Research Paper

Volume : 2 | Issue : 5 | May 2013 • ISSN No 2277 - 8179

Synthesis, and Dielectric Study of Polyaniline / Cr_2O_3 Composites

Physics

KEYWORDS : conductivity; polyaniline composites; Cr_2O_3 ; dielectric permittivity

Samba Siva Rao Gorthi Department of Physics, CMJ University, Shillong, Meghalaya, India

Ameena Parveen Department of Physics, Government First Grade College, Guirmetkal, Karnataka, India

ABSTRACT

The PANI/Cr_2O_3 composites have been synthesized with various compositions viz., 05, 10, 15, 20 and 25 wt % of Cr_2O_3 in PANI. The ac conductivity was studied in the frequency range 102 – 106 Hz. It is observed from the ac conductivity studies that the ac conductivity is found to be constant up to 105 Hz and there after it increases steeply which is a characteristic feature of disordered materials. The dielectric behavior was also investigated in the frequency range 102 – 106 Hz. It is observed from the dielectric studies the value of dielectric constant increases up to 15 wt % and later it decreases. Similarly the imaginary dielectric constant increases up to 15 wt %, further it decreases rapidly up to 25 wt %. It is seen that the tan δ values increases up to 15 wt % and then decreases thereafter. At higher frequencies these composites exhibit almost zero dielectric loss the dimensions of Cr_2O_3 particles in the matrix have a greater influence on the conductivity values and the observed dielectric values.

1. Introduction

Conducting polymers have made significant impact upon a number of different technologies since their introduction over twenty years ago. Applications range from optical and electrical devices (photovoltaics, transistors, batteries, etc) to antistatic packaging and various coating applications (membranes, shielding etc.) [1]. More recently, conductive polymers have been utilized as an effective medium for chemical sensing. A variety of conductive polymers have been evaluated using microelectronic devices, such as chemiresistors (interdigitated array transducers), quartz crystal microbalances (QCMs) and field-effect transistors (FETs). Examples of these studies include that of Kunugi et al. who utilized a specially modified QCM for making electrical and microgravimetric measurements of the uptake of alcohols onto polypyrrole thin films [2], and of Josowicz and Janata who investigated the measurements of work function changes using a polypyrrole-coated FET for the detection of lower aliphatic alcohols [3]. Several companies, including Neotronics [4] and AromaScan [5], manufacture 'electronic noses' comprised of arrays of chemiresistor-based conductive polymer sensors.

The electrical transport in polymeric materials [6-7] has become an area of increasing interest in research because of the fact that these materials have great potential for solid state devices. Similarly, conducting polymer composites have attracted considerable interest in recent years because of their numerous applications in variety of electric and electronic devices. Conducting polymer composites with some suitable compositions of one or more insulating materials led to desirable properties [8]. These materials are especially important owing to their bridging role between the world of conducting polymers and that of nanoparticles. For application of conducting polymers, knowing how these conducting polymer composites will affect the behavior in an electric field in a long-standing problem and of great importance. The discovery of doping in conducting polymer has led to further dramatic increase in the conductivity of such conjugated polymers to values as high as 105 Scm-1.

Among all conducting polymers, polyaniline (PANI) achieved widespread importance because of its unique conduction mechanism and environment stability. The survey of literature reveals that the detailed conductivity studies on PANI/Cr_2O_3 are scarce. In the present study, PANI and PANI/Cr_2O_3 composite (with varying weight percentage of chromium oxide in polyaniline) have been synthesized and studies have been made on the the on AC conductivity as well as dielectric properties of PANI/Cr_2O_3 composites.

2. Experimental

Aniline (AR grade) was purified by distillation before use and ammonium per sulphate $[(NH_4)_2S_2O_8)]$, HCl were used as received. 0.1 mole aniline monomer is dissolved in 1 mole hydrochloric acid to form polyaniline. Fine graded pre-sintered chromium oxide (AR grade, SD-Fine Chem.) powder in the weight percentages (wt %) of 05, 10, 15, 20 and 25 is added to the polymerization mixture with vigorous stirring in order to keep the chromium oxide powder suspended in the solution. To this reaction mixture, $[(NH_4)_2S_2O_8)]$ which is used as an oxidant is added slowly drop-wise with continuous vigorous stirring for the period of 4-6 hours at temperature 0-50 C. Polymerization of aniline takes place over fine grade chromium oxide particles. The resulting precipitate is filtered under suction and washed with distilled water until the filtrate becomes colorless. Acetone is used to dissolve any unreacted aniline. After washing, the precipitate is dried under dynamic vacuum at 60-800C for 24 hrs to get resulting composites. In this way, five different polyaniline chromium oxide composites with different weight percentage of chromium oxide (05, 10, 15, 20 and 25) in polyaniline have been synthesized. All the composites are crushed into fine powder in an agate mortar in the presence of acetone medium. The composite powder so obtained is pressed to form pellets of 10mm diameter and thickness which varies from 2 to 2.75 mm. The electrical measurements on these samples were made using the silver paint as electrodes on both sides. AC conductivity measurements as well as dielectric property investigation were carried out at room temperature over frequency range 102-106 Hz using Hioki impedance analyzer 3532-50 (Japan). The characterization of polyaniline and its composites by spectroscopic methods is important, as it gives information not only about various molecular-levels interactions but also on the type of charge carriers.

3. Results and discussion

Electrical measurements are known to be very sensitive for the study of electronic properties of materials. In amorphous systems, DC conductivity measurements are used to study the localization of electronic states, while AC conductivity measurements provide useful information concerning various relaxation phenomenon related to the electrical polarization process. In high frequency measurements, the characteristic hopping lengths and hopping rates of carriers between localized states can be determined. The low frequency data are however, more sensitive to slower relaxation process like the reorientation of dipoles, etc. In the latter case most relaxation process can be explained by the Debye theory of energy loss for dipole relaxations [9]. It is well known fact that frequency dependent complex conductivity in case of disordered materials such as polymers can arise from interfacial polarization at contacts, grain boundaries and other inhomogeneities present in sample [10].

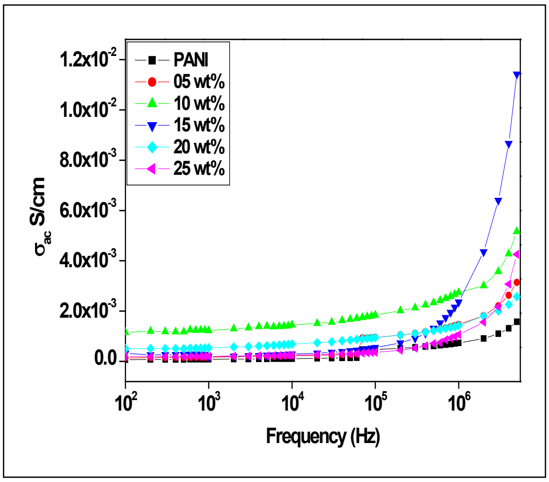

Fig.1. Variation of σ ac as a function of frequency for PANI – Cr_2O_3 composites.

Fig. 1 shows the variation of AC conductivity (σac) as a function of frequency for PANI/Cr_2O_3 composites (different wt %). It is observed from Fig 1. that in all the composites σac remains constant up to 105 and thereafter increases steeply, which is characteristic feature of disordered materials. At higher frequencies, σac increases because of contribution of polarons, which are moving along smaller and smaller distances in a polymer chain. Increase of σac at higher frequencies is due to the charge motion in the amorphous region and this supports the presence of isolated polarons in this region.

Fig. 2 shows the variation of σac as a function of wt % of Cr_2O_3 in polyaniline at two different frequencies and at room temperature. It is observed that in all the composites the conductivity increases up to 15 wt % of Cr_2O_3 in polyaniline and then decreases rapidly for 20 and 25 wt

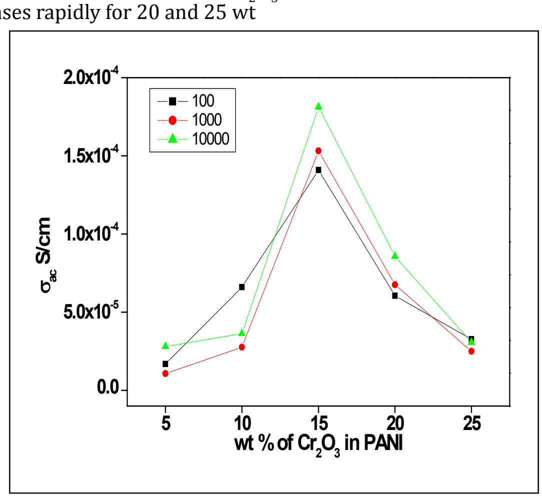

Fig.2. Variation of σ ac as a function of wt % of Cr_2O_3 at different frequencies.

%. This may be due to the extended chain length of polyaniline which facilitate the hopping of charge carriers when the content of Cr_2O_3 is up to 15 wt %. Further decrease in conductivity for 20 and 25 wt % may be attributed due to the trapping of charge carrier hop.

Dielectric materials – or, as they are also called, dielectrics – are such a media that has an ability to store, not conduct, electrical energy. A measure for this property is the permittivity or dielectric constant of the material. In fact, permittivity is only a higher-level invention to calculate approximately the electric response of matter. Matter – although electrically neutral – is composed of charged elements. The ideal dielectric does not allow the electrons to be carried around by the electric field. Instead, the force that an applied field exerts on charges displace these from their equilibrium positions, in which case there is a net displacement of positive charges in the direction of the electric field and electrons in the opposite direction. The separation of charges is equivalent to a dipole moment and the polarizability is a measure for the relation between dipole moment and electric field. Fig. 3 represents the variation of dielectric constant (ε′) as a function of wt % of Cr_2O_3 at room temperature and at two different frequencies. It is observed that initially the values of dielectric constant increases up to 15 wt % and later it increases. ε′ exhibits high value at low frequency corresponding to bulk static dielectric constant εo and then decreases with increase in frequency, finally forming low value around 106 Hz, which may be attributed to Debye-like relaxation mechanism [17, 18]. The variation of imaginary dielectric constant with wt % of Cr_2O_3 for PANI/Cr_2O_3 composites is shown in fig. 4. It is clear from this figure that the imaginary dielectric constant deceases up to 10 wt %. Further it increases rapidly up to 15 wt % and decreases slowly up to 25 wt %. Imaginary dielectric constant ε′′ is high at low frequency with changing concentration and this may be due to electric charges being displaced inside the polymer and / or their lower concentration [19]. Two possible causes may exist. The first one is increase in the counteranion size that led to an increasing interchain distance, which makes hopping between chains more difficult and hence resulting in reduction in conductivity. Another possible assumption depends on the changing concentration of Cr_2O_3. All these results go in accordance with the conductivity behavior. The observed change in conductivity is mainly responsible for the anomaly in the dielectric constant behavior of these composites.

.

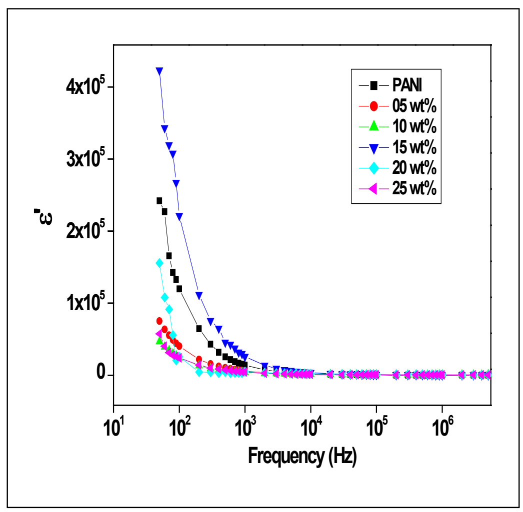

Fig.3. Variation of ε′ as a function of wt % of Cr_2O_3 at different frequencies.

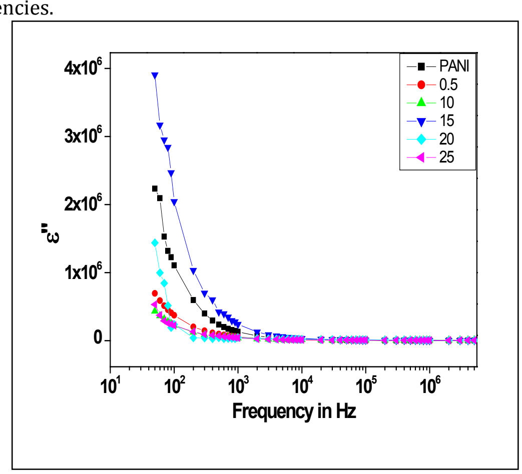

Fig.4. Variation of ε′′ as a function of wt % of Cr_2O_3 at different frequencies.

Volume : 2 | Issue : 5 | May 2013 • ISSN No 2277 - 8179

Fig. 5 shows the variation of tan δ as a function of wt % of Cr_2O_3 in polyaniline at room temperature and at two different frequencies. It is seen from the fig. 5 that the tan δ values decreases upto 30 wt % and then increases thereafter. At higher frequencies these composites exhibit almost zero dielectric loss which suggests that these composites are lossless materials at frequencies beyond 1 MHz. The observed behavior is consistent with conductivity and dielectric constant results in these composites.

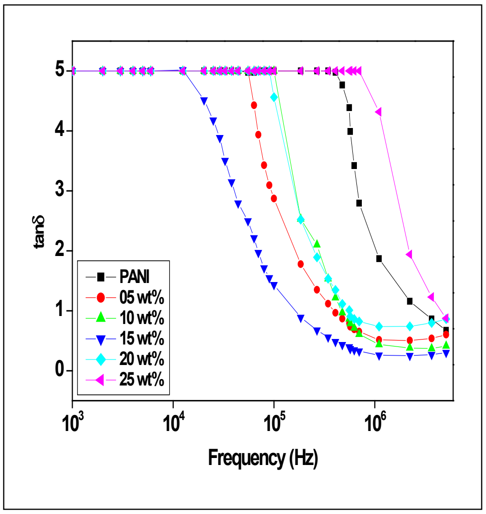

Fig.5. Variation of tan δ as a function of wt % of Cr_2O_3 at different frequencies

4. Conclusion

Efforts have been made to synthesize polyaniline - Cr_2O_3 composites to tailor make their properties. The results of AC conductivity as well as dielectric property show a strong dependence on the wt % of Cr_2O_3 in polyaniline.

REFERENCE

[1]. D.O. Cowan and F.M. Wlygul, Chem. Eng. News, 64 (1986) 28. | [2]. Y. Kunugi, K. Nigorikawa, Y.Harima and K. Yamashita, J. Chem. Soc., Chem. Commun., (1994) 873. | [3]. M. Josowicz and J. Janata, Anal. Chem., 58 (1986) 514. | [4]. T.C. Pearce, J. W. Gardner, S. Friel, P.N. Bartlett and N. Blaur, Analyst, 118 (1993) 371. | [5]. J. V. Hatfield, P. Neaves, P.J. Hicks, K. Persaud and P. Travers, Sensors and Actuators B, 18 – 19 (1994) 221. | [6]. R. Singh, R.P. Tandon, V.S. Panwar, S. Chandra, J. Appl. Phy. 64 (4) (1991) 2504. | [7]. S. Kivelson, Phys. Rev. Lett. 46 (1981) 1344. | [8]. S.C. Raghavendra, S. Khasim, M. Revanasiddappa, M.V.N. Ambika Prasad, A.B. Kulkarni, Bull. Mater. Sci. 26 (7) (2003) 733. | [9]. N.F. Mott, E.A. Davis, Electron Process in Non-linear Materials. | [10]. M. Raghu, S.V. Subramanyam. Phy. Rev. B 43 (1991) 4236. | [11]. N.J. Pinto, A.A. Acosta, G.P. Sinha, F.M. Aliev, Synth Met. 113 (2000) 77. | [12]. A.N. Papthanassiou. I. Sakellis, J. Grammatikakis, E. Vitoratos, S. Sakkopoulos, E. Dalas, Synth Met 142 (2004) 81. | [13]. M.G. Han, S.S. Im, J. Appl. Polym Sci. 82 (2001), 2760. |