Conductivity of surface modified TiO$_2$ dope nanocomposites

CrossMark

S.C. Nagaraju [a,b], Aashis S. Roy [c], G. Ramgopal [d,*]

[a] *Department of Physics, Bharathiar University, Coimbatore, Tamil Nadu, India*
[b] *Department of Physics, Vidyavahini College, SIT Extn., Tumkur, Karnataka, India*
[c] *Horizon School, Sindhanur, Raichur, Karnataka, India*
[d] *Department of Physics, Maharani's Science College, Palace Road., Bangalore, Karnataka, India*

ABSTRACT

Dielectric properties of TiO$_2$ nanoparticles doped *O*-chloropolyaniline nanocomposites have been prepared using Camphorsulfonic acid. The prepared composites were characterized by FTIR for structural studies, SEM and TEM for surface morphology. The characteristic peaks of benzeniod ring, quiniod ring and M—O bending confirm the formation of nanocomposites. TEM image shows that the TiO$_2$ nanoparticles are about 10 nm embedded in OPANI. Among all composites, 15 wt.% of nanocomposites shows high DC conductivity 4×10^{-3} S/cm compare to other compositions. The dielectric constant decreases as a function of applied frequency due to the multiple polarizations occur in polymer nanocomposites. Among all composites 15 wt.% of *O*-chloropolyaniline/TiO$_2$ nanocomposite shows low dielectric constant and high AC conductivity of 3×10^{-4} S/cm. Tangent losses of these very low that is 2.5 Ω and it almost constant after 10^5 Hz hence these materials would be great importance in low *k*-dielectric application. Therefore these composites are suitable for electronic applications.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Conducting polymer has become an interesting field for scientific community because of its wide applications in engineering and technology. The designing of new supra-molecules with the desired structure and properties for different application has attracted in recent years [1]. These conducting polymers got more attention because of its easily tunable electrical property by incorporating filler materials to in it [2]. Among all conducting polymers, polyaniline is extensively studied because of its easy synthesis, low cost, environmental stability and tunable electrical property by adding small quantity of inorganic or organic materials [3].

The nano-dimension fillers incorporated into the matrix changes tremendously, its electrical properties due to the

high surface energy, homogeneous distribution and proper orientation of nanoparticles results isotropy throughout the matrix [4]. However the composite property also depends on the way of preparation, reaction mechanism, matrix composition and filler concentration. One of the co-authors earlier reported AC conductivity of polyaniline–n-TiO$_2$ composites and found that the σ_{AC} conductivity greatly influenced by nanoparticles due to the nanodimension and orientation of nanoparticles in polyaniline matrix [5]. It is observed that the substituted polyaniline shows high conductivity because the π-electron of benzene ring delocalize cause resonant for longer time and hence conductivity is higher than polyaniline [6,7]. Lakshmi et al. reported that preparation of OPANI–NiTiO$_3$ composites and found that the NiTiO$_3$ influence the conductivity up to 0.3×10^{-2} S/cm and the tangent losses is about 10 at 10^5 Hz [8]. In this connection we made an effort to improve the conductivity of *Ortho*-chloropolyaniline (OPANI) by adding TiO$_2$ nanoparticles using camphor

---

* Corresponding author. Tel.: +91 8022 262796.
  E-mail address: dr_gramgopal@yahoo.co.in (G. Ramgopal).

sulphonic acid as surfactant which will be improve the interface and avoid the agglomeration becomes easy in the electron transport mechanism. The prepared composites were characterized by Fourier transform infrared (FTIR) spectroscopy, Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM). Further the DC and AC properties were studied by Kelvin two probe methods using Hioki LCR meter in the range of 50–5 MHz.

2. Experimental

2.1. Materials and method

The monomer *Ortho*-chloroaniline, Ammonium persulphate (APS) ($(NH_4)_2S_2O_8$), sulphuric acid (H_2SO_4) (AR grade), Camphorsulfonic acid, TiO_2 nanoparticles (99.999% purity) and acetone were procured from Sigma–Aldrich, India. All chemicals were of analytical reagent (AR) grade and were used as received without any further purification.

2.2. Synthesis of Ortho-chloroaniline

The 500 ml volumetric flask containing 1 M solution of *Ortho*-chloroaniline (100 ml) and 1 M sulphuric acid which acts as proton donor were dissolved in distilled water in equimolar ratio and stirred for 20 min to get *Ortho*-chloroaniline sulphuric acid solution. To the above mixture 10 ml surfactant of 0.1 M Camphorsulfonic acid is added and then to which oxidizer is added 0.25 M Ammonium persulphate of 100 ml solution to the above solution slowly drop by drop at the rate of 5 ml per minute and the resulting solution is stirred for an hour at 0–5 °C temperature using magnetic stirrer. The reaction mixture is allowed to keep for 24 h to complete the polymerization of monomers and get better yield without formation of oligomers. Next day, the reaction mixture is filtered using vacuum pump and *Ortho*-chloropolyaniline (OPANI) precipitate is washed with 300 ml of 0.2 M sulphuric acid to remove the unreacted monomer, followed with distilled water and acetone to remove SO_4^- ions and excess APS from *Ortho*-chloropolyaniline. Further, the *Ortho*-chloropolyaniline precipitate is dried under vacuum to achieve a constant weight [8,9].

2.3. Synthesis of Ortho-chloroaniline–TiO$_2$ nanocomposites

1 M solution of *O*-chloroaniline (100 ml) and 100 ml of 1 M sulphuric acid are dissolved in double distilled water and TiO_2 nanoparticles in various weight percentage (05, 10, 15, 20 and 25 wt.%) and stirred for 40 min and form *Ortho*-chloroaniline sulphuric acid solution which contains homogenously distributed suspended TiO_2 nanoparticles. To the above mixture 10 ml of 0.1 M Camphorsulfonic acid is added and then to which 0.25 M Ammonium persulphate of 100 ml solution is added drop by drop slowly to the above at the rate of 5 ml per minute and the resulting solution is stirred for an hour at 0–5 °C temperature using magnetic stirrer. The reaction mixture is left in the ice bath for 24 h to complete polymerization of monomers. Next day, the reaction mixture is filtered using vacuum pump

and *Ortho*-chloropolyaniline–TiO_2 nanocomposites are washed with 300 ml of 0.2 M sulphuric acid to remove the unreacted monomer, followed with distilled water and acetone to remove SO_4^- ions and excess APS from *O*-PANI–TiO_2 nanocomposites. Further, the nanocomposites precipitate is dried under vacuum to achieve a constant weight [10].

2.4. Characterization and experimental techniques

The Fourier transform infrared spectra of the samples were recorded on a Perkin Elmer 1600 spectrophotometer in KBr medium (sample to KBr ratio is 1:5) in the wave number range 400–4600 cm^{-1}. The surface morphology of *Ortho*-chloropolyaniline and its composites in the form of pellets was investigated using Philips XL 30 ESEM scanning electron microscope on Au substrate. The transmission electron microscopy (TEM) image of the sample was obtained using JEOL Model 1200KVEX instrument operated at 120 kV. Sample for TEM analysis was prepared by dispersed the *O*-chloropolyaniline and its nanocomposites on carbon-coated copper grids, has been kept for 5 min. The samples on the TEM grid is exposed to IR light for 30 min for drying. The DC conductivity was studied by preparing pellets of 10 mm diameter with thickness varying up to 2 mm by applying pressure of 10 Tons in a UTM–40 (40 Ton Universal testing machine). For temperature dependent conductivity and sensor studies, the pellets are coated with silver paste on either side of the surfaces to obtain better contacts. The DC measurement was carried by two probe method and the change in resistance is measured using Keithley meter. Frequency-dependent electrical conductivity was measured by two probe technique using laboratory made setup. The dielectric tangent loss and dielectric constant are studied by sandwiching the pellets of these composites between the silver electrodes in the frequency range of 50–5 MHz using the Hioki LCR Q meter.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy

The molecular structure is carried out by Fourier transform infrared spectroscopy (FTIR) for TiO_2 nanoparticle doped *O*-chloropolyaniline nanocomposites with different weight percentages. Fig. 1(a) shows the FTIR spectra of pure *O*-chloropolyaniline and is observed that characteristic peaks around 2922 cm^{-1} corresponds to C—H stretching of aromatic ring, 1566 cm^{-1} is due to the C=C stretching vibration of quinoid ring, 1493 cm^{-1} for stretching vibration of benzenoid ring, 1406 cm^{-1} is the characteristic mode of vibration of C—H bonding of aromatic nuclei, 1302 cm^{-1} assigned for the stretching of C—N bonds of aromatic amine, 1142 cm^{-1} is one of the important peaks assigned for measure of degree of delocalization of electron in aromatic ring, 796 cm^{-1} corresponds to N—H rocking vibration mode out of the plain, 592 cm^{-1} and 472 cm^{-1} are due to the bonding of C—H in aromatic ring out of the plain respectively [11–13].