEM micrograph of pure $NiCoFe_2O_3$ and Polyaniline–MOC composite (50wt % of MOC in PANI) respectively.

Figure 2 shows the micrograph of $NiCoFe_2O_3$. The image shows the metallic particle with crystalline cluster and few vacancies. Figure 3. reveals the presence of $NiCoFe_2O_3$ in polymer matrix, which is homogeneously distributed throughout the polymer sample. The presence of such mettallic crystals of MOC has a strong influence on various electrical parameters. The contrast in the images is due to the differences in scattering from different surface areas as a result of geometrical differences between Polyaniline and MOC

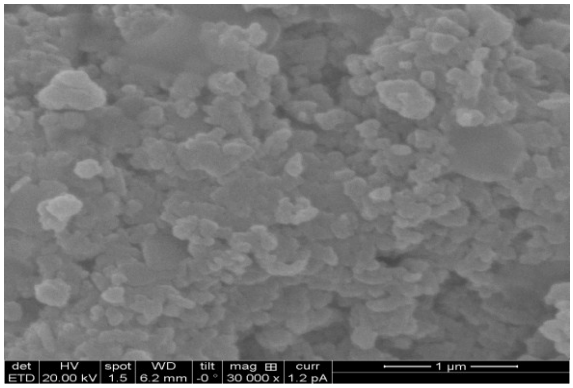

Figure 1: SEM Micrograph of Polyaniline

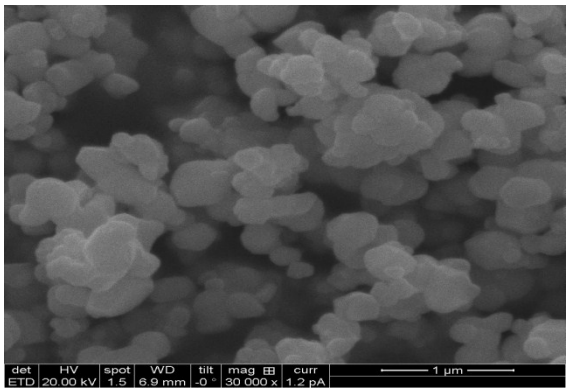

Figure 2: SEM Micrograph of pure – $NiCoFe_2O_3$

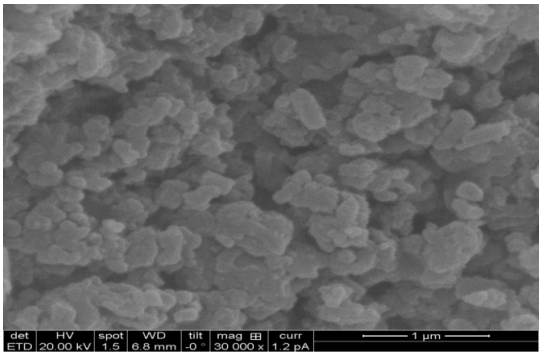

Figure 3: SEM Micrograph of Polyaniline – MOC composites (50wt %)

Figure 4 shows X-ray diffraction pattern of Polyaniline. Careful analysis of x-ray diffraction of Polyaniline suggests that it has amorphous structure with a broad peak centered on $2\theta \approx 25^0$. Figure 5 shows the X-ray diffraction pattern of $NiCoFe_2O_3$ and Figure 6 shows X-ray diffraction pattern of Polyaniline–$NiCoFe_2O_3$ MOC composite with 50wt % of MOC in Polyaniline. The resulting diffractogram shows a perfect crystalline structure due to the presence of MOC. It is observed by comparing X-ray diffraction pattern of composites with that of MOC, The comparison of XRD pattern of MOC and composite suggests that there is no change in the structure of MOC due to its dispersion in polyaniline during polymerization reaction.

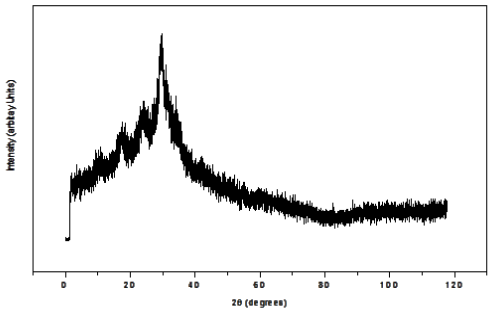

Figure 4. X-ray diffraction pattern of pure Polyaniline

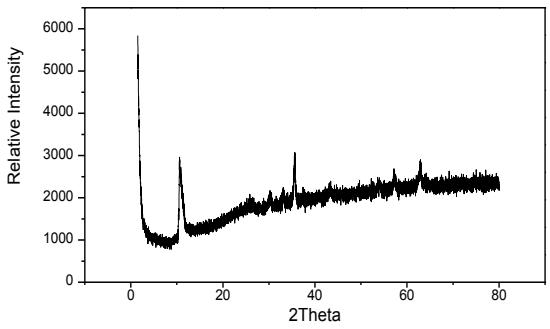

Figure 5: X-ray diffraction pattern of pure $NiCoFe_2O_3$

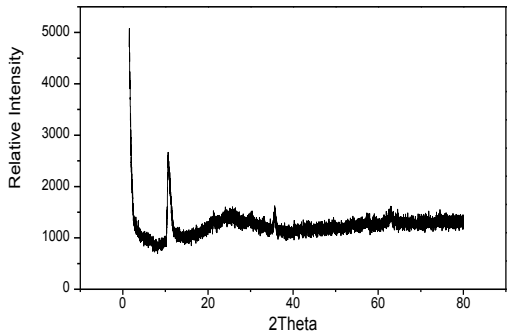

Figure 6: X-ray diffraction pattern of Polyaniline- MOC (50wt %)

Figure 7 shows IR spectra of pure Polyaniline where the percentage transmittance is plotted as a function of wave number (in cm^{-1}). Careful observation in the IR spectra reveals the presence of intensity peaks at 2322.42, 2039.90, 1780.70, 1537.79, 1403.15, 1230.34, 925.41, 833.13, 576.93, 552.64, 545.81 and 533.82 cm^{-1}. The spectrum shows the presence of characteristic stretching frequencies at 1780.70, 1537.79, 1403.15, 1230.34, 925.41cm^{-1}. The intensity peaks at 1537.79, 1403.15 and 925.41may be attributed due to the presence of C = N, N–H and C–N stretching frequencies. The occurrence of various bands in IR spectra may be attributed due to the following factors.

Frequency (cm^{-1})	**Observed band due to**
1610, 1593 and 1503	C = C stretching
1550 and 1500	C = N stretching
1040, 960 and 790	C – N stretching
1050	N – H bending deformation
726 and 1326	C – H bending deformation

The IR spectrum of pure MOC is shown in Figure 8. The important peaks is observed in MOC are 1001.3 and 532.32 cm^{-1} are due to the presence of M–M bond and M–O stretching frequencies respectively. The IR spectrum of polyaniline and MOC composites is shown in Figure 9. The characteristic stretching frequencies are observed at 1567.50, 1470.19, 1427.28, 1300.91, 1066.20, 979.73, 802.07, 689.89, 577.91, 569.96, 558.56, 547.26 and 538.79 cm^{-1}. The characteristic stretching frequencies are shifted toward higher frequency side indicates that homogeneous distribution of MOC particle in the polymeric chain. This may be attributed due to the Vander walls force of attraction between MOC and polymeric chain. The important peaks observed in case of polyaniline, MOC and polyaniline – MOC composites are listed in the following table.

Sample	**Observed band due to (cm^{-1})**
Pure Polyaniline	2322.42, 2039.90, 1780.70, 1537.79, 1403.15, 1230.34, 925.41, 833.13, 576.93,552.64, 545.81 and 533.82
Pure $NiCoFe_2O_3$	3388.92, 2358.71, 1001.3, 578.45, 574.09, 566.54, 562.7, 556.3, 550.93, 547.37, 543.63, 539.62, 535.43 and 532.32
Polyaniline – MOC composite	3042.63, 1567.50, 1470.19, 1427.28, 1300.91, 1066.20, 979.73, 802.07, 689.89, 577.91, 569.96, 558.56, 547.26 and 538.79

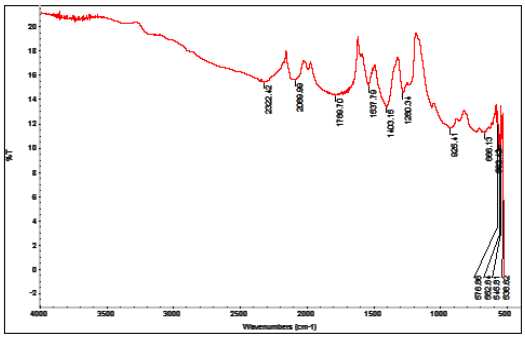

Figure 7. Infrared spectra of polyaniline,

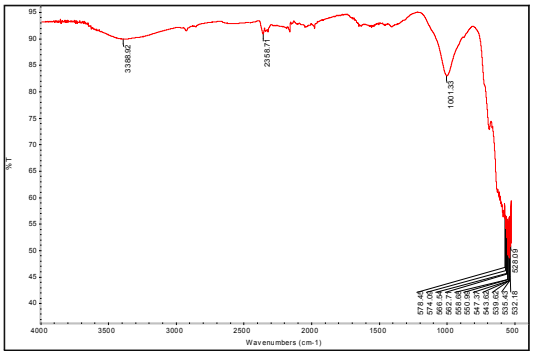

Figure 8: Infrared spectra of $NiCoFe_2O_3$

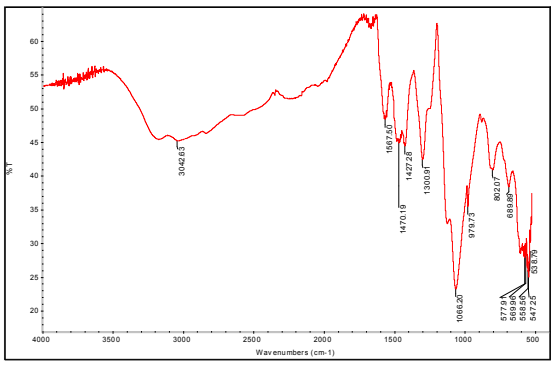

Figure 9. Infrared spectra of Polyaniline- MOC (50wt%)

Figure 10 shows the variation of AC conductivity (σ_{ac}) of pure polyaniline measured as a function of frequency in the range 10^2 Hz to 10^6 Hz. The conductivity increases with increase in frequency. The ac conductivity of Polyaniline exhibit two phases in the frequency range 10^2 Hz to 10^5 Hz. In frequency between 10^2 Hz to 10^4 Hz, the conductivity values are almost constant. The conducive increase suddenly in the frequency range 10^5 – 10^6 Hz. Lattice polarization around a charge in localized state may be responsible for multiple phases of conductivity in polyaniline. Localization occurs in the disordered regions owing to the one dimensional electronic nature of the polymer chains in these regions. The transport is then dominated by hopping and phonon-induced delocalization in the disordered regions, or even tunneling between metallic islands, depending on the morphology.

Figure 11 show the variation of AC conductivity (σ_{ac}) of Polyaniline – MOC composites (for three different wt%) measured as a function of frequency. It is observed that for 10wt% MOC in Pani shows saturated AC conductivity for all the frequencies, however, for 30wt% MOC in PANI shows two phase of conductivity, viz one saturated till the frequency of 100KHz and the thereafter an exponential increase in the AC conductivity (σ_{ac}) up to 5MHz. The anomaly in the conductivity behavior of these composites is contributed to the variation in the distribution of MOC in PANI. However, the AC conductivity for 50wt% MOC in PANI shows the reduced trend in compression with the AC conductivity of 30wt% MOC in Pani. This decrease in conductivity is contributed to trapping of hopping charge carriers.

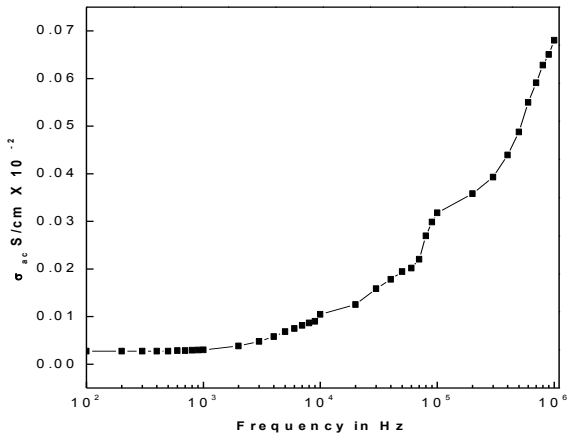

Figure 10: Variation of AC conductivity as a function of frequency for polyaniline

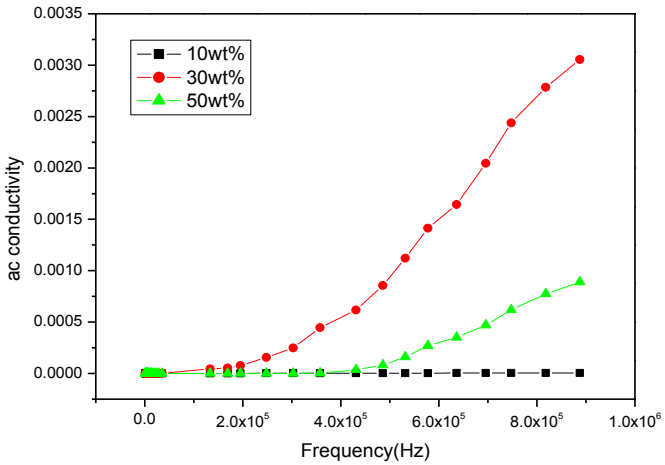

Figure 11: Variation of ac conductivity as a function of frequency for Polyaniline-MOC Composites

CONCLUSION

Polyaniline composites with different wt% of MOC in PANI were synthesized by in-situ polymerization of monomer aniline. Detailed characterizations of the composites were carried out using XRD, SEM and IR techniques. The result of XRD and SEM reveals the semicrystalline nature of the PANI / MOC composites. FTIR spectra shows the signature of MOC has been observed in the PANI / MOC. The results of AC conductivity show a strong dependence on the wt% of MOC in Polyaniline with anomaly at 30wt%. The values of conductivity of these composites are found be in the semiconducting range.

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