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Dielectric Property Study of Polyaniline–$PbTiO_3$ Composites

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ABSTRACT

Chemical route for the synthesis of polymer composites with oxide materials enhances the composite technology. Polyaniline (PANI) and Polyaniline- $PbTiO_3$ (PANI- $PbTiO_3$) composite material was prepared by insitu polymerization of aniline with $PbTiO_3$ 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 $PbTiO_3$sample and PANI. The dielectric behavior is also investigated in the frequency range 102–107 Hz at room temperature. The dimensions of $PbTiO_3$ particles in the matrix have a greater influence on the observed dielectric values

KEYWORDS : Synthesis, Composites, Dielectric Constant, Polyaniline, $PbTiO_3$

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 R (2002)**,** Lagashetty et al (2010)]. Conducting polymers have a variety of applications in the Industrial, Scientific and Medical (ISM) fields[1-3]. 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[4-7].

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 L H, Leu C MWei K H (2002), Caruso F (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)**]**.

The present work reports the synthesis of PANI and PANI composite materials by dispersing $PbTiO_3$ in the PANI matrix through chemical oxidation method. As prepared PANI its $PbTiO_3$ composites are characterized by characterization techniques[8-11]. Dielectric constant of the above samples were carried out to know the polarization.

EXPERIMENTAL

Materials and Methods

Chemicals used in the preparation PANI and PANI composites are Ammonium persulphate $(NH4)_2S_2O_8$, Hydrochloric acid (HCl), aniline and lead titanate ($PbTiO_3$) are of AR grade. The synthetic process was carried out using double distilled water. Polyaniline and its composite materials were prepared by chemical oxidative method.

Synthesis of Polyaniline-$PbTiO_3$ Composites

0.1M aniline was dissolved in 1M HCl to form aniline hydrochloride. Lead 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 lead 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^{0}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- $PbTiO_3$ composites with different weight of $PbTiO_3$ (10, 20, 30, 40 and 50) in PANI have been synthesized [12-16]. Pure polyaniline was prepared by chemical oxidation of aniline without adding lead titanate [Parvatikar and Ambika Prasad (2006), Patil et. al (2007)].

RESULTS AND DISCUSSION

X-ray diffraction

The structure of prepared PANI and PANI composite are studied by X-ray diffraction study. XRD pattern of as prepared pure PANI is shown in figure-1. The pattern shows the broad peak at about 2Əvalues of 25°. This is a characteristic peak of PANI which is ascribed to the periodicity in parallel and perpendicular directions of the polymer chain.

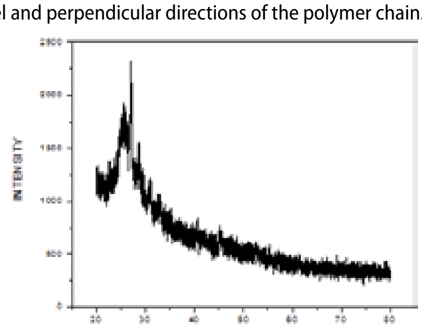

Figure 1: XRD pattern of as prepared PANI

Figure-2 shows XRD pattern of PANI- $PbTiO_3$ at 50% weight composition. Presence of lead titanate reflections are observed in the composite pattern and are identified in the composite pattern on comparison with lead titanate JCPDS file. This oxide peaks in the composite pattern confirms the formation of lead titanate dispersed polyaniline composite.

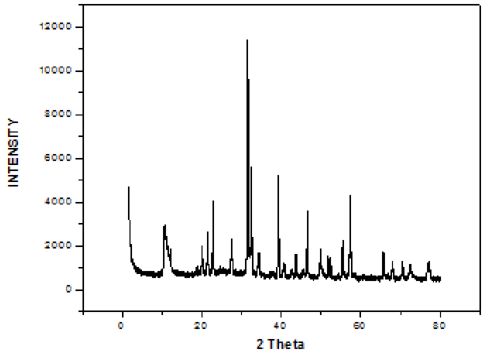

Figure 2: XRD pattern of pure PANI- $PbTiO_3$ (50 wt%) composite

Scanning Electron Microscopy (SEM)

The morphology of the $PbTiO_3$, pure PANI and PANI-$PbTiO_3$ composite materials were studied by Scanning electron microscope toll.

Figure-3 shows SEM image of lead titanate sample. This image shows the fine spherical particles are closed each other. Most of the particles forms globular arrangement with compact structure. This clearly shows the crystalline nature of the sample.

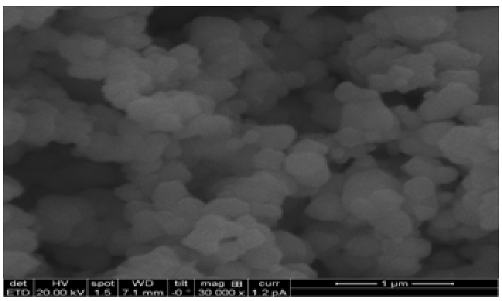

Figure 3: SEM image of $PbTiO_3$

Figure-4 shows SEM image of pure PANI obtained by chemical oxidation route. This image shows the irregular particles are in micro range and particles are spherical agglomeration without uniform packing.

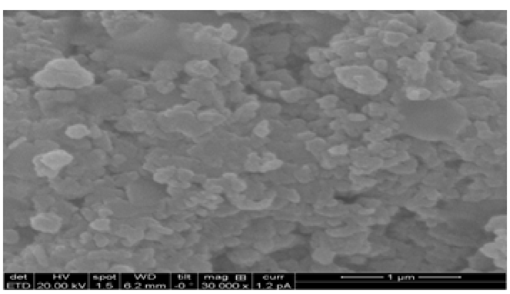

Figure 4: SEM image of pure PANI

Figure-5 shows the SEM image of PANI- $PbTiO_3$ at 50% weight percentage. The image shows the fine flecks of $PbTiO_3$ particles in the PANI matrix forms cluster morphology. Some smooth solid blocks are due to the presence of oxide particles, which increases the crystallinity of the composite materials.

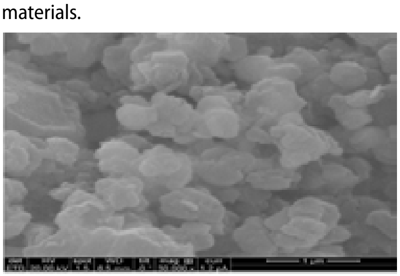

Figure 5: SEM image of PANI- $PbTiO_3$ (50wt%) composite

Figure- 6 shows a representative energy-dispersive X ray (EDX) spectrum of as prepared lead titanate. The pattern shows that the material consists of Pb and Ti metals. The atomic ratios of these elements are given in the table-1

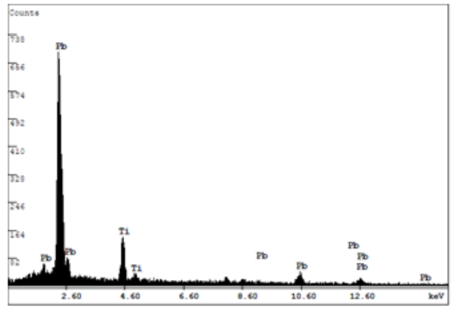

Figure 6: EDAX of PANI- $PbTiO_3$ (50 wt%) composite

Infrared Study

The bonding nature in the $PbTiO_3$, pure PANI and bonding variation in the composite was well studied by infrared tool. This study is to ascertain the metal- oxygen (M-O) bond and nature of the synthesized of $PbTiO_3$ sample. Metal oxides generally give absorption bands below $1000 cm^{-1}$ arising from inter-atomic vibrations [Rao C N R (1963)].

Figure-6 shows FTIR spectrum of commercially obtained $PbTiO_3$ sample. The spectrum shows number of peaks at 500cm-1 range confirms the formation of metal-oxygen (Pb-O and Ti-O) vibrational modes of the spinal compound. Absorption peaks in the region 2545, 2160 and $1416 cm^{-1}$. Band at 2545 and 2160cm-1may be due to water of hydration and the peak 416 may due the presence of some overtones. This conform the formation of $PbTiO_3$.

Figure-7 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.

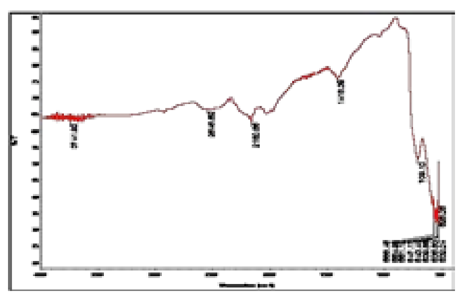

Figure 7: FTIR spectrum of $PbTiO_3$ sample

Figure-8 shows the FTIR spectrum of PANI- $PbTiO_3$ composite. The spectrum shows some peaks below 1000cm-1clearly shows presence of lead titanate. Some additional peaks and shift in vibrational frequency were also observed on comparison with pure PANI and $PbTiO_3$ spectrum. This confirms the formation PANI- $PbTiO_3$ composite.

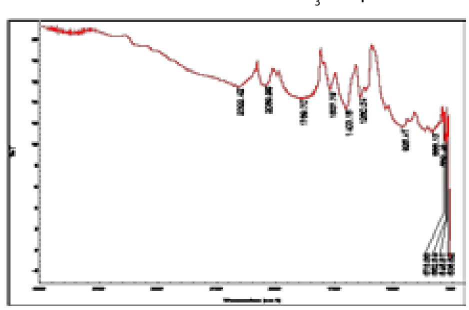

Figure 8: FTIR spectrum of pure PANI

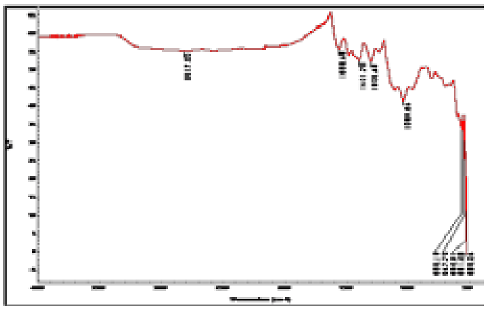

Figure 9: FTIR spectrum of PANI- $PbTiO_3$ (50 wt %) composite

Dielectric Study

Figure 10(a) shows the variation of ε' as a function of frequency for Polyaniline – $PbTiO_3$ composites for different wt%. It is found that dielectric constant decreases as frequency increases for pure PANI and PANI /$PbTiO_3$ composites. It is observed that Debye type relaxation mechanism is responsible for higher values of dielectric constant at low frequencies, which decreases as the applied frequency increases.

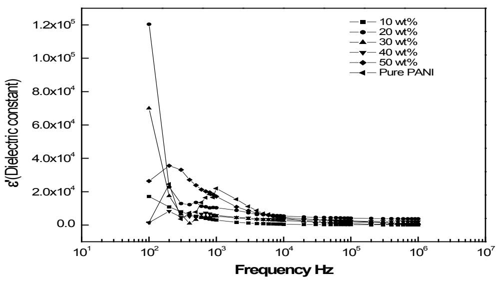

Figure 10(a): Variation of ϵ' as a function of frequency of PANI-$PbTiO_3$ Composite

Figure 10(b) represents the variation of ε' as a function of wt% of $PbTiO_3$ in polyaniline at room temperature at three different frequencies. It is observed that for all the frequencies, the value of ε' is found to decrease up to 20wt% and thereafter increases, which is a characteristic of Debye type relaxation mechanism . This is also due to the additional contribution of hopping of polarons in the localized state.

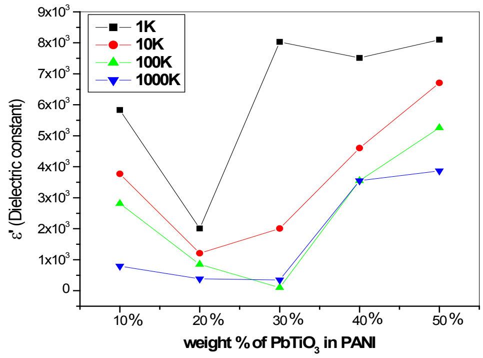

Figure 10(b) Variation of ϵ' as a function of wt % of PANI-$PbTiO_3$ Composite

Conclusion

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 a c conductivity as well as dielectric property show a strong dependence on the wt. % of $PbTiO_3$ in PANI. Increases in dielectric constant in the composite are also observed.

Table-1
EDX data of pure PANI- $PbTiO_3$ at 50% weight composition

Element	Weight%	Atomic %
TiK	15.88	44.96
PbM	84.12	55.00
Total	100	100

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