

Synthesis, characterization and electrical properties of polyaniline/SrTiO₃ composites

AMEENA PARVEEN¹, ANIL KUMAR KOPPALKAR²,
M. REVANASIDAPPA³ and M.V.N AMBIKA PRASAD^{2*}

Department of Physics¹, Department of Materials Science²,
Gulbarga University, Gulbarga - 585 106 (India).
Department of Chemistry³, PES School of Engineering, Bangalore (India).

(Received: March 10, 2009; Accepted: April 12, 2009)

ABSTRACT

In the present work, synthesis of Polyaniline (PANI) is carried out by chemical oxidation method by using ammonium persulphate as an oxidant. PANI- SrTiO₃ composites were synthesized by using various weight percentages (10, 20, 30, 40 and 50wt %) of SrTiO₃ in PANI by insitu polymerization. The composites are characterized by using various techniques such as XRD and SEM. XRD micrographs indicate that SrTiO₃ is homogeneously distributed in the PANI. SEM micrograph indicates that PANI / SrTiO₃ have many aggregated pores. The Dielectric constant and Dielectric tangent loss are studied by sandwiching the pellets of these composites between the silver electrodes. It is observed that dielectric constant decreases with increasing frequency where as at higher frequencies dielectric constant remains constant. PANI and its composites exhibit small value of dielectric loss at higher frequency. The AC conductivity is studied in the frequency range from 10²Hz-10⁶Hz. From these studies it is found that, AC conductivity remains constant at lower frequency and increase rapidly at higher frequency, which is characteristics behaviour of disordered materials. Hence, this composite finds applications such as sensor devisees.

Key words: Polyaniline (PANI); Polyaniline composites (PANI/ SrTiO₃); Transport properties.

INTRODUCTION

Conducting polymers, more commonly known as, synthetic metals possess a striking ability of getting switched 'on' and 'off'. It is possible to switch between conducting and insulating stages by virtue of doping and undoping, which can be attained by applying electric potentials. The novel concept that plastic can be fabricated into wires, films and other accessories carrying electric current is fascinating, if scientists can regulate the electrical, mechanical, and optical properties of these substances. Thus these conducting polymers have tremendous potential for making of many application devices. The studies on these conducting polymers has offered many advantages in today's industries in the field of synthetic metals because of its versatile applications right from rechargeable

storage battery, sensors to artificial muscles¹. The most consequential application of conductive polymers is the development of sensors for biochemical species. A bio-sensor is an analytical tool assembling a biological or biologically derived component. Thus this development of effective sensing devices for industrial process control and environmental monitoring is a fast growing need. Also in recent years, the synthesis and characterization of electro-active polymers have become important research area in Polymer Science². Polyaniline (PANI) is one of the most promising amongst conductive polymers because of inexpensive monomer, ease of synthesis, good environmental stability, moderately high value of dc conductivity and excellent chemical stability in conductive form³⁻¹¹. It can be prepared either by a chemical or an electrochemical oxidative

polymerization. The electrical insulator form of polyaniline is the emeraldine base consisting of two amine nitrogen atoms followed by two amine nitrogen atoms. Polyaniline emeraldine base can be converted into a conducting form by two different doping processes: the protonic acid doping and the oxidative doping. Protonic acid doping of emeraldine base corresponds to the protonation of the amine nitrogen atoms in which there is no electron exchange¹². In the oxidative doping, emeraldine salt is obtained from leucoemeraldine through electron exchanges¹³. Organic polymer Ceramic composites have also received a greater attraction in today's industry. The dielectric composites are made up of an active ceramic phase embedded in a passive polymer. The properties of these composites depend on the connectivity of the phases, volume percent of ceramic, and the spatial distribution of the active phase in the composite. The concept of connectivity developed by Neunhham¹⁴ describes the arrangement of the component phases within a composite. Many excellent reviews on the processing and properties of Piezoelectric /polymer composites have been reported in the last few years¹⁴⁻¹⁵.

The present work is thus an investigation of the electrical properties of PANI / SrTiO₃ Composites.

EXPERIMENTAL

Material and Synthesis

Ammonium peroxi-di-sulphate and Aniline used were of AR grade. Strontium Titanate (SrTiO₃) is commercially procured from Sigma Aldrich. The monomer aniline was synthesized chemically by oxidative polymerization of aniline in an aqueous HCl solution. Aniline (0.1M) was dissolved in 1M aqueous HCl solution before 5°C and an aqueous solution of Ammonium peroxi-disulphate (0.1 M) was added to the above solution over a period of 30 min with vigorous stirring and it is added to polyaniline (PANI) solution in order to keep SrTiO₃ suspended in the solution. This process of treatment with the solvents was repeatedly done for three hours. The precipitated was finally obtained after the filtrate was dried in vacuum oven at 60-80°C for 24 h so as to achieve a constant weight. Further, PANI/SrTiO₃ composites were prepared in weight

percent ratio in which the concentration of SrTiO₃ (10, 20,30,40,50 wt %) was varied. The test samples were prepared in the forms of pellets of diameter 10mm and thickness 2mm by applying pressure of 5-6 tones using hydraulic pressure. The pellets thus obtained are coated with silver paste on both the surfaces.

Characterization instruments

The X-ray diffraction patterns were recorded for these materials with CuK α radiation of wavelength $\lambda=1.5420 \text{ \AA}$ in the 2θ range 8-90°. The powder morphology of polyaniline and its composites sintered in the form of pellets are investigated using Philips XL30 ESEM scanning electron microscope (SEM).

Conductivity measurement

The frequency dependent AC conductivity of PANI and PANI/SrTiO₃ composites are studied in the frequency range 10^2 Hz - 10^6 Hz at room temperature using Hiokie LCR Q meter Japan. The Dielectric constant and Dielectric tangent loss are also studied by sandwiching the pellets of these composites between the silver electrodes and is studied in the frequencies 10^2 Hz - 10^6 Hz , using Hiokie LCR Q meter Japan.

RESULTS AND DISCUSSIONS

Figure 1 shows the X-ray diffraction pattern for PANI and PANI/SrTiO₃ composite. The XRD diffraction studies of the samples were found that the peaks are broadened and were possible due to the formation of oxide particles. By comparing the XRD patterns of the PANI / SrTiO₃ composite, it is confirmed that SrTiO₃ has retained its structure even though it is dispersed in PANI during polymerization reaction. The structure of the composite resembles with that of cubic system with $a=b=c=3.936 \text{ \AA}$ and $a = b = c = 90^\circ$. Prominent four peaks of PANI/SrTiO₃ correspond to (110), (111), (200) and (211). (No. 40-1500, 1997 JCPDS- International Centre for Diffraction Data. PCPDFWIN. V 1.30). The SEM study performed on these samples indicates many aggregated particles and pores that have been reduced due to the homogeneous distribution of strontium titanate in PANI/ SrTiO₃ composites as shown in Fig. 2a) and 2b).

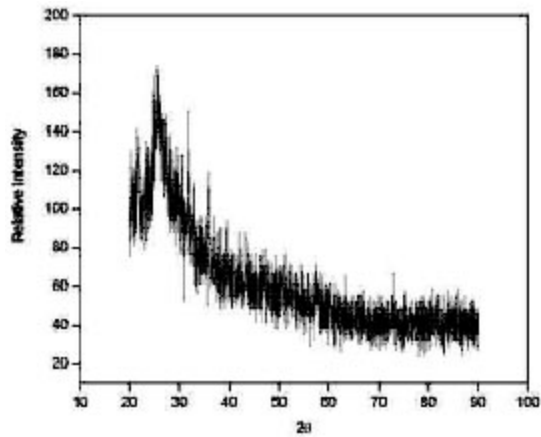


Fig. 1(a): XRD Pattern of pure PANI

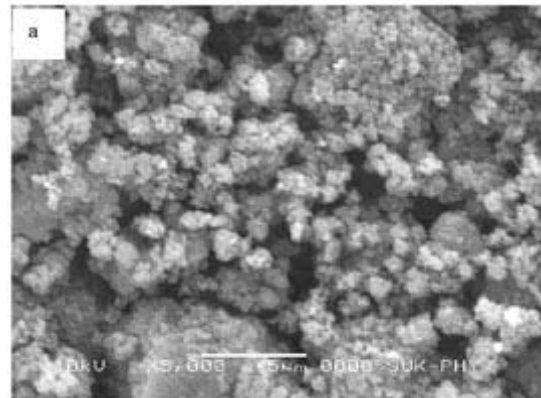


Fig. 2(a): SEM image of PAN

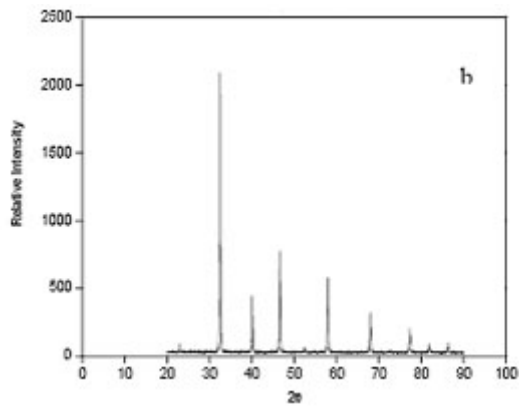


Fig. 1(b): XRD Pattern of pure SrTiO₃

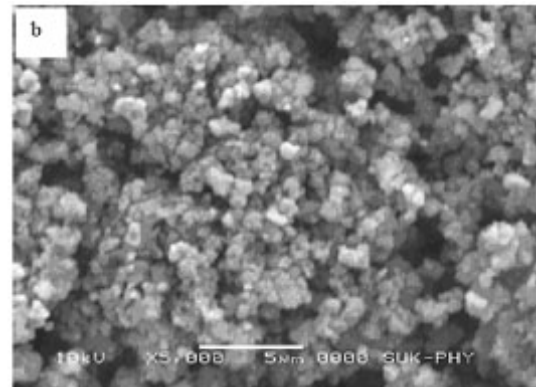


Fig. 2(b): PANI/SrTiO₃ (50wt%)

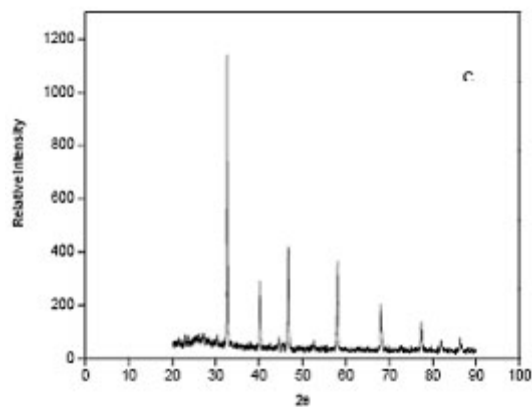


Fig. 1(c): XRD Pattern of pure PANI/SrTiO₃ (50wt%)

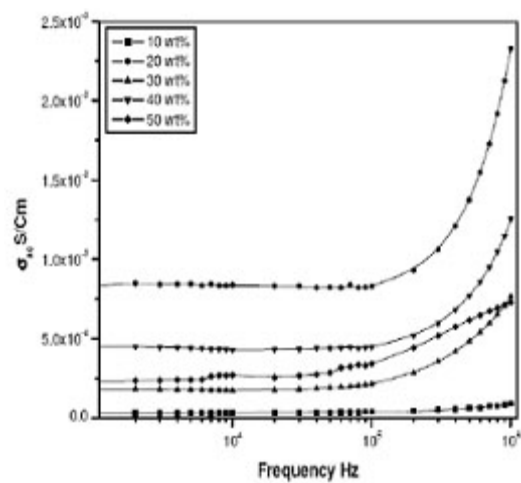


Fig. 3(a): Shows the AC conductivity versus frequency for different weight percentages SrTiO₃ in PANI

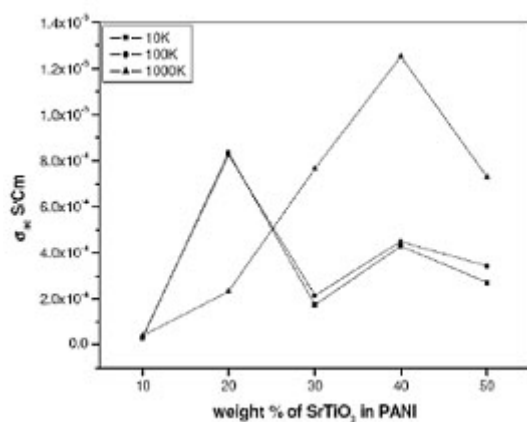


Fig. 3(b): Shows the AC conductivity versus weight percentages of SrTiO_3 in PANI for different frequency

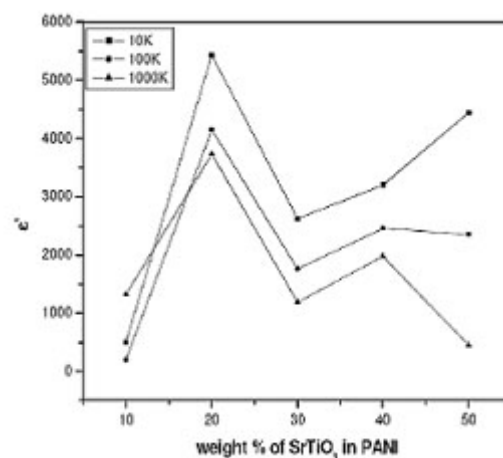


Fig. 4(b): Shows the variation of dielectric constant (ϵ') as function of weight percentage at different frequency

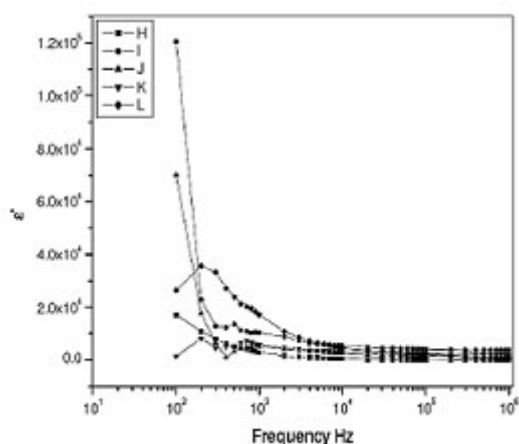


Fig. 4(a): Shows the variation of dielectric constant (ϵ') as function of frequency

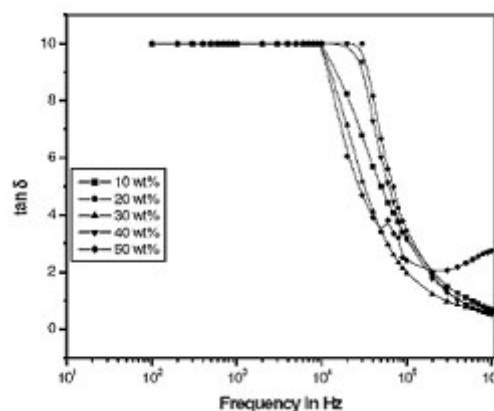


Fig. 5: Shows the variation of $\tan \delta$ as function of frequency for PANI/ SrTiO_3 composites of different weight percentages

AC Conductivity

Fig 3(a) illustrates the AC Conductivity of PANI/ SrTiO_3 composites. It is found that AC conductivity remains constant up to 10^6Hz and there after it increases steeply, which is a characteristics feature of disordered materials. In Fig. 3(b) the values of σ_{ac} are plotted as a function of different weight percentage of SrTiO_3 in PANI at room temperature with different frequencies (10 KHz, 100K Hz and 1000 KHz). It is observed that for all

the frequencies, the value of σ_{ac} is found to increase for 20 wt% and 40 wt%, and decrease for 30 wt% and 50 wt%. The initial increase in the value of σ_{ac} is due to the extended chain length of PANI, between which the localized charge carriers polarons under going polarization significantly leading to increase in conductivity. As the wt% of SrTiO_3 exceeds more than 20 or 40 wt% the partial blocking of polarons takes place, which makes the polarization condition more difficult, as a result, the conductivity decreases.

Dielectric constant

Fig. 4 (a) shows the variation of dielectric constant ϵ' with frequency for different wt% of PANI/SrTiO₃ composite. It is found that dielectric constant decreases as frequency increases. Figure 4 (b) shows the variation of dielectric constant as a function of weight percentage of SrTiO₃ in PANI. It is found that the dielectric constant increases for 20wt% and 40 wt% for all the frequencies (10, 100 and 1000 KHz). This means that at higher frequencies they behave as dielectric materials. The dielectric tangent loss (tand) as a function of frequency for PANI and PANI/SrTiO₃ is shown in Figure 5 for the different wt%. It is observed that the dielectric loss decreases as a function of frequency. PANI and PANI/ SrTiO₃ exhibit small value of dielectric loss at higher frequencies, which suggests that these materials are lossless materials beyond 10⁶ Hz. The observed behaviour is consistent with the conductivity and dielectric constant results in these composites.

CONCLUSION

The efforts have been made to synthesize Polyaniline /SrTiO₃ composite to tailor these properties. Detail characterizations of the composites were carried out using XRD and SEM techniques. The result of AC conductivity and dielectric constant shows a strong dependence on weight percentage of SrTiO₃ in PANI.

ACKNOWLEDGEMENTS

The authors express sincere thanks to Department of Physics, Gulbarga University, Gulbarga for providing basic facilities and also to Prof A. Venkataraman and Dr. R.L. Raibagkar of Department of Materials Science, Gulbarga University, Gulbarga. I acknowledge my thanks to Prof. B.K. Chougale and Prof A.V. Rao, Department of Physics, Shivaji University, Kolhapur for their kind support.

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