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Dielectric Study of Polyaniline–Nitio$_3$ Composites

KEYWORDS: In Situ, Ac Conductivity, Dielectric Constant, Polyaniline, $NiTiO_3$

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ABSTRACT *Polymers with oxide materials constitute a new class of polymer composite materials, which integrates materials science and technology. Chemical oxidation of aniline is carried out for Polyaniline (PANI) and insitu polymerization for Polyaniline- NiTiO3 (PANI- $NiTiO_3$) composite material. To know detailed changes different characterization tools are used i.e. SEM, XRD and IR. The dielectric behavior is also investigated in the frequency range 102–107 Hz at room temperature. The $NiTiO_3$ particles in the matrix have a greater influence on the observed dielectric values*

INTRODUCTION

Research on conducting polymer composite materials integrates the science and technology of polymeric materials. Polymers containing metal oxides constitutes polymer composites are well studied for its properties (Devindrappa et al., 2006; Sinha, 2002; Lagashetty et al., 2010). Conducting polymers have a variety of applications in the Industrial, Scientific and Medical (ISM) fields. Applications like anticorrosion, static coating electromagnetic shielding etc comes under first generation. Second Generation of electric polymers have applications such as transistors, LEDs, solar cells batteries etc. Controlled conductivity, high temperature resistance, low cost and ease of bulk preparation make these materials attractive in the engineering and scientific world[1-4].

The features of conducting polymers such as reversibility, availability in film form and good environmental stability enhance their potential use for practical applications. One of the most widely studied conducting polymers; Polyaniline can be obtained chemical or electrochemical route[5-7]. Polymeric materials has become an area of increasing interest in research because of the fact that these materials have great potential for solid state devices (Jiang et al., 2002; Caruso, 2001; Mallikarjuna et al., 2004). Polyaniline has received much attention because of its unique reversible proton doping, high electrical conductivity, ease of preparation and low cost[8-9]. The demand of high quality materials for electromagnetic compatibility is alarmingly increasing (Murgendraappa and Ambika Prasad, 2006; Raghavendra et al., 2003**)**. Metal oxides dispersed polymer composites have attracted a great deal of interest from researchers, because they frequently exhibit unexpected hybrid properties synergistically derived from both components. $NiTiO_3$ is one of the examples of pervoskite oxide material, which is known for functional oxide materials with applications (Leu et al.,2002; Lagashetty et al., 2010).

Conducting PANI containing such metal oxide materials called PANI composite with variable compositions my lead to desirable properties. These materials are especially important owing to their bridging role between the worlds of conducting polymers (Parvatikar et al.,2007; Mallikarjuna et al., 2005)[10-12].

However, in this paper we report the synthesis of PANI and PANI-$NiTiO_3$ composites. The characterization of $NiTiO_3$, PANI and PANI-$NiTiO_3$ are carried out by characterization tools. Electrical study like dielectric constant is under taken for the above materials.

MATERIALS AND METHODS

Ammonium persulphate $(NH4)_2S_2O_8$, Hydrochloric acid (HCl), aniline and nickel titanate ($NiTiO_3$) used were of AR grade. Double distilled water is used as a solvent for chemical synthesis process. Polyaniline is prepared by oxidative method and its composites were prepared by insitu polymerization aniline with dispersion of $NiTiO_3$.

1. Synthesis of Polyaniline-$NiTiO_3$ Composites

0.1M aniline was dissolved in 1M HCl to form aniline hydrochloride. Nickel titanate was added in the weight percent of 10, 20, 30, 40 and 50 to the above solution with vigorous stirring in order to keep the nickel titanate suspended in the solution. 0.1M of ammonium persulphate $[(NH_4)_2S_2O_8]$ as an oxidant was added slowly to the reaction mixture with continuous stirring for 4-6 hours at 0-5^{O}C. The precipitated powder recover was vacuum-filtered and washed with deionizer water. Finally, the resultant precipitate was dried in an oven for 24 hours to achieve a constant weight. Similarly five different PANI- $NiTiO_3$ composites with different weight of $NiTiO_3$ (10, 20, 30, 40 and 50) in PANI have been synthesized. Pure polyaniline was prepared by chemical oxidation of aniline without adding nickel titanate (Parvatikar and Ambika Prasad, 2006; Patil et al., 2007).

2. Results and discussion

2.1 X-ray diffraction

Figure 1. shows the XRD pattern of as prepared PANI. The pattern shows the broad peak at about 2Ə values of 25°. This is a characteristic peak of PANI which is ascribed to the periodicity in parallel and perpendicular directions of the polymer chain.

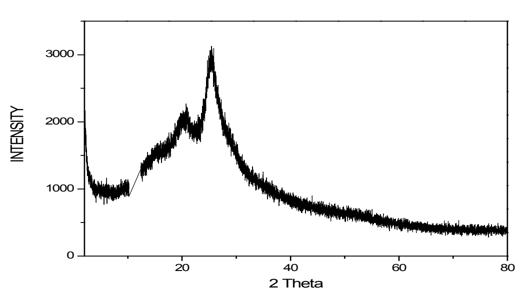

Figure 1: XRD pattern of as prepared PANI

Figure-2 Shows indexed XRD pattern of pure PANI- $NiTiO_3$ at 50% weight composition. The pattern show the presence of nickel titanate reflections and are identified in the composite pattern by the reference of nickel titanate JCPDS file. This oxide peaks in the composite pattern confirms the formation of nickel titanate dispersed polyaniline composite and

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enhances the crystallinity of the PANI.

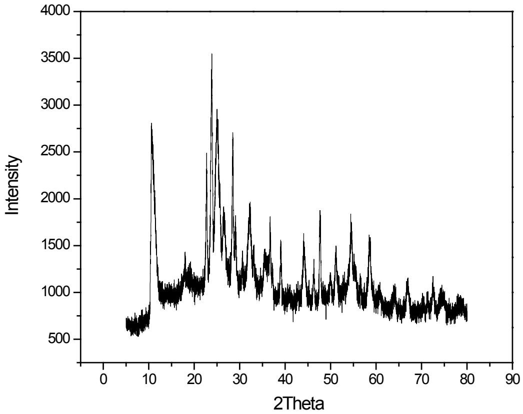

Figure 2: XRD pattern of PANI- $NiTiO_3$ (50wt%) composite

2.3 Scanning Electron Microscopy (SEM)

Scanning electron microscope stoll is using to know the morphology of the $NiTiO_3$, pure PANI and PANI- $NiTiO_3$ composite materials.

Figure-3 shows SEM image of pure PANI obtained by chemical route. This image shows the irregular particles are in nano range and particles are spherical agglomeration with uniform packing.

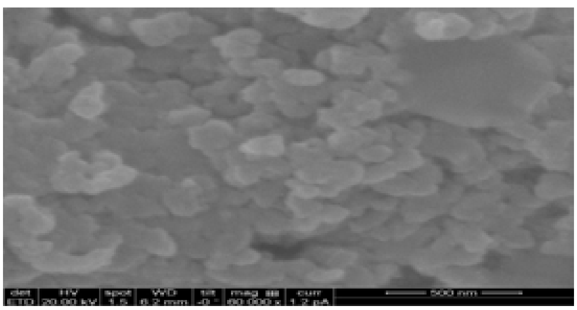

Figure 3: SEM image of pure PANI

Figure-4 shows the SEM image of PANI- $NiTiO_3$ at 50% weight percentage. In this image one can observe the fine dispersion of $NiTiO_3$ particles in the PANI matrix. Formation of sheet like structure and deagglomaration of $NiTiO_3$ takes place. The image also shows the cluster morphology due to inserted oxide particles in the PANI matrix, which enhances the crystallinity of the composite.

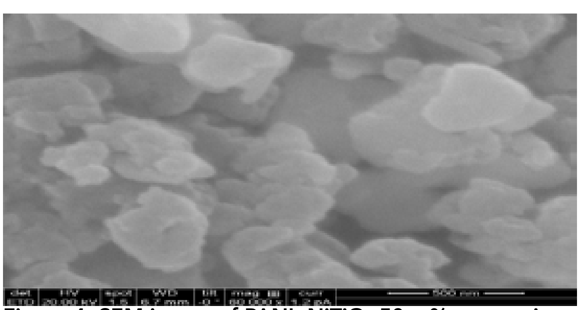

Figure 4: SEM image of PANI- $NiTiO_3$ 50wt% composite

2.3 Infrared Study

The aim of infrared study is to ascertain the metal- oxygen (M-O) bond and nature of the synthesized of $NiTiO_3$ sample. Metal oxides generally give absorption bands below 1000cm^{-1} arising from inter-atomic vibrations (Rao C N R (1963)].

Figure-5 shows FTIR spectrum of pure PANI obtained by chemical route. The peak at 1103cm-1 is due to the B-NH+ = Q vibration, indicating that the PANI is conductive and is in the form of emeraldine salt. The absorption peak at 925 cm-1 is due the C-H bonding of the aromatic ring. The peak 666 is attributed to the out of plane deformation of C-H aromatic ring. Additional peaks at 2322, 2089, 1537 and 1280cm-1 are may be due to overtones.

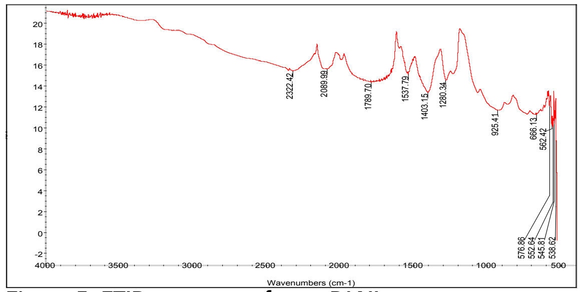

Figure 5: FTIR spectrum of pure PANI

Figure-6 shows the FTIR spectrum of as prepared PANI- $NiTiO_3$ composite. The spectrum shows some peaks below 1000cm-1clearly shows presence of $NiTiO_3$. Some additional peaks and shift in vibrational frequency were also observed on comparison with pure PANI and $NiTiO_3$ spectrum. This confirms the formation PANI- $NiTiO_3$ composite.

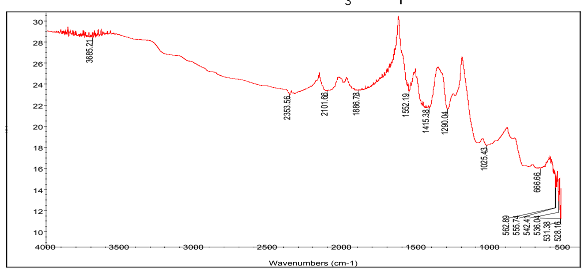

Figure 6: FTIR spectrum of PANI- $NiTiO_3$(50wt%) composite

Figure 7 shows the variation of ε' as a function of frequency for different wt% of polyaniline PANI/$NiTiO_3$ composite. It is found that dielectric constant decreases as frequency increases for all the weight percentage. The observed behavior may be due to Debye like relaxation mechanism taking place in these materials.

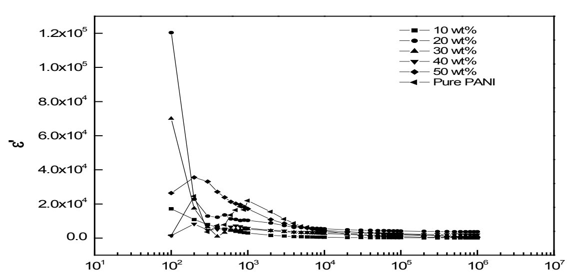

Figure 7: Dielectric constant of PANI- $NiTiO_3$ composites at variable frequency

Figure 8 represents the variation of ε' as a function of wt% of $NiTiO_3$ at room temperature at three different frequencies. It is found that the dielectric constant increases for pure PANI, 20wt% and 40wt% which is a characteristic of Debye relaxation mechanism and decreases for 10wt%, 30wt% and 50wt% .From the above studies, it is confirmed that at lower frequencies these composites behave as dielectric materials.

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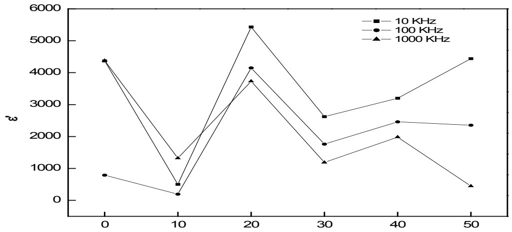

Figure 8: variation of ε' as a function of wt% of $NiTiO_3$ at three different frequencies.

CONCLUSIONS

Insitu polymerization is a simple method for preparation of conducting PANI composites. This method may be used for the preparation of other than PANI composites. Structural changes of pure PANI and pure metal oxide is taken place due to the presence of oxide material in the PANI is observed by XRD pattern. Similarly, morphology and bonding changes is observed in composite material compared to pure PANI and pure metal oxide. The results of dielectric property show a strong dependence on the wt. % of $NiTiO_3$ in PANI. Increase in dielectric constant in the composite are also observed.

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