Synthesis, transport and dielectric properties of polyaniline/Co$_3$O$_4$ composites

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Abstract. Conducting polyaniline/cobaltous oxide composites have been synthesized using *in situ* deposition technique by placing fine graded/cobaltous oxide in polymerization mixture of aniline. The a.c. conductivity and dielectric properties are studied by sandwiching the pellets of these composites between the silver electrodes. It is observed that the values of conductivities increase up to 30 wt% of cobaltous oxide in polyaniline and decrease thereafter. Initial increment in conductivity is due to extended chain length of polyaniline where polarons possess sufficient energy to hop between favourable sites. Beyond 30 wt% of cobaltous oxide in polyaniline, blocking of charge carriers takes place reducing the conductivity values. It can be noted that the value of dielectric constant increases up to 10 wt% of cobaltous oxide. Thereafter, it decreases up to 30 wt% of cobaltous oxide and again increases up to 40 wt% of cobaltous oxide and decreases thereafter. The observed behaviour is attributed to the variation of a.c. conductivity. And it is observed that the dielectric loss increases up to 10 wt% of cobaltous oxide in polyaniline, decreases to a lower value of 20 wt% of cobaltous oxide and increases to 35 wt% and thereafter decreases. These values go in accordance with the values of dielectric constant. The results obtained for these composites are of greater scientific and technological importance.

Keywords. Transport properties; polyaniline; cobaltous oxide; composites.

1. Introduction

The conducting polymers have emerged as a new class of materials because of their unique electrical, optical and chemical properties. By proper doping the conductivity of these materials can be varied from semiconducting to metallic regime, which has offered new concept of charge transport mechanism. Conductive polyaniline (PANI) has been studied extensively because of its ease of synthesis in aqueous media, its environmental stability and special electrical and other properties. PANI has become a suitable candidate for a variety of technological applications (Matsunaga *et al* 1990; Gustafsson *et al* 1992; Olcani *et al* 1993) such as solar cells, electromagnetic shielding, electrodes for rechargeable batteries, sensors, etc. Preparation of composites of conducting polymer (PANI) has been considered to provide a suitable solution to the processibility problem. These composites have the ability to enhance their material properties with desirable mechanical and physical characteristics. One way of making these composites involves synthesizing the conductive polymer inside the matrices of conventional polymers using chemical (Mohammadi *et al* 1993; Chakraborty *et*

al 1999) or electrochemical (Niwa and Tamamura 1984; Wang *et al* 1990) polymerization. There are many reports pertaining to the chemical preparation of conductive polymer composites without using any insulating polymers (Gill *et al* 1992; Maeda and Armes 1995). The most preferred method for synthesis of PANI composites is to use either HCl or H$_2$SO$_4$ with ammonium peroxydisulfate as an oxidant (MacDiarmid *et al* 1985; Armes and Miller 1988). In these approaches, monomer is polymerized in the presence of commercially available inorganic acid particles which act as colloidal substrate for the precipitating polymer nuclei leading to the formation of conducting polymer–inorganic oxide composite.

2. Experimental

2.1 *Materials and methods*

All chemicals used were of analytical reagent (AR) grade. The monomer aniline was doubly distilled prior to use. Ammonium persulphate ((NH$_4$)$_2$S$_2$O$_8$), hydrochloric acid (HCl) and cobaltous oxide (CO$_3$O$_4$) (Sigma) were used as received. 0·1 mol of aniline was dissolved in 1 M HCl to form polyaniline (PANI). Cobaltous oxide was added to PANI solution with vigorous stirring in order to keep the

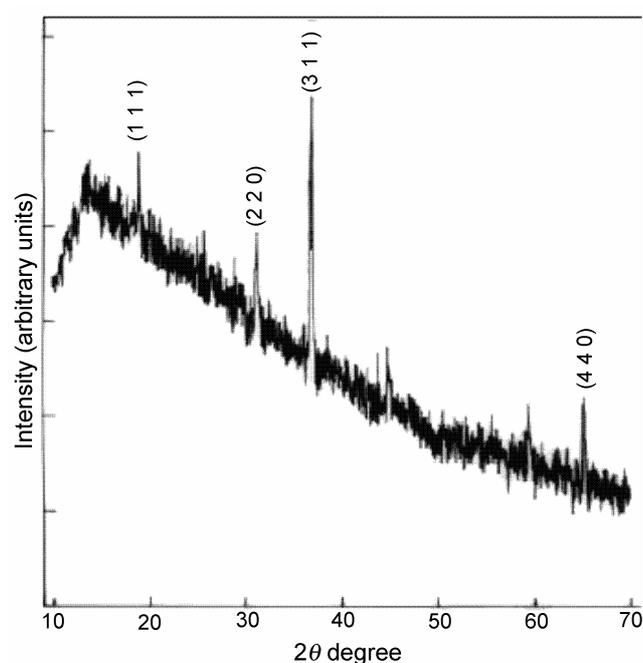*Author for correspondence (prasad1_amb@rediffmail.com)

cobaltous oxide suspended in the solution. To this reaction mixture, 0·1 M of ammonium persulphate which acts as the oxidant was added slowly with continuous stirring for 4–6 h at 0–5°C. The precipitated powder recovered was vacuum filtered and washed with deionized water. Finally, the resultant precipitate was dried in an oven for 24 h to achieve a constant weight.

The FTIR spectra of the samples were recorded on a Perkin-Elmer 1600 spectrophotometer in KBr medium. X-ray diffraction studies were performed by using Philips X-ray diffractometer with Cu K_α as the radiation source. The powder morphology of the composites in the form of pellets was investigated using Philips XL 30 ESEM scanning electron microscope (SEM).

3. Results and discussion

Figure 1 shows XRD pattern of the composite having 50 wt% cobaltous oxide in polyaniline. In this figure, sharp peak is observed at about 30–40°. There are new peaks attributed in composite due to the presence of cobaltous oxide. It is observed that there is homogenous distribution of cobaltous oxide in PANI, which is confirmed by SEM photographs.

The typical IR spectra of PANI/Co_3O_4 composite is shown in figure 2. From the figure the IR spectra is observed at higher sensitivity in the region of interest i.e. 1600–500 cm^{-1}. Further the intensities of some of the peaks, e.g. 1560, 1480, 1290, 1130 and 807 cm^{-1}, are affected by the presence of Co_3O_4 during PANI synthesis. These differences in the IR spectra can be explained on the basis of constrained growth and restricted modes of vibration in PANI grown in the presence of Co_3O_4. In such a case, the aniline monomer gets absorbed on the oxide particles, which were dispersed in the reaction mixture and the polymerization proceeds initially on the surface of these oxide particles when $(NH_4)_2S_2O_8$ (ammonium per sulphate) is added to the solution. This leads to adhesion of the polymer to the Co_3O_4 particles and this explains the constrained growth around these particles. As a result, the characteristic stretching frequencies are shifted towards lower frequency side, as compared with pure PANI. Hence, there is a kind of weak Van der Waals force of attraction between the polymer chain and the cobaltous oxide.

Figure 3 displays the scanning electron micrograph of PANI/CO_3O_4 composite. The SEM of polyaniline synthe-
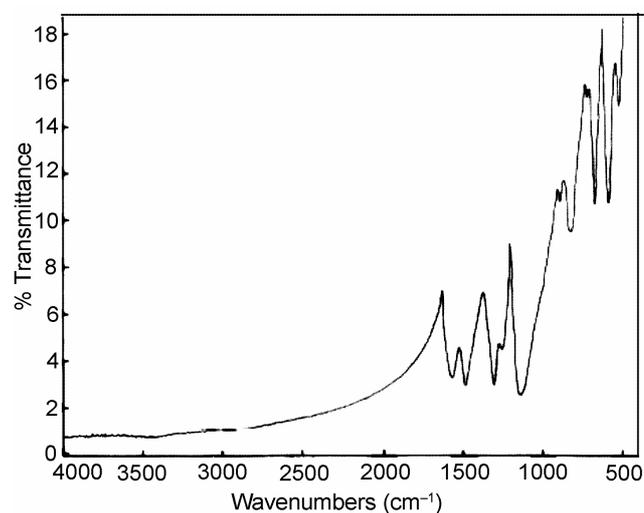
Figure 2. Infrared spectroscopy of polyaniline–cobaltous oxide composite (50 wt%).

**Figure 1.** X-ray diffraction of polyaniline–cobaltous oxide composite (50 wt%).
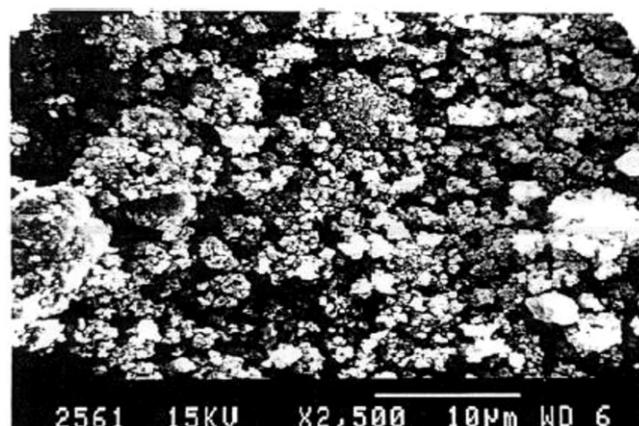
Figure 3. Scanning electron micrograph of polyaniline–cobaltous oxide composite (50 wt%).

sized by chemical oxidative method shows the presence of microcrystallites which are uniformly distributed as shown in figure 3. This is confirmed from the XRD studies. It is observed from this figure that the cobaltous oxide is uniformly dispersed in the polyaniline matrix.
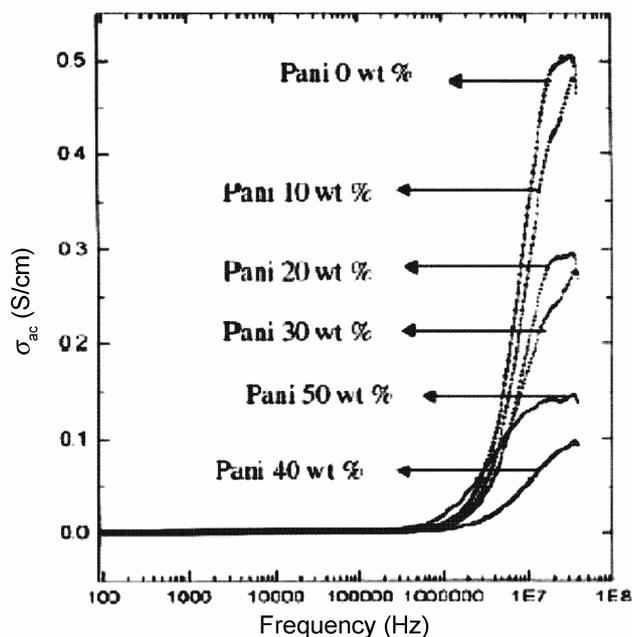
Figure 4. Variation of a.c. conductivity as a function of frequency for pure polyaniline and Co_3O_4 composite (different wt%).
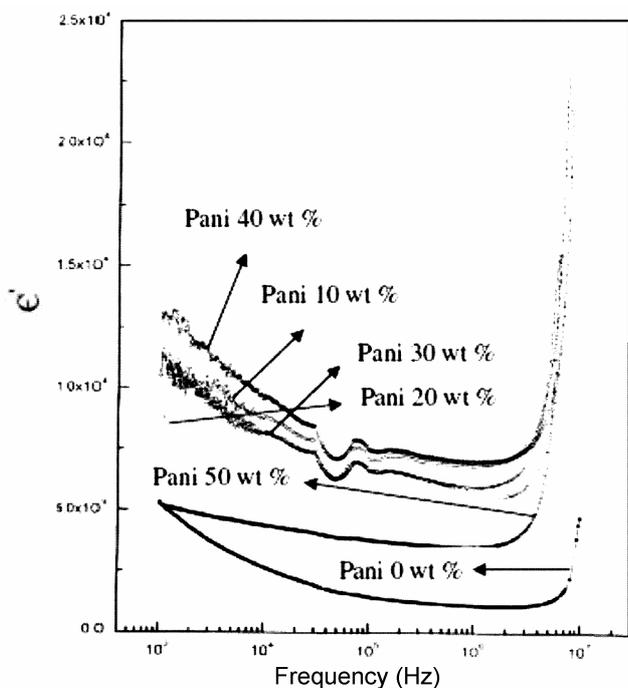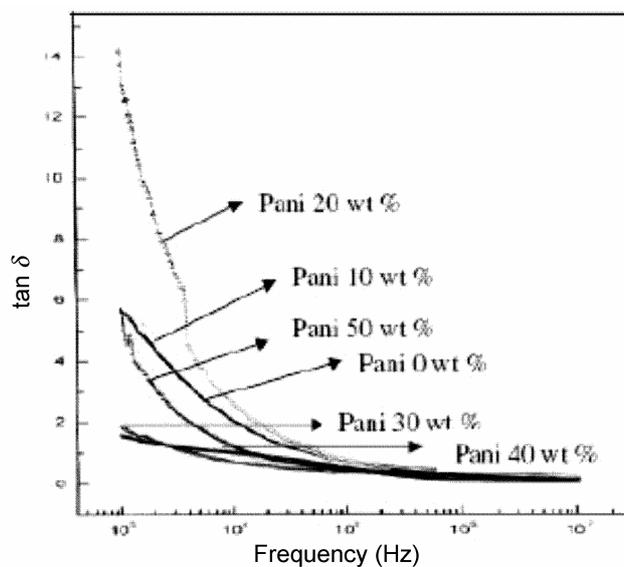

Figure 5. Variation of frequency for pure polyaniline and Co_3O_4 composite (different wt%).

Figure 4 shows variation of a.c. conductivity as a function of frequency for pure polyaniline and Co_3O_4 composite (different wt%). It is observed that in all the cases, $\sigma_{a.c.}$ remains constant up to about 1 MHz and then increases rapidly thereafter. At higher frequencies beyond 1 MHz, the conductivity increases because of contribution of polarons, which are moving along smaller and smaller distances in the polymer chain. Increased $\sigma_{a.c.}$ at higher frequencies is denoted by the charge motion in the amorphous region and this supports the presence of isolated polarons in this region. An in depth study is required to understand the anomaly in conductivity behaviour with respect to wt% of Co_3O_4 in polyaniline at molecular level using theoretical simulation techniques.

Figure 5 shows variation of dielectric constant as a function of frequency for pure polyaniline and Co_3O_4 composite (different wt %). It is observed that at low frequencies dielectric constant was found to decrease with increasing frequency. And then above 1 MHz dielectric constant is found to increase with increase in frequency, which is the characteristic feature of disordered materials. This could be due to the fact that ions are unable to oppose the effects of the field and/or tightly pinned to the polymer chain.

Figure 6 shows variation of dielectric loss as a function of frequency for pure polyaniline and Co_3O_4 composite (different wt%). It is observed that the dielectric loss tangent in case of polyaniline and its composite decreases as a function of frequency. Both polyaniline and its composites exhibit small value of dielectric loss at higher frequency. Therefore, these samples of polyaniline and its composites are used in the present study.

Figure 6. Variation of dielectric loss as a function of frequency for pure polyaniline and Co_3O_4 composite (different wt%).

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