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# Structural and dielectric properties of polyaniline / $TiO_2$ Nano-composites

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**Abstract:**

*Titanium oxide ($TiO_2$) doped polyaniline (PANI) i.e. PANI-$TiO_2$ nanocomposites with different fractions of $TiO_2$ were synthesized with a chemical polymerization method in HCl medium. The structure of the PANI-$TiO_2$ composites was confirmed by X-ray diffraction (XRD) technique. It showed that the $TiO_2$ of the composites was anatase crystalline and PANI contained some degree of crystallinity. The interesting behavior of the XRD patterns around 6% $TiO_2$ content was marked as critical concentration of the dopent. Dielectric measurements revealed about the strong interactions between PANI and $TiO_2$ nano particles causing a beneficial effect on stability of the composites. The hydrogen bonding was assigned as the mode of interaction between PANI and $TiO_2$ apart from other weak interactions. The synthesized polyaniline–TiO2 nano composite materials were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Dielectric properties of polyaniline–TiO2 nanocomposites were measured at 1 MHz–2.4 GHz and higher dielectric constants and dielectric losses of polyaniline–TiO2*

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*nanocomposites than neat PANI were found. Dielectric properties of composites are considered to be improved due to the addition of TiO2, which can improve the formation of a more efficient network for charge transport mechanism in the base polyaniline matrix.*

**Key words:** Conducting polymers, chemical synthesis, composite materials, Titanium oxide, and Electronic properties.

## 1. Introduction:

The conducting polymers have emerged as a new class of materials because of their unique electrical, optical and chemical properties. These properties may lead to a variety of practical applications such as information storage and optical signal processing, substitutes for batteries [1] and materials for solar energy conversion [2]. Furthermore, electroluminescence from conjugated polymers is a rapidly expanding field of interest since the reports of poly (p-phenylene vinylene) based devices [3-4]. These possible applications are to some degree limited by the low stability towards atmospheric oxidation and the lack of processability. As a result, considerable research effort has been directed towards the preparation of well-defined conjugated polymers with improved processability and stability characteristics. Conductive polyaniline (PANI) has been studied extensively because of its ease of synthesis in aqueous media, its environmental stability and special electrical and other properties. It is a suitable candidate for a variety of technological applications [5] such as solar cells, electromagnetic shielding, electrodes for rechargeable batteries, sensors, etc. Preparation of composites of the conducting polymer (PANI) has been considered to provide a suitable solution to the processability problem. A class of nano materials is nano clusters. The materials based upon nanoclusters are a topic of great importance [6-7]. Nano clusters are ultrafine particles of nanometer dimensions located in the transition region between atoms and bulk solids. Quantum states in the nanoclusters are size-dependent, leading to novel properties that are sometimes dramatically different from those of the atomic and bulk counterparts [8, 9]. For example, $TiO_2$ clusters can absorb the ultraviolet (UV) energy that is why they are used as protectant against external irradiation and sunlight. The absorbed organic compounds on $TiO_2$ clusters can be decomposed by oxidation due to presence of a radical released by irradiation. Therefore, such nanoclusters of $TiO_2$ are known as photo catalyst. Among the semiconductors being studied, $TiO_2$ is one of the most efficient photo catalysts. The advantage of utilizing $TiO_2$ includes its low cost, radiation stability, and the fact that there is no need to use strong oxidizing agents, such as $O_3$ or $H_2O_2$ .As Titanium dioxide ($TiO_2$) is concerned, several studies have focused on the influence of different crystalline structures. Titanium (IV) oxide, occurring in three polymorphic forms – rutile, anatase, brooked, is a very common pigment utilized in various industries [10]. Rutile and anatase are produced commercially in large quantity for the use as pigments, catalysts and in the production of ceramic and electronic materials. Their electrical conductance is between $1.1 \times 10^{-5} - 3.4 \times 10^{-3}$ S/cm [11]. It is generally shown that anatase is more efficient as a photo catalyst than rutile the poor photocatalytic activity of rutile was proposed due to its higher electron-hole recombination rate [12-14].

Indeed, a variety of $TiO_2$ materials synthesized in recent years including $TiO_2$ aerosols [15, 16], aerogels [17-19], nanorods [20, 21], nano tubes [22, 23], nano crystals [24–28] and meso porous materials [29-32] show promising photoreactivity. Also, photo-induced superhydrophilicity and generation of reactive oxygen species (ROS) by photoactivated $TiO_2$ were linked to its antimicrobial properties [33]. $TiO_2$ is widely used in welding-rod coatings, specific paints, inks, acid-resistant vitreous enamel, etc. owing to its high refractive index, durability, dispersion, tinting, strength, chemically inert nature and non toxicity. Titanium dioxide has also been studied to prepare its composite with conducting polymers, such as poly(3-methylthiophene) supported on $TiO_2$ for solid-state photoelectron chemical device [34]. The conducting polyaniline/$TiO_2$ composites were investigated, which exhibit high piezo sensitivity being maximum at a certain PANI- $TiO_2$ composition [35, 36].

## 2. Experimental:

### 2.1. Materials:

Aniline (Merck) was distilled under reduced pressure and stored at low temperature prior to use. Ammonium per sulfate (APS) was obtained from SIGMA ALDRICH. Titanium oxide ($TiO_2$) was supplied by SIGMA ALDRICH and used as obtained. All materials were used as provided without any further.

### 2.2. Synthesis of polyaniline (PANI):

Aniline was added dope wise in 30ML distilled water for about 1h and the solution was left stirring for 6 hrs. HCl was added dope wise in it to keep PH between 0 and 1. After this Ammonium per sulphate (APS) was added drop wise for about 30 minutes period, whereas molar ratio of oxidant to monomer was kept 1:2. As the Ammonium per sulphate (APS) mixed with the solution, it turned to greenish black color, indicating that the organic polymerization reaction has begun. The solution was left overnight, the next day the solution was filtered and a dark black-green paste of Polyaniline was obtained which was washed with plenty of distilled water until the filtrate become colorless. The paste was kept at 70°C in a vacuum oven for 24 hours.

### 2.3. Synthesis of PANI/ $TiO_2$ nanocomposites:

Titanium oxide ($TiO_2$) mixed in 100mL distilled water and the mixture was stirred for about 1h in order to disperse Titanium oxide ($TiO_2$) in the solution. Aniline was added dope wise for about 1h and the solution was left stirring for 6 hrs. HCl was added in it to keep PH between 0 and 1. After this, Ammonium per sulphate (APS) was added drop wise for about 30 minutes period and Titanium oxide ($TiO_2$) was varied from 0% to 40%, whereas molar ratio of oxidant to monomer was kept 1:2. As the Ammonium per sulphate (APS) mixed with the solution, it turned to greenish black color, indicating that the organic polymerization reaction has begun. The solution was left overnight, the next day the solution was filtered and a dark black-green paste of Polyaniline / $TiO_2$ was obtained which was washed with plenty of distilled water until the filtrate become colorless. The paste was kept at 70°C in a vacuum oven for 24 hours.

## 2.4. Measurements:

Electronic properties (Dielectric and Conductivity) were measured in pressed pellets in a press machine at 10 ton pressure in stainless steel die of 0.85 mm diameter and 0.5 mm thickness by using a two-point method in the frequency range 1MHz to 2.4GHz. The samples were connected to a Keithley 2400 electrometers and a current source electrometer. The dielectric constant of all the samples and reproducibility were checked. X rays powder diffraction analysis was carried out using an automated diffractometer, Panalytical X' Pert PRO equipped with Cu Kα radiations ($\lambda$=1.54 A°). The instrument was operated at 40 kV and 30 mA and diffraction patterns of PANI and PANI-$TiO_2$ Composites samples mounted on a standard holder were recorded over the range of 10° to 80° counting time was 0.5 s and the step size was 0.02. .The crystalline size was calculated from Scherer equation and d-spacing was calculating from Bragg's equation. Scanning electron microscopy was carried out on an EVO50 ZEISS instrument.

## 3. Results and discussion:

### 3.1. XRD Analysis:

X-ray diffraction of Synthesis PANI, Pure $TiO_2$ and PANI/$TiO_2$ composites with different $TiO_2$/monomer weight ratio ranging from 6% to 42% are shown in Figures 1, 2 and the corresponding diffraction data are arranged in Table 1.

X-ray diffraction patterns of the polyaniline exhibits no sharp peak except a broad peak in the range of $18^0$-$28^0$, (Fig.1a) which is characteristic peak of PANI and suggests that the structure of pure polyaniline is amorphous as reported in the literature [37]. The XRD pattern of the $TiO_2$ nano particles is in good accordance with that on the JCPD card 21-1272 , Which corresponds to d-spacing = 3.49 Å, 2.38 Å, 1.89 Å, 1.70 Å, 1.66 Å, 1.48 Å and 1.36 Å respectively and average grain size of $TiO_2$ is 27.1nm. X-ray diffraction patterns of the PANI-$TiO_2$ composites having 18% $TiO_2$ represented in Fig.1 PT-18. When doping percentage of $TiO_2$ is increased to 18% then resulting peaks at $2\theta$ = $25.659^o$, $38.040^o$, $48.411^o$, $54.180^o$, $55.377^o$, $62.949^o$, $68.936^o$ which corresponds to d-spacing =3.46 Å, 2.36 Å, 1.88 Å, 1.69 Å, 1.66 Å, 1.48 Å and 1.36 Å respectively are observed and average grain size of this composite is 27.14nm shows a little shift of peaks towards greater angle side .It is due to the increasing concentration of $TiO_2$ and increase in grain size is also measured. Polyaniline deposited on the surface of $TiO_2$ particles have no effect on the crystallization behavior of $TiO_2$ particles in composites [38] and Lee et al [39] have recorded similar observations on the XRD pattern of PANI-$TiO_2$ composites. X-ray diffraction patterns of the PANI-$TiO_2$ composites having 30% $TiO_2$ represented in Fig.1 PT-30 (30 % weight ratio of $TiO_2$/monomer) change in d-spacing observed, resulting peaks at $2\theta$ = $25.7^o$, $38.040^o$, $48.411^o$, $54.180^o$, $55.377^o$,$62.949^o$, $69.138^o$ which corresponds to d-spacing =3.47 Å, 2.36 Å, 1.88 Å, 1.69 Å, 1.66 Å, 1.48 Å and 1.35 Å respectively are observed and average grain size of this composite is 27.2nm and very small shift of last peak towards right takes place. It is due to the increase in $TiO_2$ concentration. X-ray diffraction patterns of the PANI-$TiO_2$ composites having 6% $TiO_2$ represented in Fig.2 PT-6 (6 % weight ratio of $TiO_2$/monomer) where peaks at 2θ = 25.33°, 37.883°, 48.118°, 53.756°, 55.035°, 62.732°, 68.629° which corresponds to d-spacing = 3.51 Å, 2.37 Å, 1.89 Å, 1.70 Å, 1.67 Å, 1.48 Å and 1.37 Å respectively are observed and average grain size of this composite is 24.317nm. These peaks show the crystalline structure of composite and corresponding results are in good agreement with the literature [40]. The intensity of this composite is lower than pure $TiO_2$ Because $TiO_2$ is more crystalline than composite. The presence of non-crystalline polyaniline reduces mass-volume percentage of $TiO_2$ and hence reduces the intensity of $TiO_2$. When $TiO_2$ concentration is further increased to 42% then grain size increased largely to 50.8nm and corresponding peaks at 2θ = 25.03°, 37.532°, 47.789°, 53.69°, 54.81°,62.410°, 68.509° which corresponds to d-spacing =3.56 Å, 2.396 Å, 1.90 Å, 1.707 Å, 1.67 Å, 1.488 Å and 1.369 Å respectively are observed and peaks are little shifted towards left and corresponding d-spacing increased and hence grain size increased .It is due to the increase in doping concentration of $TiO_2$.These results are in good agreement with the literature [41].There is no difference between XRD pattern of $TiO_2$ and PANI-$TiO_2$ composites, which reveals that deposition of PANI on the surface of $TiO_2$ nano particles has no effect on the crystallinity of $TiO_2$ particles , this result suggest that crystallization of PANI molecular chain has been hampered in PANI-$TiO_2$nanocomposites[42] d-space is the characteristic distance between the planes of benzene rings in adjacent planes and is the inter chain distance or the close interaction distance between two adjacent chains. Further, it is a general thought that the polymer chain array and the inter chain distance are affected by the size and shape of the interlying dopants which result in an increase in electron delocalization length till a saturation value [43]. In the samples studied the grain size start increasing with the addition of $TiO_2$. The peculiar behavior of $TiO_2$ in this range points towards some interesting changes in the electrical and magnetic properties of the material.

| **S.No** | **Sample Code** | **Average grain size (nm)** |
|---|---|---|
| **1** | **T** | 27.1 |
| **2** | **PT-6** | 24.32 |
| **3** | **PT-18** | 27.14 |
| **4** | **PT-30** | 27.2 |
| **5** | **PT-42** | 50.8 |

**Table 1: The observed Grain size values of $TiO_2$ and PANI-$TiO_2$ composites**

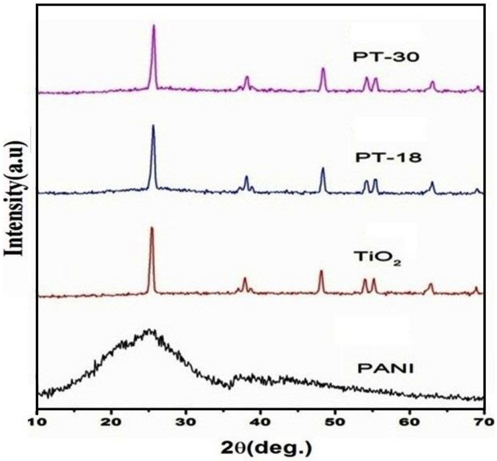

**Figure 1: XRD pattern of Synthesis PANI, Pure $TiO_2$and PANI- $TiO_2$ Composites.**

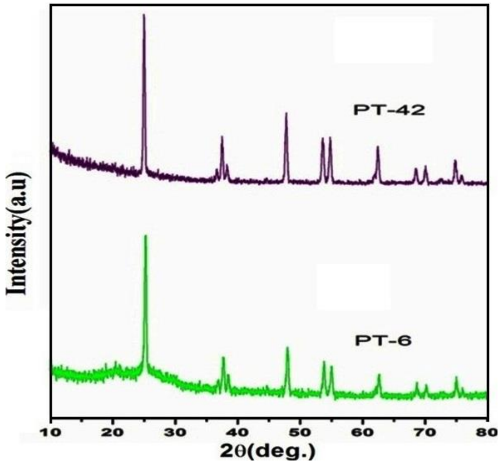

**Figure 2: XRD Pattern of PANI-$TiO_2$ composites.**

## 3.2. Scanning Electron Microscopy (SEM)

In order to confirm the crystallinity of polyaniline doped with $TiO_2$ the SEM images of polymers have been obtained and are shown in Fig. 3. SEM of Synthesis PANI exhibit bright granular agglomerates without much inter-particle spacing and pure $TiO_2$ have platelet structure. However the particle size of doped Polyaniline increases and the structure is flaky. Also the composite PANI-$TiO_2$ is showing increment in particle size and a mixture structure of platelet as well as flaky structure is achieved. The doped PANI with $TiO_2$ is more crystalline as matched to PANI because grain size is increasing as polyaniline is shifting to PANI-$TiO_2$. According to the SEM images, it was considered that the nano structured TiO2 particles implanted within the netlike structure built by PANI chains.

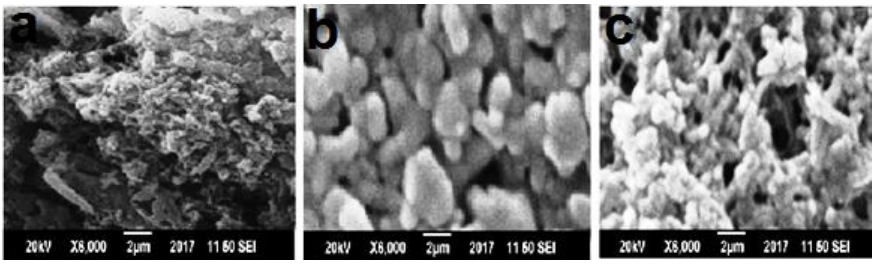

**Figure 3: ( a) SEM of Synthesis PANI (b) SEM of TiO2(c) SEM of PANI-$TiO_2$ composite.**

## 3.3. Frequency dependent dielectric Properties:

### 3.3.1 Dielectric constant:

Dependence of dielectric constant, dielectric loss and tan loss as a function of frequency ranging from 1MHz–2.4GHz at room temperature for the Synthesis (PANI) and PANI-$TiO_2$ composites is plotted in figures 4 - 6 respectively. It was observed that dielectric constant an dielectric loss are high at low frequency and decreases sharply as frequency increases and nearly becomes constants at high frequencies indicating the usual dispersal. As capacitance and dielectric constant are directly proportional to each other shown by equation

$$\varepsilon' = Cd/A\varepsilon_0 \qquad (1)$$

Dielectric constant also decreases with the increase in frequency just like capacitance, Average dielectric constants and average dielectric Loss of PANI, PT-6 and PT-42 are shown in table 2.

The electric field effects on polyaniline depend on the different factors temperature, electric field frequency, acid doping, and water content. The dielectric function $\varepsilon^*$ gives the information of transport mechanism in the system. The dielectric response is described by the complex permittivity

$$\varepsilon^* = \varepsilon' - i\varepsilon \qquad (2)$$

Where $\varepsilon'$ is storage energy in each cycle of applied electric field, $\varepsilon''$ loss of energy in each cycle of applied electric field. At high frequency the value of $\varepsilon'$ is nearly constant in assessments to at low frequency and high temperature [44]. The increase of the dielectric permittivity with doping is a result of helps from the backbone emeraldine base and the formed polaron and bipolarons to the polarization [44]. The increasing dielectric constant and loss with decreasing frequency is due to the conductivity which is directly related to the increase in mobility of localized charge carriers. This may be ascribed the dipoles resulting from changes in valence states of cations and space charge polarization. At high frequencies, electric dipoles are unable to follow the alternating applied electric field, so dielectric constant remains independent of frequency [45].These frequency independent values are known as static values of the dielectric constant. At low frequencies ($f<f_r=1/2\pi t_r$) dipoles follow the field in each dispersion region, where $f_r$ is mean relaxation frequency and $\varepsilon'_r=\varepsilon'_s$ where $\varepsilon'_s$ is static dielectric constant in the plateau region. With increasing frequency, the dipoles do not follow the field an lag behind according to their mobility which results in slight decrease of $\varepsilon'_r$. After relaxation frequency $f_r=1/2\pi t_r$ ($t_r$ is relaxation time), the dipoles are unable to follow the applied electric field so sharp decrease in dielectric constant is observed. Very high values of dielectric constant at the lower frequencies as compared to those at the higher can be ascribed to the presence of all types of polarization such as electrode, interfacial and dipolar, atomic, ionic and electronic contribution So our These results are in good agreement with the literature [45,46].

Dielectric loss is loss of energy that goes into heating a dielectric material in a varying electric field. During the alternation of polarity of the plates, the charges must be displaced through the dielectric first in one direction and then in the other direction. Dielectric loss increases with the increase in dielectric constant and PANI-TiO2 composites shows higher dielectric constant and dielectric loss [47].

$$\varepsilon'' = \varepsilon' \tan\delta \qquad (3)$$

| **Sr No** | **Sample code** | **Average dielectric constant ( ε')** | **Average dielectric Loss ( ε")** |
|---|---|---|---|
| 1 | P | 4.1x$10^2$ | 1.42x$10^2$ |
| 2 | PT-6 | 4.6x$10^3$ | 3.13x$10^3$ |
| 3 | PT-42 | 3.85x$10^2$ | 1.06x$10^2$ |

**Table 2: The observed average Dielectric constant and average Dielectric Loss of PANI and PANI-$TiO_2$ composites observed in frequency range from 1MHz to 2.4GHz.**

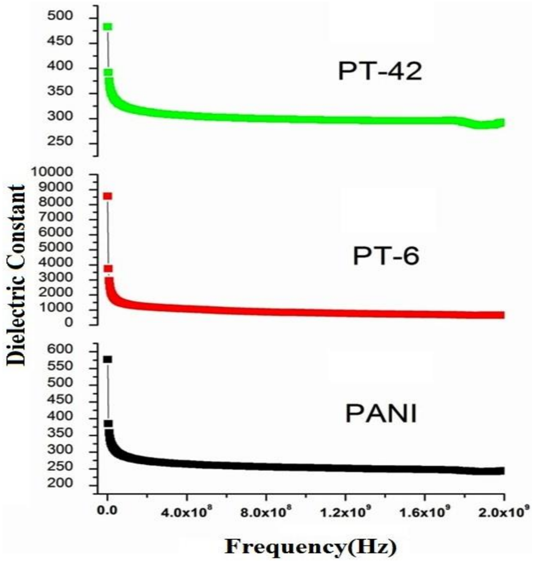

**Figure 4: Dielectric constant Vs frequency of PANI and PANI-$TiO_2$ composites**

### 3.3.2 Dielectric Loss factor or tangent Loss

The energy lost in a dielectric is measured by the angle$\delta$ between the current and charging potential in dielectric systems relaxation effects occur if dielectric displacement D(ω) lags behind in phase with electric field E(ω). For vacuum this angle is $90^o$ but if dielectric material of some dielectric constant is placed, this phase angle does not remain $90^o$. The angle by which dielectric displacement D(ω) deviates from $90^o$ is termed as loss angle or tangent loss. It is the ratio of dielectric loss to the dielectric constant. Frequency dependent dielectric measurements were carried out using Wayne Kerr LCR meter Model 4275 in the frequency range 1MHzto 2.4 GHz at room temperature (300 K). The higher values of tanδ at low frequency and decrease in tanδ at higher frequency for pure PANI and PANI-$TiO_2$ composites of different concentration are shown in figure 6. As frequency increases, dielectric constant and dielectric loss decreases sharply and hence tanδ decreases sharply Decrease in dielectric constant, dielectric loss and tanδ with increasing frequency is a typical characteristics of conducting polymer. Our observed measurements are in good agreement with literature [48]. Figure 6 Shows high tangent loss for 6% PANI-$TiO_2$ composite because dielectric constant and dielectric loss of this sample is quite high than those of pure PANI and 42% PANI-$TiO_2$.

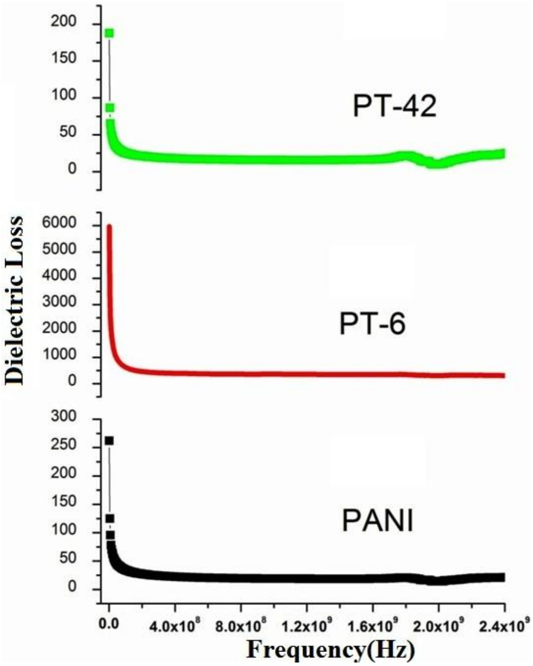

**Figure 5 Dielectric Loss Vs frequency of PANI and PANI-$TiO_2$ composites**

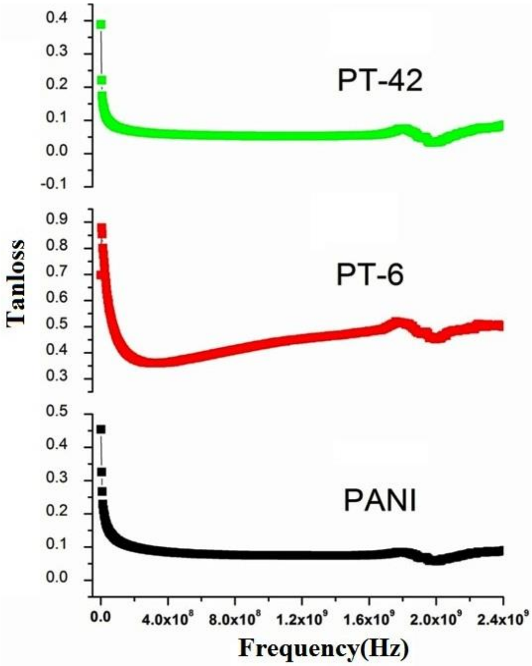

**Figure 6 tanδ Loss Vs frequency of PANI and PANI-$TiO_2$ composites**

### 3.3.3 A.C conductivity ($\alpha_{a.c}$)

AC conductivity is measured using the equation;

$$\alpha_{a.c} = 2\pi f \varepsilon o\ \varepsilon' \tan \delta \qquad (4)$$

The a.c conductivity ($\alpha_{a.c}$) increases with an increase in frequency. The frequency dependent behavior can be explained by Maxwell-Wagner double layer model [50] .As PT-6 shows high a.c conductivity than PANI and PT-42 composite.PT-6 composite shows high dielectric constant than Pure PANI and PT-42 composite .But behavior of conductivity is opposite to that of dielectric constant. Dielectric constant decreases with the increase in frequency but conductivity increases with the increases in frequency and this behavior can be explained by Maxwell-Wagner double layer model. The increase of $\alpha_{a.c}$ with frequency is due to the presence of various kinds of in homogeneity present in the materials [51]. The conductivity of PANI–$TiO_2$ nanocomposites is higher than free PANI. Imene*et al*[52]suggested that increase in conductivity of composite than pure conducting polymer is due to the fact that for this loading amount of monomer a larger amount of aniline has been intercalated by solid–solid reaction into the $TiO_2$ and has been polymerized in the $TiO_2$ interlayer with an extended chain conformation which has for effect the decreasing of p defects and the polymer bridges and hence the amelioration of the conductivity of the nanocomposites[52] average a,c conductivity of PANI and PANI-$TiO_2$composites. that PT-6 has large a.c conductivity than PANI and PT-42 composite. It means conductivity decreases when concentration of $TiO_2$ is increased to 42%. The increasing trend of conductivity for PANI–TiO2 was also described by Xu*et al*[38]and Su*et al*[53]. From the results described above, it has been considered that the improved dielectric constants and losses might originate from the increased conductivity. The addition of $TiO_2$ might encourage the formation of a more efficient network for charge transport in the base polyaniline matrix, resulting in higher conductivities [38] showed that Electrical conductivity measurements direct that the conductivity of composites at low $TiO_2$ content is much higher than that of pure PANI, while with the increasing percentage of $TiO_2$, the conductivity indicates an orderly decrease So our measured experimental results show good agreement with the literature[38,53].

| **Sr. No** | **Sample code** | **Average ac conductivity ($\alpha_{a.c}$) (S/cm)** |
|---|---|---|
| 1 | P | $1.44x10^{-2}$ |
| 2 | PT-6 | $20.40x10^{-2}$ |
| 3 | PT-42 | $1.66x10^{-2}$ |

**Table 3: The observed average a.c conductivity of PANI and PANI-$TiO_2$ composites**

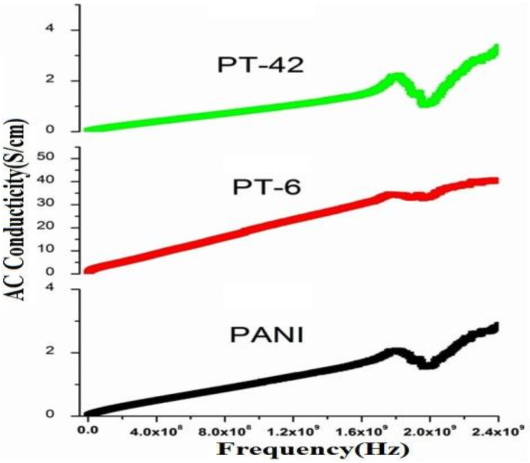

**Figure 7: A.C conductivity Vs frequency of PANI and PANI-$TiO_2$ composite**

## Conclusions

Nanocomposites of PANI/ $TiO_2$ were successfully synthesized by chemical polymerization method. The crystallinity of synthesized samples was studied by XRD diffraction pattern and was found to be improved due to crystalline nature of $TiO_2$ in PANI/ $TiO_2$ composite. Dielectric characterization demonstrated that TiO2 nano particles exhibit a strong effect on the dielectric properties of resultant PANI/ $TiO_2$ nanocomposites. The increased Dielectric constant is attributed to the formation of a better charge transport network in the relatively insulating polyaniline matrix. Increase in a.c conductivity observed with the increase in frequency for PANI and PANI-$TiO_2$ composite and small electric modulus is observed for PANI-$TiO_2$ composites than pure PANI.

## BIBLIGRAPHY

1. F. Brandstetter, Eur. Chem News Speciali O' Chemical Suppl, 32 (1988).
2. M. J. Sailor, E. J. Ginsburg, C. B. Gorman, A. Kumar, R. H. Grubbs, and N. S. Lewis, Scienc*e* 249, 1146 (1990).
3. J. H. Buroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. MacKay, R. H. Friend, P. L. Burn, and A. B. Holmes, Nature (London), 347, 539(1990).
4. D. D. C. Bradley, Synth. Met.54, 401(1993).
5. M. G. Han, S. Soon; Journal of Applied Polymer Science. 82, 2760 (2001).
6. S. D. Patil, S. C. Raghavendra, M. Revansiddappa, P. Narsimhaand M. V. N. A. Prasad: Bull. Mater. Sci. 30, 89 (2007).
7. S. C. Raghavendra, S. Khasim, M. Revanasiddappa, M. V. N. Ambika Prasadand A. B. Kulkarni*:* Bull. Mater. Sci. 26*,* 733(2003).
8. M. D. Butterworth, R. Corradi, J. Johal, S. F. Lascelles, S. Maeda and S. P. Armes: Journal of Colloid and Interface Science. 174*,* 510 (1995).
9. Ananya Dan, P. K. Sengupta:Journal of Applied Polymer Science.91, 991(2003).
10. J. Tang, F. Redl, Y. Zhu, T. Siegrist, L.E. Brus, M.L. Steigerwald: *Nano Lett*. 5, 543 (2005).
11. X. Jiang, T. Herricks, Y. Xia: *Adv. Mater*. 15, 1205 (2003).
12. A. Braun, E. Pelizzetti and M. Schiavello, Photochemical Conversion and Storage of Solar Energy, Kluwer, Dordrecht, 551, (1991)
13. R. S. Carmicheal, Handbook of Physical Properties of Rocks. CRC Press. Fluorida: (1982).
14. S. I. Nishimoto, B. Ohtani, H. Kajiwara and T. Kagiya: J. Chem. Soc. Faraday Trans. 181, 61 (1985).

15. K. Tanaka, T. Hisanaga and A.P. Rivera and H. Al-Ekabi, Photocatalytic Purification and Treatment of Water and Air Elsevier,Amsterdam, 169, (1993).
16. M.A. Fox and M.T. Dulay: *Chem. Rev.* 93, 541 (1993).
17. C.R. Bickmore, K.F. Waldner, R. Baranwal, T. Hinklin, D.R. Treadwell, R.M. Laine*:* J. Eur. Ceram. Soc. 18, 287 (1998).
18. C.B. Almquist, P. Biswas: *J. Catal.* 212, 145 (2002).
19. L.K. Campbell, B.K. Na, E.I. Ko: *Chem. Mater.* 4, 1329 (1992).
20. V. Strengl, S. Bakardjieva, J. Subrt, J. Szatmary, *Micropor. Mesopor. Mater.* 911 (2006).
21. S. Yoda, D.J. Suh, T. Sato: *J. Sol–Gel Sci. Technol.* 22, 75 (2001).
22. J. Joo, S.G. Kwon, T. Yu, M. Cho, J. Lee, J. Yoon, T. Hyeon: J. Phys. Chem. *B* .109, 15297(2005).
23. X. Peng, A. Chen: J. Mater. Chem. 14, 2542(2004).
24. P. Hoyer: Langmuir. 12, 1411 (1996).
25. C. Aprile, A. Corma, H. Garcia, Phys. Chem. Chem. Phys. 10, 769 (2008).
26. M. Qamar, C.R. Yoon, H.J. Oh, N.H. Lee, K. Park, D.H. Kim, K.S. Lee, W.J. Lee, S.J. Kim, *Catal. Today* 13, 3(2008).
27. M. Wu, G. Li, D. Chen, G. Wang, D. He, S. Feng, R. Xu: *Chem. Mater.* 14, 1974 (2002).
28. A.J. Maira, K.L. Yeung, J. Soria, J.M. Coronado, C. Belver, C.Y. Lee, V. Augugliaro: *Appl. Catal. B.* 29, 327 (2000).
29. A.J. Maira, J.M. Coronado, V. Augugliaro, K.L. Yeung, J.C. Conesa, J. Soria*, :J. Catal.* 202, 413 (2001).
30. J.M. Coronado, A.J. Maira, J.C. Conesa, K.L. Yeung, V. Augugliaro, J. Soria: Langmuir . 17, 5368, (2001).
31. D.M. Antonelli, J.Y. Ying, Angew: Chem. Int. 34, 2014 (1995).
32. F. Bosc, A. Ayral, P.A. Albouy, L. Datas, C. Guizard, *Chem. Mater.* 16, 2208 (2004).

33. J.G. Yu, J.C. Yu, W.L.K. Ho, Z.T. Jiang, *New J. Chem*. 26, 607 (2002).
34. Y. Yamauchi, F. Takeuchu, S. Todoroki, Y. Sakka, S. Inoue *: Chem. Lett.* 37, 72 (2008).
35. A.F. Nogueira, L. Micaroni, W.A. Gazotti, M.A. De-Paoli *: Electrochem. Commun.* 1, 262(1999).
36. P.R. Somani, R. Marimuthu, U.P. Mulik, S.R. Sainkar, D.P. Amal- nerkar: *Synth. Met.* 106, 45 (1999).
37. A. Shakoo: Preparation, Characterization and Studies of Conducting Polymer Composites and Blends, department of physics, quaid-i-azam University, islamabad, Pakistan, (2009).
38. J.C. Xu, W.M. Liu, H.L. Li: Mater. Sci. Eng. 25, 447 (2005).
39. I.S. Lee, J.Y. Lee, J.H. Sung, H.J. Choi: Synth. Met. 152, 173 (2005).
40. Xueyan Li, Desong Wang, Guoxiang Cheng, Qingzhi Luo, Jing An, Yanhong Wang, 81, 267 (2008).
41. S. Sathiyanarayanan, S. Syed Azim, G. Venkatachari: Electrochemical Acta. 52, 2068(2007).
42. Te-Cheng Mo, Hong-Wen Wang , San-Yan Chen , Yun-ChiehYeh: Ceramics International 34, 1767(2008).
43. R. Murugesan, and E. Subramanian: *Mat. Chem. And Phys*. 77, 860(2002).
44. Pinto N.J, Sinha G.P, Aliev F.M : Synthetic Metals. 94, 199(1998).
45. K.K. patankar,P.D. Dombale,V.L. Mathe, S.A. Patil, R.N. Patil: Material science Engineering. 8, 53 (2001).
46. M. Idrees,M. Nadeem, M. Atif, M. Siddique, M. Mehmood, M.M. Hassan,ActaMaterialia, 59 1338(2011).
47. Te-Cheng Mo, Hong-Wen Wang , San-Yan Chen , Yun-ChiehYeh: Ceramics International. 34, 1767(2008).
48. A.K.Himansh, D.K. Ray,T.P. Sinha: Indian J physics.79, 1049(2005).
49. E.S. Matteeva: Synth Met.79, 127 (1996).

50. K. W. Wagner: Arch Elektrotech. 2, 371(1914).
51. D.J.E. Albuquerque, L.H.C. Mattoso, D.T. Balogh, R.M. Faria, J.G. Masters A.G.MacDiarmid: Synth. Met. 113, 19(2000).
52. ImeneBekri-Abbes ,EzzeddineSrasra,: Elsevier Reactive & Functional Polymers, 70, 11 (2010).
53. S.J.Su, N. Kuramoto: Synth. Met. 114 , 147 (2000).