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AC Conductivity study on Polyaniline-Pr_2O_3 Composites

KEYWORDS: Polymeric materials, Oxidation, SEM, XRD, IR, Pr_2O_3

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ABSTRACT *Chemical route for the synthesis of polymer composites with oxide materials enhances the composite technology. Polyaniline (PANI) and Polyaniline- Pr_2O_3 (PANI- Pr_2O_3) composite material was prepared by insitu polymerization of aniline with Pr_2O_3 as composite material. Variation in the oxide composition with polymer matrix is maintained to know its detailed changes. The structural characterization of prepared composite materials and metal oxide material are carried out by X-ray diffraction (XRD), morphological study by Scanning Electron Micrograph (SEM) and bonding by Infrared (IR) study. Variation in Structural, morphology and bonding is observed in composite materials compared to Pr_2O_3 sample and PANI. The ac conductivity is also investigated in the frequency range 102–107 Hz at room temperature. The dimensions of Pr_2O_3 particles in the matrix have a greater influence on the observed ac conductivity values*

1. INTRODUCTION

Synthesis of polymer composites of core shell inorganic particle-polymer has attracted much research attention in recent years because its properties [1-2]. In particular, the composites of core shell metal oxide particles-conducting polymer combine the electrical properties of the polymer shell and the magnetic, optical, electrical or catalytic characteristics of the metal oxide core, which could greatly widen their applicability in the fields of catalysis, electronics and optics [3]. Many efforts have been made to successfully prepare composites such as Fe_2O_3.polypyrrole by chemical preparation and electrochemical method [4-5]. Besides the preparation of MO-Polymer, the synthesis of hollow conducting polymer capsules is expected to become much feasible by the chemical removal of the metal oxide core of the MO-Polymer. The resulting conducting polymer capsules with controllable hollow structure have shown promising prospective applications [6]. The challenge for the preparation of the MO-Polymer is how to generate the polymer coating uniformly and completely on the surface of the metal oxide core by a polymerization reaction in a solution phase. The key issue aims at slowing down the rate of polymerization and controlling the polymerization on the surface of the core rather than in the solution. The fabrication of MO-Polyaniline is particularly of interest because polyaniline (PANI) is one of the most important conducting polymers with high conductivity, ease of synthesis, and good environmental stability [7].

In this paper, we describe the synthesis of PANI and Pr_2O_3 dispersed PANI composite materials through oxidative polymerization of aniline. As prepared PANI and its Pr_2O_3 composite is well characterized by various characterization techniques. Ac conductivity study of the prepared PANI composite material is also well studied for its conductivity behavior.

2. EXPERIMENTAL

1.1. Materials and Methods

PANI and PANI composites were prepared by chemicals i.e Ammonium persulphate $(NH4)_2S_2O_8$, Hydrochloric acid (HCl), Aniline and Pr_2O_3 are of AR grade. Double distilled water was used in the synthetic process. In situ polymerization of aniline was carried out for PANI and Pr_2O_3 composite materials.

2.2. Synthesis of PANI- Pr_2O_3 Composites

0.1 M aniline was dissolved in 1M HCl to form aniline hydrochloride. Pr_2O_3 was added in the weight percent of 10, 20, 30, 40 and 50 to the above solution with vigorous stirring in order to keep the Pr_2O_3 material suspended in the solution. 0.1M of ammonium persulphate $[(NH_4)_2S_2O_8]$ as an oxidant was added slowly to the reaction mixture with continuous stirring for 4-6 hours at 0-5^{O}C. The precipitated powder recover was vacuum-filtered and washed with deionizer water. Finally, the resultant precipitate was dried in an oven for 24 hours to achieve a constant weight. Similarly five different PANI- Pr_2O_3 composites with different weight of Pr_2O_3 (10, 20, 30, 40 and 50) in PANI have been synthesized. Pure polyaniline was prepared by chemical oxidation of aniline without adding oxide [8].

2.3. Preparation of Pellets

Varied concentrations of prepared composites were pressed under pressure for its pellet form. The test samples to be used were prepared in pellet form of diameter 10mm and thickness 3mm by applying pressure of 7t using Pye-Unicam dye. The contacts for these composites were made using silver paste as electrodes on both sides.

2. RESULTS AND DISCUSSION

X-ray diffraction

Figure 1(a) Shows X-ray diffraction pattern of Polyaniline. Careful analysis of X-ray diffraction of polyaniline suggests that it has semi-crystalline nature with a broad peak centered around $2\theta \approx 27^0$. XRD spectra of pure PANI, shows a broad reflection at lower Bragg angle 2θ value of 25.38° corresponding to (200) diffraction plane of ES-I structure of HCl doped PANI.

Figure 1 (b) shows the X-ray diffraction pattern of Polyaniline - Pr_2O_3 composite (50 wt % of Pr_2O_3 In PANI). By comparing the XRD pattern of composite with that of Pr_2O_3 (JCPDS No. 47-1111) the prominent peaks corresponding to 2θ = 26.75 ^{0}56.09 are due to (100), and (100) planes of Pr_2O_3. By comparing the XRD patterns of the composite and Pr_2O_3, it is confirmed that Pr_2O_3 has retained its structure even though it is dispersed in PANI during polymerization reaction

The SEM micrograph of polyaniline & Polyaniline – Pr_2O_3 composite with 50 wt % of Pr_2O_3 in polyaniline is shown in figure 2.The composites possess grains and porous structure. Further the composites have capillary pores connected by pores. Such composites are likely to facilitate the adsorption of water vapors due to the large surface area and capillary pores [9]. The presence of such sharp crystals of Pr_2O_3 has a strong influence on various electrical properties such as conductivity and dielectric behavior of these composites.

Figure 3(a) shows the IR spectra of Polyaniline where the transmittance is plotted as a function of wave number (cm

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[1]). Careful analysis of the spectra from the figure reveals the presence of intensity peaks 1578 cm^{-1}, 1486 cm^{-1}, 1300 cm^{-1}, 1239 cm^{-1} ,1140 cm^{-1} and 880cm^{-1} ,819cm^{-1} , 707cm^{-1} , 516 cm^{-1}. The spectra show the presence four intense bands at 1578 cm^{-1}, 1480 cm^{-1}, 1300 cm^{-1} and 1239 cm^{-1}. The intense peaks at 1578 cm^{-1} and 1486 cm^{-1} may be attributed due to the presence of quinoid rings. The FTIR spectra of the thin film confirmed the presence of amino group [10].

The IR spectra of polyaniline – Pr_2O_3 composite (50 wt % of Pr_2O_3 in PANI) is shown in figure 3(b). The prominent peaks that are observed in polyaniline – Pr_2O_3 composite are 1572 cm^{-1}, 1486 cm^{-1}, 1307 cm^{-1}, 1251 cm^{-1}, 1146 cm^{-1},880 cm^{-1} ,819 cm^{-1} 707 cm^{-1} ,596 cm^{-1} and 504 cm^{-1} . By careful observation of IR the characteristic stretching frequencies are considerably shifted towards higher frequency side. The data suggest that, there is a Vander walls kind of kind of interaction between the polymeric chain and Pr_2O_3.

4.2.4.1. Polyaniline

Figure 4(a) shows the variation of ac conductivity as a function of frequency for polyaniline. 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 and 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 [11].

Figure. 4(b) show the variation of ac conductivity as a function of frequency for polyaniline – Pr_2O_3 composites (for different weight %). It is observed that in all the cases, σ_{ac} almost remains constant up to10^5 Hz. and there after increases. The anomaly in the conductivity behavior of these composites is due to the variation in the distribution of Pr_2O_3 in polyaniline.

Figure. 4(c) shows the variation of σac as a function of weight % of Pr_2O_3 in polyaniline at three different frequencies and at room temperature. It is observed that in all the composites, the conductivity slightly increases up to 20wt%, then decreases up to 30wt % of Pr_2O_3 in polyaniline and then increases up to 50wt %. This may be due to the extended chain length of polyaniline, which facilitate the hopping of charge carriers when the content of Pr_2O_3 is up to 20wt %. Further the decrease in conductivity for 30wt % is attributed due to the trapping of charge carrier hop.

Conclusion

In this paper ac conductivity of PANI- Pr_2O_3 composites in the frequency range 10^2-10^7have been presented. Results clearly demonstrate that conducting PANI composite with Pr_2O_3show better ac conductivity and observed that 50 wt% Pr_2O_3 in PANI shows maximum ac conductivity. These composites may be used for the technological development

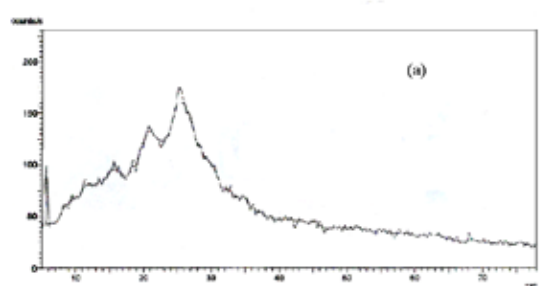

Figure 1(a). X – Ray diffraction pattern of Polyaniline

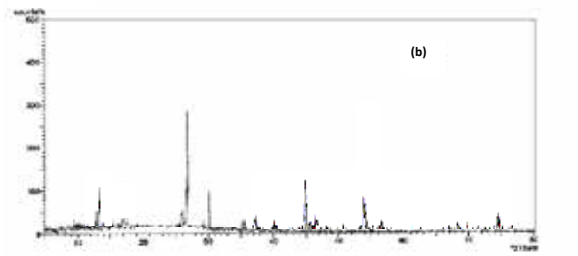

Figure 1(b). X – Ray diffraction pattern ofPANI/ Pr_2O_3(50wt%)

Figure : 2(a) FTIR spectra of pure PANI

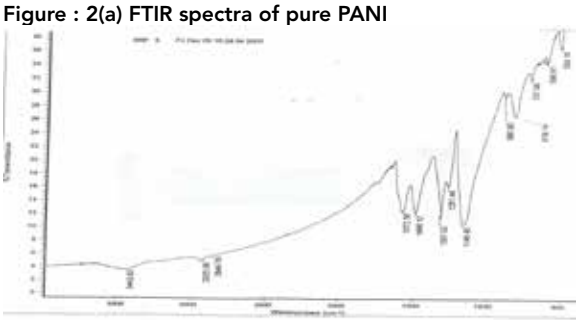

Figure : 2(b) FTIR spectra of PANI - Pr_2O_3 composite (50 wt%)

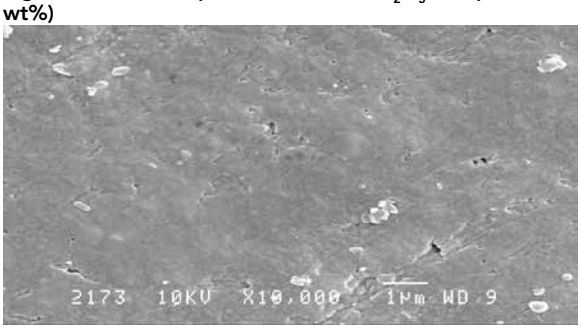

Figure 3(a) SEM Micrograph of Polyaniline

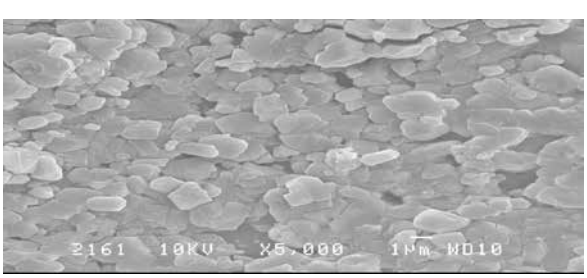

Figure: 3(b) SEM Micrograph of Polyaniline - Pr_2O_3 (50 wt %)

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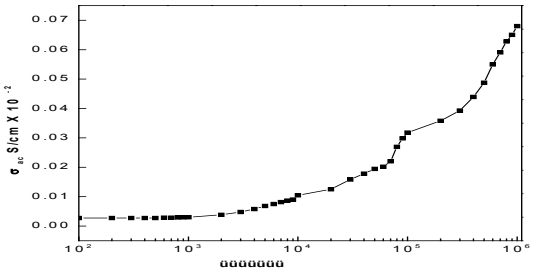

Figure 4(a) Variation of ac conductivity as a function of frequency for polyaniline

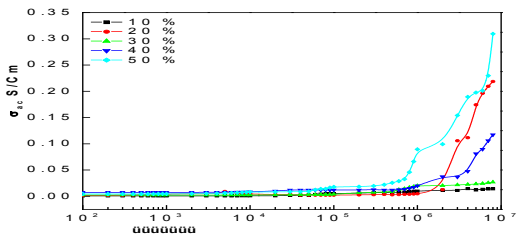

Fig 4(b) Variation of ac conductivity as a function of frequency for Polyaniline- Pr_2O_3 composites

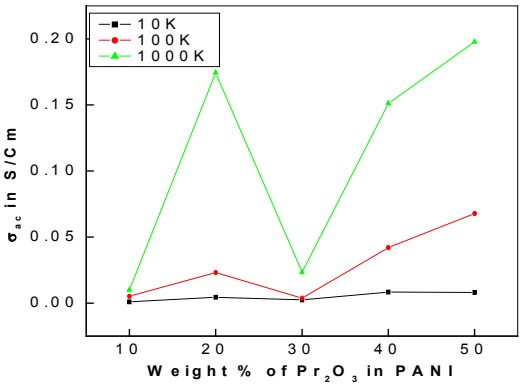

Fig 4(c) Variation of ac conductivity as a function of wt % for Polyaniline Pr_20_3 at different frequencies

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