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FREQUENCY – DEPENDENT CONDUCTIVITY AND DIELECTRIC PERMITTIVITY OF POLYANILINE / Y_2O_3 COMPOSITES

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ABSTRACT

Conducting polyaniline/Yattrium oxide (PANI/Y_2O_3) composites have been synthesized by insitu deposition technique by placing fine graded Y_2O_3 in polymerization mixture of aniline. The PANI/ Y_2O_3 composites have been synthesized with various compositions viz., 10,20,30,40 and 50 wt % of Y_2O_3 in PANI. The ac conductivity was studied in the frequency range 10^2 – 10^6 Hz. It is observed from the ac conductivity studies that the ac conductivity is found to be constant up to 10^5 Hz and there after it increases steeply which is a characteristic feature of disordered materials. The dielectric behaviour was also investigated in the frequency range 10^2 – 10^6 Hz. The dimensions of Y_2O_3 particles in the matrix have a greater influence on the conductivity values and the observed dielectric values.

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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.) (Cowan and Wlygul, 1986). 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 (Kunugi *et al.*, 1994), 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 (Josowicz and Janata, 1986). Several companies, including Neotronics (Pearce *et al.*, 1993) and AromaScan (Hatfield *et al.*, 1994), manufacture 'electronic noses' comprised of arrays of chemiresistor-based conductive polymer sensors. The electrical transport in polymeric materials (Singh *et al.*, 1991; Kivelson, 1981) 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 (Raghavendra *et al.*, 2003). 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 polymer 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 unique conduction mechanism and environment stability. The survey of literature reveals that the detailed conductivity studies on PANI/ Y_2O_3 are scarce. In the present study, PANI and PANI/Y2O3 composite (with varying weight percentage of Yattrium oxide in polyaniline) have been synthesized. In the present work we report the study on AC conductivity as well as dielectric properties of PANI/ Y_2O_3 composites.

MATERIALS AND METHODS

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 Yattrium oxide (AR grade, SD-Fine Chem.) powder in the weight percentages (wt %) of 10, 20, 30, 40 and 50 is added to the polymerization mixture with vigorous stirring in order to keep the Yattrium 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 0-5^0 C. Polymerization of aniline takes place over fine grade Yattrium 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 un-reacted aniline. After washing, the precipitate is dried under dynamic vacuum at 60-80^{0}C for 24 hrs to get resulting composites. In this way five different polyaniline Yattrium oxide composites with different weight percentage of Yattrium oxide (10, 20, 30, 40 and 50) 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 is pressed to form pellets of 10mm diameter and thickness which varies from 2 to 2.65 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 10^2-10^6 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.

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 (Mott and Davis). 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 (Raghu and Subramanyam, 1991).

Composites (different wt %). It is observed that in all the cases AC conductivity remains constant up to 10^5 and thereafter increases steeply, which is characteristic feature of disordered material. At higher frequencies, AC increases because of contribution of polarons, which are moving along smaller and smaller distances in a polymer chain. Increase of AC conductivity 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 AC conductivity as a function of wt % of Y_2O_3 in polyaniline at two different frequencies and at room temperature.

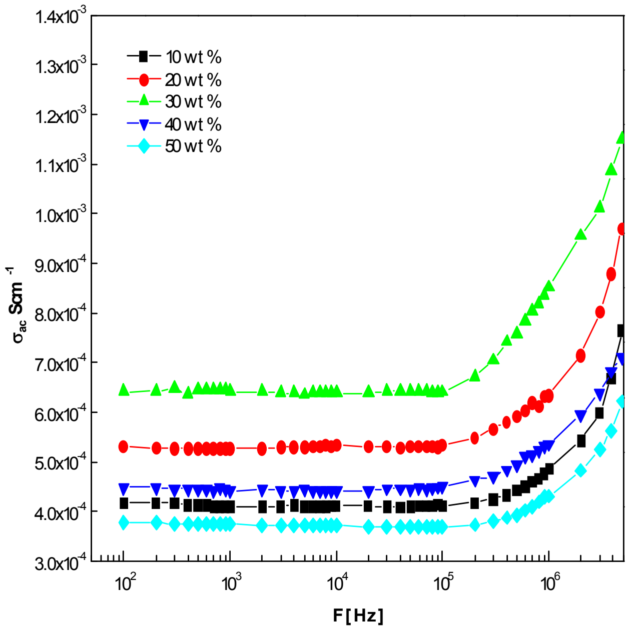

Fig.1. Variation of σ_{ac} as a function of frequency of Polyaniline – Y_2O_3 composites

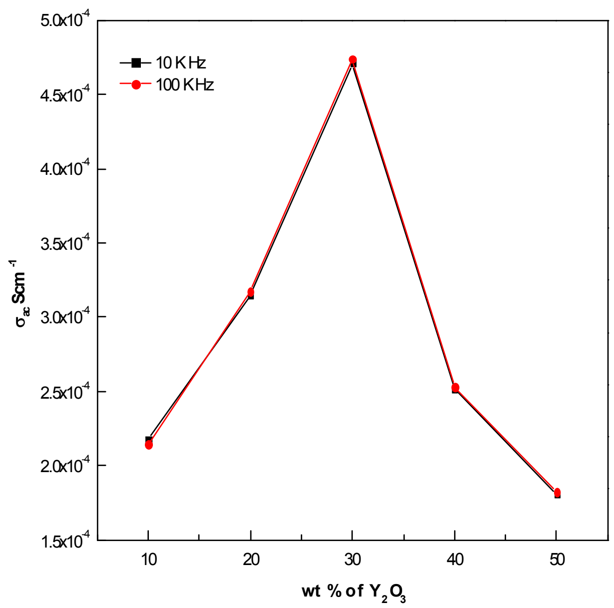

Fig.2. Variation of σ_{ac} as a function of wt % of Y_2O_3 at different frequencies

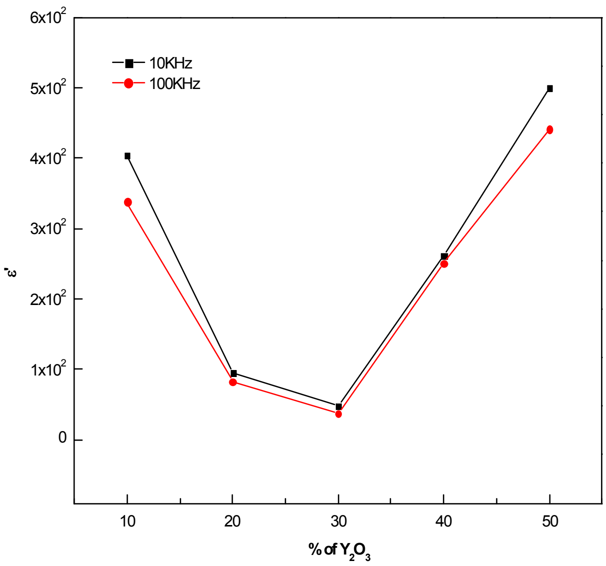

Fig.3. Variation of ε′ as a function of wt % of Y_2O_3 at different frequencies

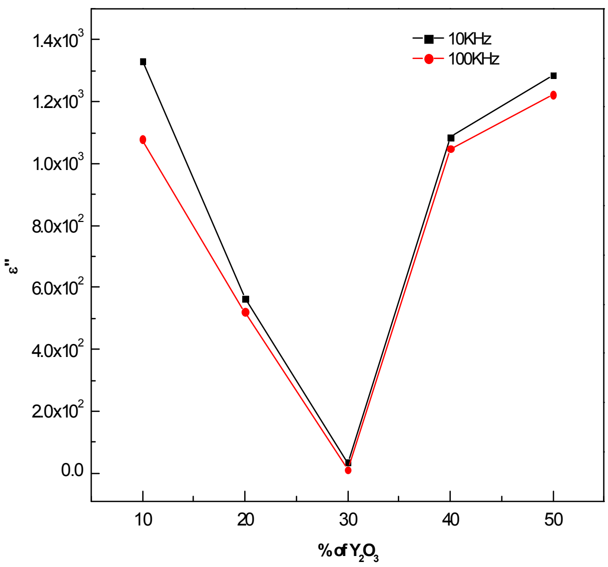

Fig.4. Variation of ε′′ as a function of wt % of Y_2O_3 at different frequencies

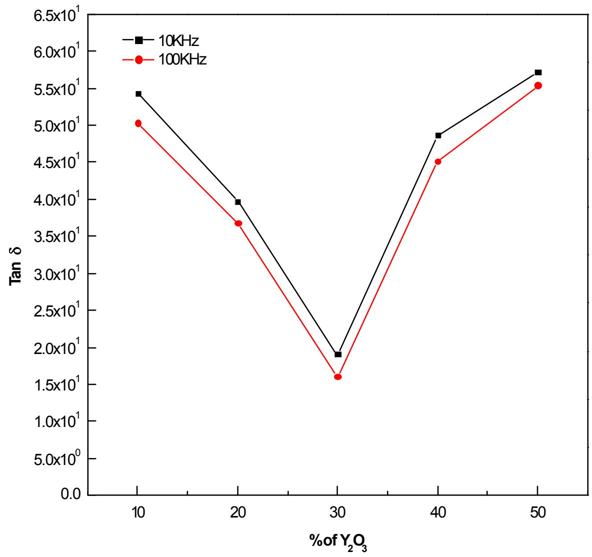

Fig.5. Variation of tan δ as a function of wt % of Y_2O_3 at different frequencies

It is observed that in all the composites the conductivity increases up to 30 wt % of Y_2O_3 in polyaniline and then decreases rapidly for 40 and 50 wt %. This may be due to the extended chain length of polyaniline which facilitate the hopping of charge carriers when the content of Y_2O_3 is up to 30 wt %. Further the decrease in conductivity for 40 and 50 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 ε′ as a function of wt % of Y_2O_3 at room temperature and at two different frequencies. It is observed that initially the values of dielectric constant decreases up to 30 wt % and later it increases. The variation of imaginary dielectric constant with wt % of Y_2O_3 for PANI/ Y_2O_3 composites is shown in fig. 4. It is clear from this figure that the imaginary dielectric constant slowly deceases up to 30 wt % and further it increases rapidly. 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.

As a function of wt % of Y_2O_3 in polyaniline at room temperature and at two different frequencies. It is seen 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.

Conclusion

Efforts have been made to synthesize polyaniline - Y_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 Y_2O_3 in polyaniline.

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