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Research Article

IN SITU POLYMERIZATION SYNTHESIS FOR POLYANILINE–$NiTiO_3$ COMPOSITES: STRUCTURE, MORPHOLOGY, BONDING AND DIELECTRIC STUDY

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ABSTRACT
Chemical route for the synthesis of polymer composites with oxide materials enhances the composite technology. Polyaniline (PANI) and Polyaniline-$NiTiO_3$ (PANI-$NiTiO_3$) composite material was prepared by insitu polymerization of aniline with $NiTiO_3$ as composite material. Variation in the oxide composition with polymer matrix is maintained to know its detailed changes. The structural characterization of prepared composite materials and metal oxide material are carried out by X-ray diffraction (XRD), morphological study by Scanning Electron Micrograph (SEM) and bonding by Infrared (IR) study. Variation in Structural, morphology and bonding is observed in composite materials compared to $NiTiO_3$ sample and PANI. The dielectric behavior is also investigated in the frequency range 10^2–10^7 Hz at room temperature. The dimensions of $NiTiO_3$ particles in the matrix have a greater influence on the conductivity values and observed dielectric values

Key Words: *In Situ, Ac Conductivity, Dielectric Constant, Polyaniline, $NiTiO_3$*

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.
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. 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. 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**)**.

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 $NiTiO_3$.

Synthesis of Polyaniline-$NiTiO_3$ Composites

M 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).

Preparation of Pellets

Varied concentrations of prepared composites were pressed under pressure for its pellet form. The test samples to be used were prepared in pellet form of diameter 10mm and thickness 3mm by applying pressure of 7t using Pye-Unicam dye. The contacts for these composites were made using silver paste as electrodes on both sides (Mahesh *et al*., 2009).

Characterization

The structures of as prepared polymer composite were studied by X – ray diffraction using Phillips X – ray diffractometer (PW3710) with Cu Kα as source of radiation. Morphology and bonding of the above polymer composites were studied by Phillips XL 30 ESEM and Perkin–Elmer 1600 spectrophotometer in KBr medium tools respectively. Dielectric measurements were carried out at room temperature over the frequency range 10^2-10^7Hz using the Hiokie LCR Q meter.

RESULTS AND DISCUSSION

X-ray diffraction

Figure-1

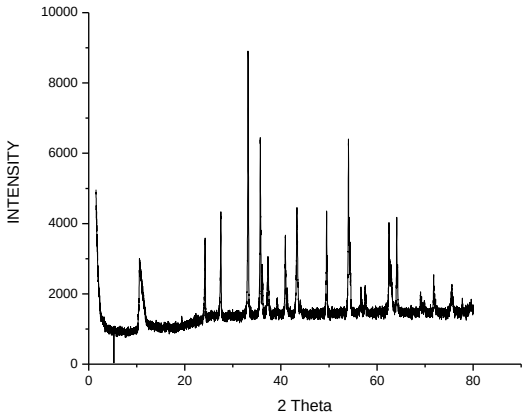

Figure 1: XRD pattern of pure $NiTiO_3$

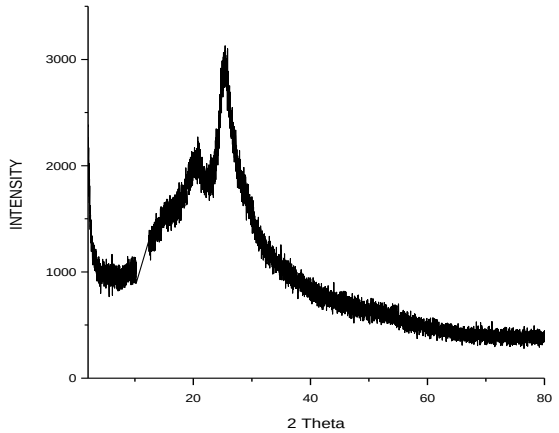

Figure 2: XRD pattern of as prepared PANI

shows XRD pattern of pure $NiTiO_3$. The pattern shows large number of peaks confirms the formation of rhombohedral phase of NiTiO3. The d-spacing values of the sample matches well with standard 33-0960 JCPDS file. Unit cell parameters ware obtained by least –square refinement of the powder XRD data. This study reveals that the sample is monophasic $NiTiO_3$ with rhombohedral structure having nanosized particles. Figure-2 shows the XRD pattern of as prepared PANI. The pattern shows the broad peak at about 2Ɵ values of 25^o. This is a characteristic peak of PANI which is ascribed to the periodicity in parallel and perpendicular directions of the polymer chain. Figure-3

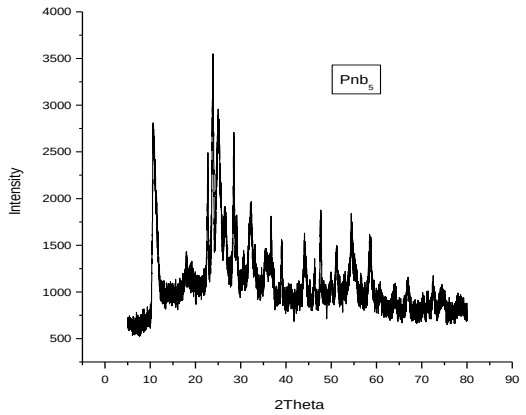

Figure 3: XRD pattern of pure PANI- $NiTiO_3$ at 50% weight composition

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 enhances the crystallinity of the PANI.

Scanning Electron Microscopy (SEM)

Scanning electron microscope toll is using to know the morphology of the $NiTiO_3$, pure PANI and PANI-$NiTiO_3$ composite materials. Figure-4 shows SEM image of $NiTiO_3$. This image shows the irregular shaped particles are joined together. Joints between fine particles of $NiTiO_3$ with non-chain structure is also observed.

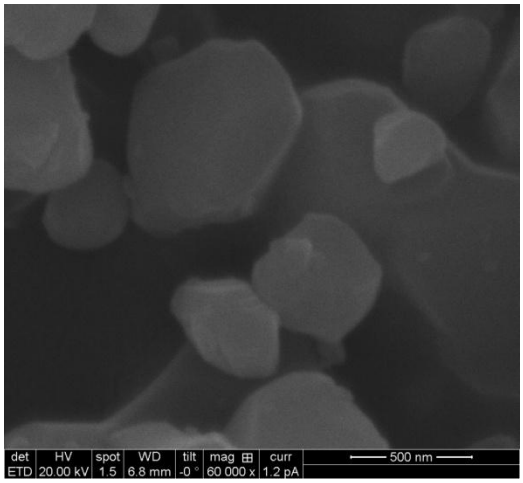

Figure 4: SEM image of $NiTiO_3$

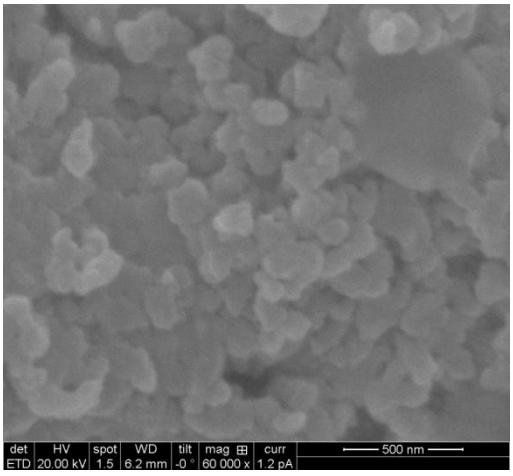

Figure 5: SEM image of pure PANI

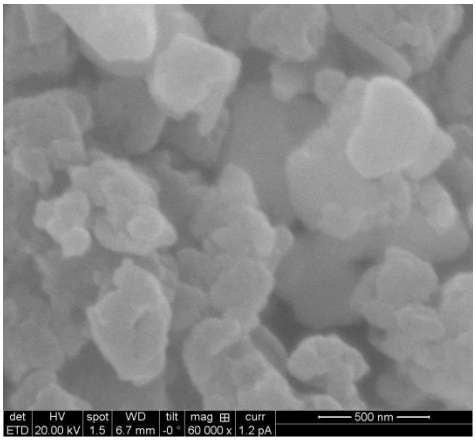

Figure 6: SEM image of PANI- $NiTiO_3$ at 50% weight composition

Figure-5 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-6 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.

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-7 shows FTIR spectrum of commercially obtained $NiTiO_3$ sample. The sample shows the absorption in the region 2160, 601, 571, 566 and 526cm^{-1}. The peak 2160cm-1 corresponds to water of absorption and other peaks at 601, 571, 566 and 526 cm^{-1}corresponds to metal-oxygen (Nb-O and Ti-O) vibrational modes of the spinal compound. This conform the formation of $NiTiO_3$. Figure-8 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-9 shows the FTIR spectrum of as prepared PANI- $NiTiO_3$ composite. The spectrum shows some peaks below 1000cm-1clearly shows presence of

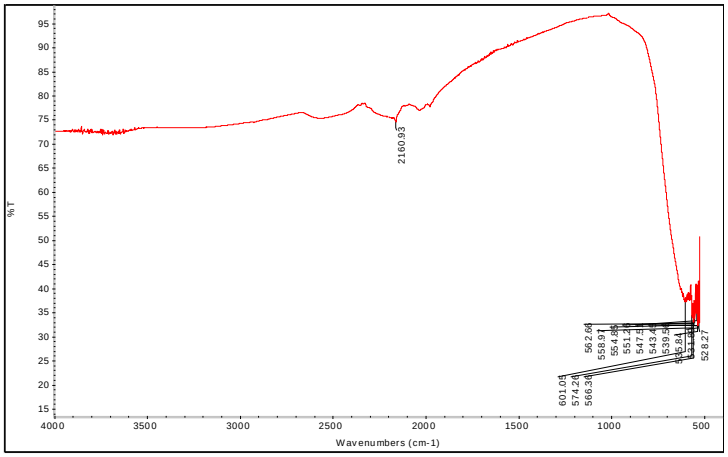

Figure 7: FTIR spectrum of $NiTiO_3$ sample

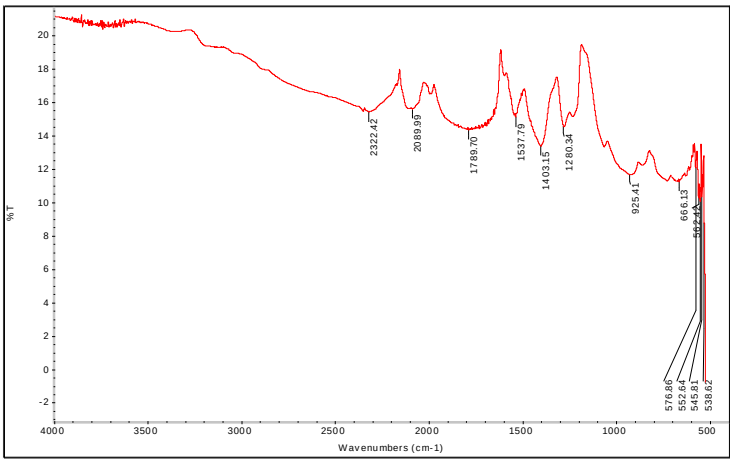

Figure 8: FTIR spectrum of pure PANI

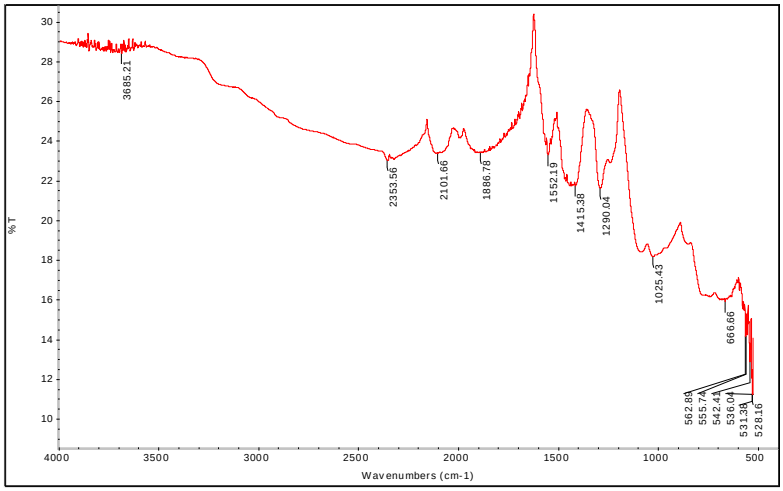

Figure 9: FTIR spectrum of PANI- $NiTiO_3$ composite

$NiTiO_3$. 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.

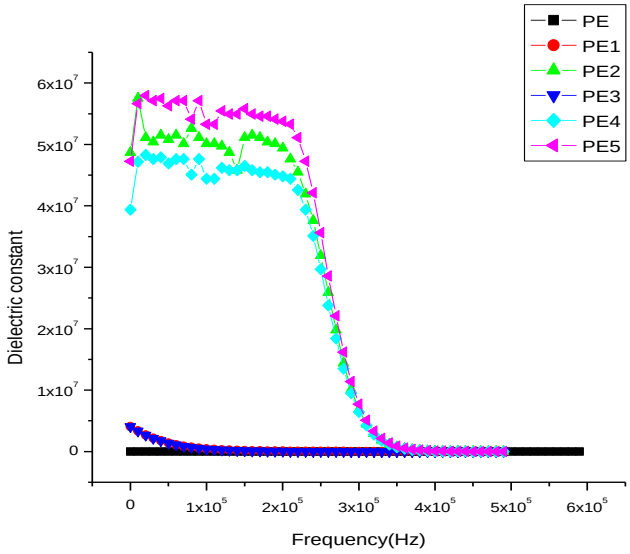

Figure 10: Dielectric constant of PANI- $NiTiO_3$ composites at variable frequency

Dielectric Study

Figure-10 represents the variation of ε' as a function of wt% of $NiTiO_3$ at room temperature at variable frequencies. It is found that, the dielectric constant decreases for 20wt%, 40wt % and 50wt% at $2.5x10^5$Hz which is a characteristic of Debye relaxation mechanism. From the above studies, it is confirmed that at lower frequencies PANI composites behave as dielectric materials.

CONCLUSIONS

In situ 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 a c conductivity as well as dielectric property show a strong dependence on the wt. % of $NiTiO_3$ in PANI. Increase in dielectric constant in the composite is also observed.

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