

## ***IN-SITU CHEMICAL SYNTHESIS AND ELECTRICAL PROPERTIES OF POLYANILINE/ TITANIUM DI-OXIDE NANO COMPOSITES***

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**Abstract.** The present paper aims to study the preparation of Polyaniline / titanium di-oxide (PANI / TiO<sub>2</sub>) Nano composites and characterize them. Polyaniline / titanium di-oxide nano composites were prepared by in-situ chemical oxidation polymerization method. The synthesis involved the formation of dark green colored Polyaniline/TiO<sub>2</sub> nanocomposites. The nanocomposites were characterized by FTIR, XRD, UV-Visible Spectroscopy and SEM. The expected structure of polymer was confirmed by the characteristic peaks in FTIR, SEM and UV-Visible spectra. The XRD pattern shows the monoclinic structure of the composite. The A.C. conductivity , dielectric constant ( $\epsilon'_{(w)}$ ) and Dielectric Loss ( $\epsilon''_{(w)}$ ) of PANI /TiO<sub>2</sub> nano composites were investigated in the frequency range 10<sup>2</sup>-10<sup>6</sup> Hz using LCR Meter .The effect of doping on the A.C. conductivity was investigated.

**Keywords:** A.C. conductivity, Chemical polymerization, dielectric constant ( $\epsilon'_{(w)}$ ), Dielectric Loss ( $\epsilon''_{(w)}$ ), Polyaniline / titanium di-oxide (PANI / TiO<sub>2</sub>), SEM , XRD.

### **1. INTRODUCTION**

The emergence of nanoscience and technology in recent years has revived the field of conducting polymers. Nano structural conducting polymers possess extraordinary properties due to its high surface area to volume ratio. Hence they are extensively used in sensor applications.[1] Conducting polymer composites with some suitable compositions of one or more insulating materials led to desirable properties .[2][3] These materials are especially important owing to their bridging role between the world of nanoparticles and that of conducting polymers. Use of nanoparticles in composite materials can increase their strength or reduce their weight . [4]

PANI is one of the mostly studied conducting polymer , because of its ease of polymerization , environmental stability and electrical conductivity.[5] One-dimensional PANI nanostructures, including nanowires, nanorods, and nanotubes, have been studied.[6] Recent studies are focused on the study of composites based on conducting PANI/metal nanoparticles for increased mechanical and electrical properties. The properties of these nanocomposites are quite different from PANI alone. By varying the particle size, shape, composition and the extent of dispersion of nanoparticles, the properties can be changed and tuned to the desired applications. [7][8] Another interesting type of polymer nanocomposites is that in which the inorganic material is doped in nano size.[9] Nano composites such as CuO , Fe<sub>2</sub>O<sub>3</sub> and SnO<sub>2</sub> have been reported.[10]

In the present study, PANI and PANI/TiO<sub>2</sub> composite(with varying weight percentage of TiO<sub>2</sub> in PANI) have been synthesized. TiO<sub>2</sub> is widely used in rod coating specific paints and in the areas such as purification of air and water. The combination of electrical conductivity of PANI and anatase TiO<sub>2</sub> find wide application in electronic devices. In the present work PANI/TiO<sub>2</sub> nanocomposites were characterized by FTIR, XRD,SEM and UV-Visible Spectroscopy. AC conductivity and dielectric properties of PANI/TiO<sub>2</sub> composites were also investigated for various doping percentage.

### **2. EXPERIMENTAL**

#### **2.1 MATERIALS**

Aniline, Ammonium peroxydisulphate (APS, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) and Methanol were purchased from S.D. Fine Chem. Ltd. Degussa TiO<sub>2</sub> (P25) nanoparticle with a primary particle size of 27 nm and the phase Composition of 80% anatase and 20% rutile was purchased from Degussa Chemicals (Hanau, Germany). All the solutions were made using double distilled water.

#### **2.2 Synthesis**

##### **Synthesis of Polyaniline (PANI)**

PANI was synthesized by Chemical Oxidation Polymerization where Ammonium Per sulfate [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] was used as an oxidant. At first, 0.2M aqueous solution of Aniline was dissolved in 0.2M HCl solution in a beaker. In another beaker, 0.2M [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] was dissolved in 100 ml deionized water.

This solution was added drop wise to the Aniline solution. The whole solution was stirred for 5 hours maintaining constant temperature bath at 0-5°C. After leaving 24 hrs in unstirred condition, the whole solution was filtered, washed with deionized water followed by Acetone several times to get clear filtrate, and dried in Oven at 70°C.

### Synthesis of Polyaniline / titanium di-oxide (PANI / TiO<sub>2</sub>) Nano composite

Fine graded pre-sintered titanium di-oxide powder in the weight percentages (wt %) of 10, 30 and 50 was added to Aniline monomer (0.2M) dissolved in 1 M HCl. This mixture was stirred for 1 hour in order to keep the titanium di-oxide powder suspended in the solution. To this reaction mixture, [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] which is used as an oxidant is added slowly drop-wise with continuous vigorous stirring for the period of 4-6 hours at an ambient temperature. Polymerization of aniline takes

place over fine grade titanium di-oxide particles. The washing of the nanocomposite is repeated same as in case of PANI alone.

### 2.3.Characterization

U.V. Visible Absorbance Spectra were recorded on Double beam UV-Visible Spectrophotometer (Systronics – 2201) using DMSO as solvent. The FTIR spectra of the PANI and PANI-TiO<sub>2</sub> composites were taken on a Thermo Nicolet Nexus 670 Spectrometer preparing pellets of samples with KBr. Wide Angle X-Ray Powder Diffraction is used to obtain information about the Structure and Composition of PANI and its Composite materials. X-ray diffractometer used to characterize the samples was Philips PW 1530 diffractometer. The morphologies of PANI/TiO<sub>2</sub> composites were investigated by scanning electron microscope (SEM) on a Zeiss EVO 18(U.K) instrument. AC conductivity as well as dielectric property were investigated over frequency range 10<sup>2</sup> – 10<sup>6</sup> Hz using WeinKerr (U.K) 41110 LCR meter.

## 3. RESULTS AND DISCUSSION

### 3.1 UV-VISIBLE SPECTRA

The UV -Visible spectra of nano TiO<sub>2</sub>, PANI and PANI / TiO<sub>2</sub> nanocomposites is shown in fig. 1. In the case of PANI, the peak in the wave length range of 300-400 nm with maximum at 340nm is due to  $\pi-\pi^*$  transition of benzenoid ring. The peak at 445 nm is due to polaron  $-\pi^*$  transition and the broad band with absorption maximum at 660 nm corresponds to the transitions from localized benzene molecular orbital (MO) to a quinonoid molecular orbital (MO).[11] NanoTiO<sub>2</sub> shows broad band absorption peak from 270nm-320nm.

The band at 660 nm is slightly shifted to lower wavelength which indicates the interaction between PANI and TiO<sub>2</sub>. The composite with 50%TiO<sub>2</sub> has very low intensity at this wavelength.

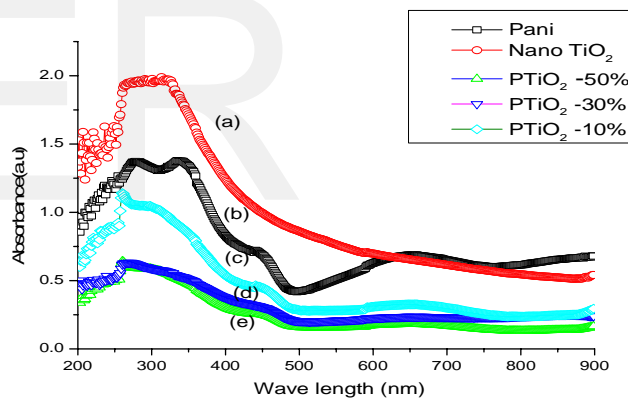


Fig 1. UV Visible spectra for PANI, Nano TiO<sub>2</sub> and PANI/TiO<sub>2</sub> composites

### 3.2 XRD studies

Fig.2 presents the XRD spectrum of pristine TiO<sub>2</sub> nanoparticles and PANI/ TiO<sub>2</sub> Nanocomposite. From the graph it is observed that that the peak of TiO<sub>2</sub> indicates the crystalline nature of the nano TiO<sub>2</sub> and PANI/TiO<sub>2</sub> nanocomposite. By comparing the XRD pattern of PANI/TiO<sub>2</sub> composite with that of TiO<sub>2</sub>, the prominent peaks of TiO<sub>2</sub> corresponding to  $2\theta = 25.61^\circ, 38.12^\circ, 47.53^\circ,$  and  $54.03^\circ$  are due to (110), (101), (111), and (211) planes are also present in PANI/TiO<sub>2</sub> composite ,

which indicates the presence of TiO<sub>2</sub> in PANI [JCPDS file no. 21-1276].[10] Also fig.2 shows that there is not much change in the XRD pattern of PANI/TiO<sub>2</sub> nanocomposite and XRD pattern of pristine TiO<sub>2</sub> nanoparticles.[12] The crystallite size of pure TiO<sub>2</sub> nanoparticles was calculated to be 30 nm according to the Debye–Scherrer formula. The Debye– Scherrer equation given by

$$t = 0.9 \lambda / \beta \cos \theta \quad (1)$$

Where t is the crystalline size of the particle, λ is the X-ray wavelength, β is the full width at half maximum (FWHM) of the peak and θ is the Bragg’s angle. By comparing curves of PANI/ TiO<sub>2</sub> and nano TiO<sub>2</sub>, it may be concluded that the PANI is deposited on the surface of nanoTiO<sub>2</sub> particles.

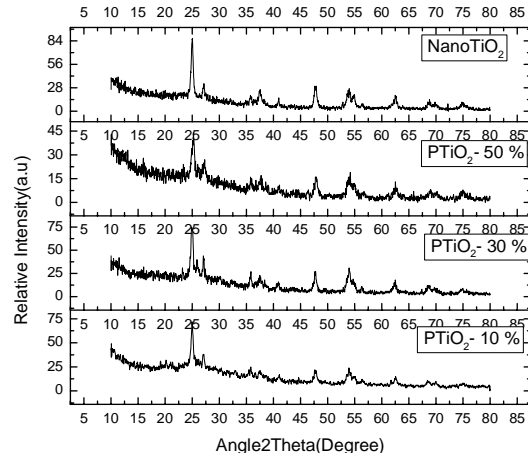


Fig 2 . XRD pattern of Nano TiO<sub>2</sub> and PANI/TiO<sub>2</sub> composites

**3.3. FTIR studies**

Fourier transform–infrared (FT-IR) spectroscopy was used to characterize the prepared PANI/TiO<sub>2</sub> nanocomposite. The ftir spectra of PANI , PANI/TiO<sub>2</sub>and TiO<sub>2</sub> is shown in fig. 3. The main characteristics peaks of PANI are 3400,1549,1439,1287and 788 cm<sup>-1</sup>. The peak 3405 cm<sup>-1</sup> is attributed to N-H stretching, 1549and 1439cm<sup>-1</sup> belong to N-H bending , 1287 cm<sup>-1</sup> belong to C-N stretching and 788 cm<sup>-1</sup> is associated with C-C and C-H of benzoid unit. All the charecteristics peak of PANI appear in all the samples of PANI/TiO<sub>2</sub> composites. Also, the characteristic peak of TiO<sub>2</sub> are 630 and 3021 cm<sup>-1</sup> which corresponds to Ti-O-Ti and O-H stretching frequencies.[13] These peaks appeared at the FT–IR spectrum of PANI/TiO<sub>2</sub>nanocomposite . The shift of PANI/TiO<sub>2</sub> nano composite charecteristics peak towards higher values indicate a strong interaction between PANI and TiO<sub>2</sub>. The FTIR results confirm the formation of PANI/TiO<sub>2</sub> composite .

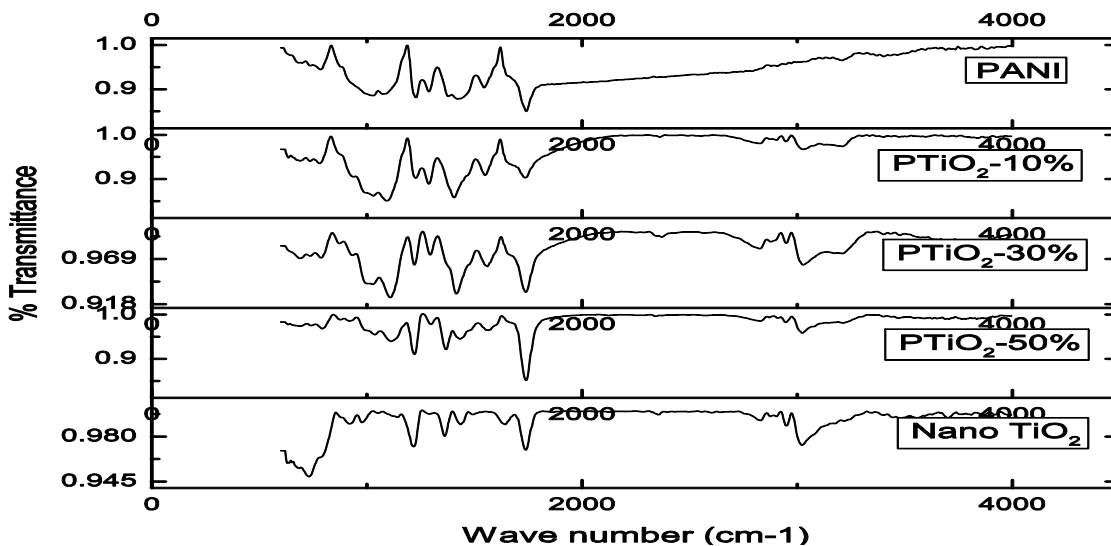
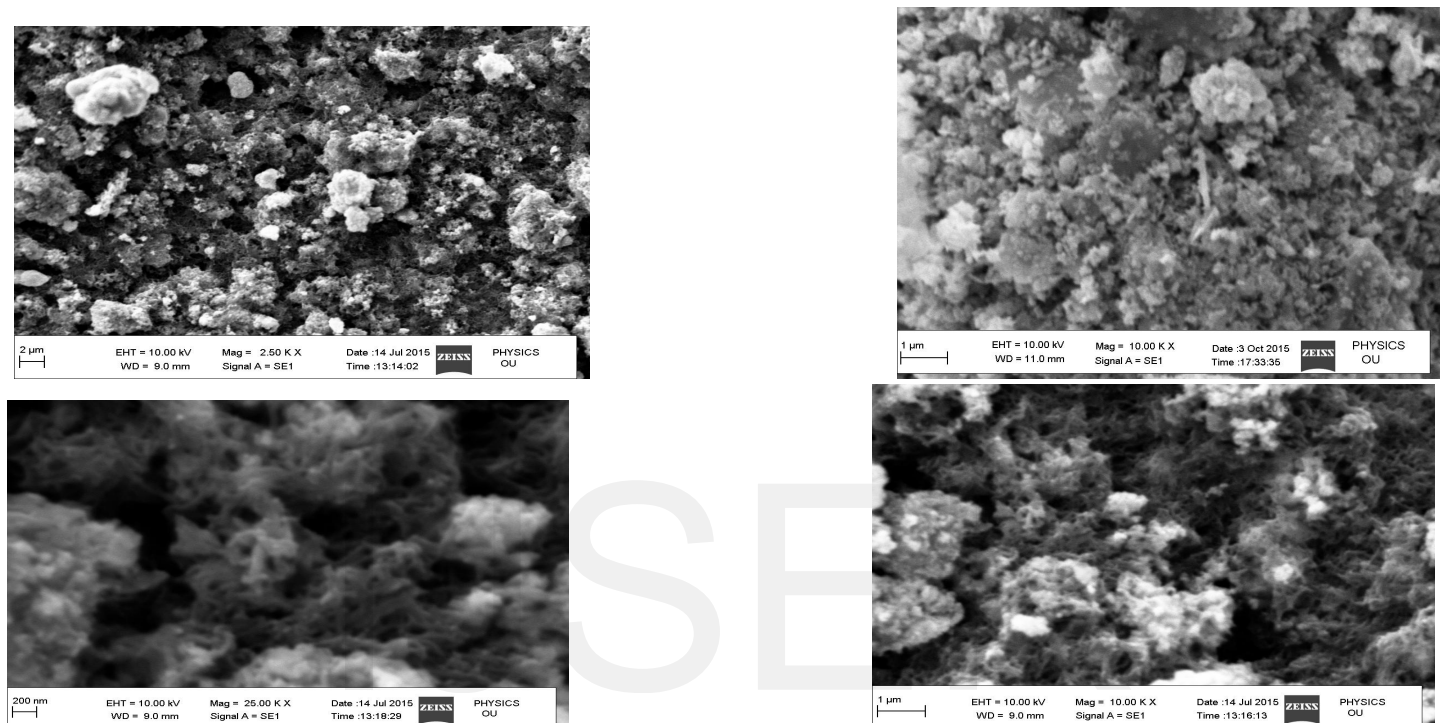


Fig 3 . FTIR pattern of PANI , Nano TiO<sub>2</sub> and PANI/TiO<sub>2</sub> composite

### 3.4 Scanning Electron Microscopy (SEM)

Morphological study confirms the formation of PANI/TiO<sub>2</sub> nano composite. Scanning electron micrographs of TiO<sub>2</sub> nano particles and PANI/TiO<sub>2</sub> nanocomposite are shown in fig. 4. The TiO<sub>2</sub> nano particles exhibit granular structures.

Comparing these images it is seen that the PANI fibers grew on the TiO<sub>2</sub> nano particle surfaces. These PANI fibers formed provide strength to the PANI/TiO<sub>2</sub> composite. It is also seen that the particles agglomerated into irregular shape as a result of polymer growth on the surface of the nano particles.



**Fig. 4 .SEM images of TiO<sub>2</sub> and PANI/TiO<sub>2</sub> composite**

### 3.5 Electrical investigation

Electrical investigation is one of the most important characteristics of a conducting polymer, especially to explore their use in electrical devices. An attempt was made to measure a.c conductivity and dielectric measurements. For electrical properties the powder was made in to pellets by uniaxial pressing.

#### 3.5.1 Dielectric measurement

For dielectric measurement the capacitance( C ) and the dissipation factor ( D ) for the sample was measured using an Wein kerr 41110 (U.K) LCR meter in the frequency range of 100Hz – 1 MHz. Fig. 5 represents the variation of dielectric constant ( $\epsilon'(w)$ ) with frequency for sample PANI/TiO<sub>2</sub> nano composites (different wt %). Dielectric constant at low frequencies

is quite high in all the samples. As frequency increases dielectric constant for all wt% decreased. This can be attributed to Debye-like relaxation mechanism. The system exhibit strong interfacial polarization at low frequency.[14][15] At low frequency the dipole can respond rapidly to follow the field and dipole polarization at its maximum value and so highest dielectric constant. At higher frequencies , dipole polarizability will be minimal as the field cannot induce the dipole moment so dielectric constant values attain minimum. [16]

Fig. 6 represent Dielectric constant with wt% of TiO<sub>2</sub> for three different frequencies (10K,100K and 1000K). It is observed that the dielectric constant is low for 30 wt% for all frequencies . It is observed that dielectric constant for PANI /TiO<sub>2</sub> 10wt% is around 204.6 at 10KHz and for PANI/TiO<sub>2</sub> 30wt% is



137 and for PANI/TiO<sub>2</sub> 50 wt% is 550 at same frequency.

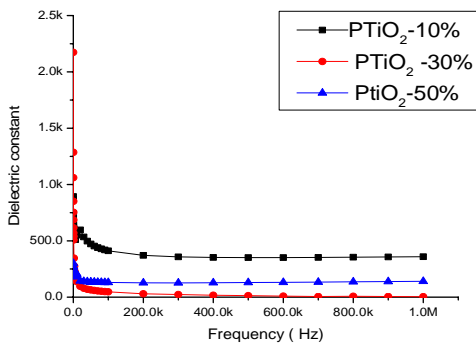


Fig. 5. Dielectric constant of PANI/TiO<sub>2</sub> Composite as a function of frequency

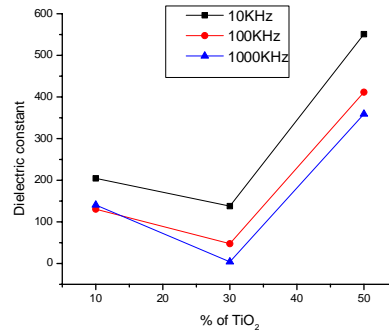


Fig. 6. Dielectric constant of PANI/TiO<sub>2</sub> composite as a function of wt % of TiO<sub>2</sub> at different frequencies

Fig. 7 shows variation of loss tangent with frequency. It is observed that as frequency increases loss tangent decreases for all composites. This suggests that dc conduction loss dominates over interfacial polarization losses present in the polymer.[17] For all the samples there is a very large value of loss at lower frequencies ( $\leq 10$  KHz). After 10KHz frequency the value falls abruptly and is constant for all samples. It is observed that there is little difference in the dielectric loss in all samples at high frequencies.[18]

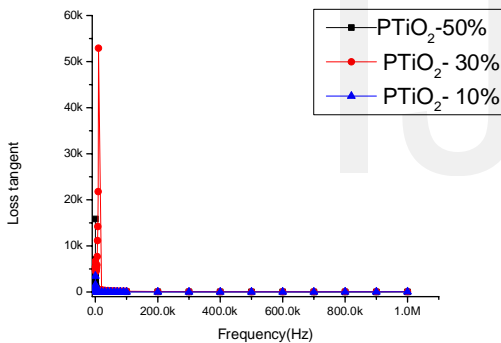


Fig. 7. Loss tangent of PANI/TiO<sub>2</sub> composite as a function of frequency

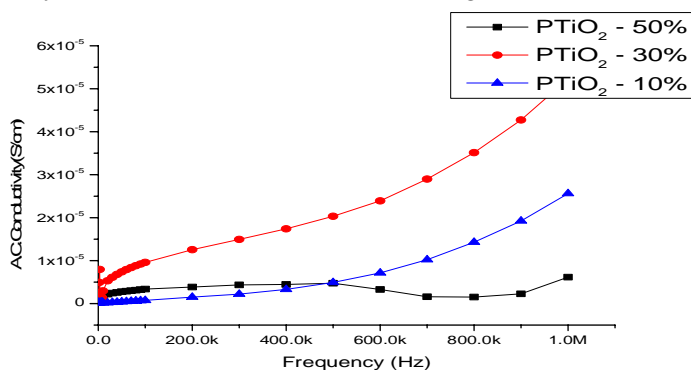
### 3.5.2 A.C. Conductivity

The A.C. conductivity ( $\sigma_{ac}$ ) is obtained from using the relation

$$\sigma_{ac} = \epsilon_0 \epsilon(\omega) \omega D \quad (2)$$

where  $\omega(=2\pi f)$  is the angular frequency and  $\epsilon_0$  is permittivity of free space ( $8.85 \times 10^{-12}$  farad per meter (F/m)). Fig. 8 shows the variation of AC conductivity as a function of frequency for PANI/TiO<sub>2</sub> (different wt%) composite. As shown in the figure it is evident that the A.C. conductivity is frequency dependent and enhanced with an increase in the frequency.[19][20] It is also observed that A.C. conductivity remains constant up to 100KHz frequencies and there after increases rapidly. This is associated with polarizability function. Doped PANI as two types of charged species,

one polaron / bipolaron system, which is free to move along the chain ,the others are bound charges which have



restricted mobility.

Fig. 8. *A.C conductivity of PANI/TiO<sub>2</sub> composite as a function of frequency*

At higher frequencies the conductivity increases because of the contribution of polarons, which are moving along shorter distances in the polymer chain. It is also observed from the figure that there is a sudden increase in the A.C conductivity for PANI/TiO<sub>2</sub> (30wt% ). This is the critical concentration for which the conductivity is maximum. For PANI/TiO<sub>2</sub> (50wt% ) the conductivity decreases. The increasing  $\sigma_{ac}$  at PANI/TiO<sub>2</sub> (30wt% ) is due to the increase of isolated polarons and bipolarons. Further increase in the doping may lead to severe pinning of polarons thus restricting their hopping hence reducing their conductivity.

#### 4 . CONCLUSIONS

PANI and PANI/TiO<sub>2</sub> composites were synthesized by in-situ polymerization. The synthesized PANI was found to be in Emeraldine Salt form as indicated by the green color. The incorporation of nanoTiO<sub>2</sub> in the PANI polymer matrix were confirmed by XRD, FTIR , SEM and UV Visible spectrum. The XRD pattern indicated the crystalline phase of TiO<sub>2</sub> . SEM analysis showed dispersion of TiO<sub>2</sub> nano particles in the PANI fiber matrix. Conductivity and dielectric properties such as dielectric constant and dielectric loss have been measured. Dielectric constant was measured and it was observed that at PANI/TiO<sub>2</sub> (30wt% ) had minimum value when compared to other PANI/TiO<sub>2</sub> composites. In all the samples dielectric constant and loss tangent decreased with increase in frequency. Similar results were observed with respect to A.C conductivity. PANI/TiO<sub>2</sub> (30wt% ) had maximum conductivity when compared to other PANI/TiO<sub>2</sub> composites. The present in situ synthesis encompasses simple method of preparing PANI/TiO<sub>2</sub> Composites.

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