

# Electrical & dielectric studies of magnesium oxide doped Polyaniline nanocomposites influenced by ammonium dichromate

Mahantappa Limbitot<sup>1</sup>, Sangshetty Kalyane<sup>2</sup>, Nagbasavanna Sharanappa<sup>3</sup>, Vidyadhara<sup>4</sup>, B.D.Malipatil<sup>5</sup>

<sup>1&2</sup>Department of Physics, Bheemanna Khandre Institute of Engineering and Technology, Bhalki, Bidar, Karnataka, India,

<sup>3&4</sup>Department of Physics, Sharnbasva University, Kalaburagi, Karnataka, India

<sup>5</sup>Department of Physics, Sharnbasveshwar College of Science, Kalaburagi, Karnataka, India

**Abstract:** *In situ chemical oxidation route has been adopted to prepare polyaniline emeraldine salt (PANI) & magnesium oxide doped Polyaniline (MgO/PANI) with different molar concentration of MgO using ammonium dichromate (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (ADC) as an oxidant & HCL as catalyst. Composite of PANI with 5%, 10%, 20 %, 30%, 40% & 50% of magnesium oxide (MgO) has been synthesized by adding magnesium oxide powder gradually in the polymerization solution of aniline & APS. Further these composites were characterized by XRD & SEM techniques to investigate their structural and morphological studies. As a part of electrical studies, AC conductivity, dielectric constant, dielectric loss and variation of tanδ of all the composites were studied as a function of frequency by using impedance analyser. DC conductivity was studied as a function of temperature.*

**Key Words:** Polyaniline, XRD, SEM, AC, DC conductivity & dielectric constant, tanδ.

## 1. Introduction:

Among the many materials, conducting polymer has unique properties such as electrical, optical and magnetic property, due to this reason polymers increasing scientific and technical interest and offering the opportunity to prepare new polymer materials [1].

Conducting polymers are characterized by a conjugated structure of alternating single and double bonds. The feature shared by all them originates from the common nature of their  $\pi$ -electron system, an enhanced conductivity in oxidized or in reduced state and reversible redox activation in a suitable environment [2].

Among all the conducting polymers, polyaniline has a unique and wide range electrical, dielectric properties and good stability. Hence polyaniline have been considered as prominent new materials for the fabrication of the devices. Polyaniline (PANI) is an important conducting polymer because of its high conductivity in doped state. PANI has wide range of application due to its flexible properties in different area. Such some applications are solar cell, LED, sensors, radiation absorbers and electromagnetic shields. It is possible to alter the properties of the PANI by the process of doping metal oxide or various types of particles with polyaniline. It is one of so called polyaniline composite, in which conductivity results from a process of partial oxidation or reduction [3]. There are many oxidation forms of the polyaniline, among these the most important form of polyaniline is green protonated emeraldine which can prepare by using chemical oxidative polymerization method. When the metal oxide or various types of particles are doped with polyaniline, the charge-transfer reaction takes place between polyaniline and doping agent. The bond length and angles changes when charges are removed from the polyaniline upon chemical doping. The charge is localized over the region of several repeating units. Since the localized charges can move along the polymer chain, they are regarded as charge carriers in conducting polymer [4]. Ammonium persulfate (APS), Ammonium Dichromate (ADC) was used as an oxidant to minimize the presence of residual aniline and to obtain the best yield of PANI.

Magnesium oxide (MgO), a versatile oxide material with assorted properties finds extensive applications in catalysis, ceramics, toxic waste remediation, and as an additive in paint and superconductor products [8]. Also, owing to its very large band gap (7.8 eV) [9], excellent thermodynamically stability, low dielectric constant and refractive index, it has been used for growing various thin film materials [10]. From literature it has been found that MgO nanostructures may be synthesized by dehydration of Mg(OH)<sub>2</sub> or by decomposition of various magnesium salts using different techniques such as sol-gel method [11], thermal evaporation [12], flame spray pyrolysis [13], combustion aerosol synthesis [14], chemical vapour deposition [15], hydrothermal [16], and surfactant methods [17] etc.

## 2. Materials and Method:

### i. Preparation of Polyaniline

Aniline solution of 0.2M is mixed with 1N of solution of hydrochloric acid at room temperature. This mixer was stirred by magnetic stirrer for 2 hrs at constant RPM for the completion of the reaction. The solution of 0.2 M of ammonium dichromate (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (ADC) was added drop wise into the mixer. This reaction mixer was continuously stirred in magnetic stirrer for 8 hrs in room temperature. The precipitate formed and separated out by filtering and washed with deionised water with acetone. The obtained final suspension was dried in oven at 50° C for 24 hrs. The final product was grinded into powder.

### ii. Preparation of MgO/Polyaniline:

Aniline solution of 0.2M is mixed with 1N of solution of hydrochloric acid at room temperature. This mixer was stirred by magnetic stirrer for 2 hrs at constant RPM for the completion of the reaction. The solution of 0.2 M ammonium dichromate (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (ADC) was added drop wise into the mixer. Magnesium oxide (MgO) powder for different additive weight percentage (5%, 10%, 20%, 30%, 40% & 50%) is dissolved in the mass fraction to the above solution with vigorous stirring in order to keep the MgO homogeneously suspended in the solution and stirring of final solution was continued for another 8 hours at room temperature. After 8 hrs the precipitate was separated out by

filtering and washed with deionised water with acetone. The obtained final suspension was dried in oven at 50°C for 24 hrs. The final product was grinded into powder.

### 3. Result and Discussions

#### i. Structural Analysis:

The structural analysis of the samples are analysed by XRD technique. Figure-1 shows the XRD pattern of pure polyaniline and Figure-2 (a, b, c, d, e & f) shows the XRD pattern of MgO/PANI (5%, 10%, 20%, 30%, 40% & 50%) respectively. Usually polyaniline is the amorphous in nature. The sharp peaks of the sample illustrates the semi-crystalline nature of the sample may be due to the presence of ammonium dichromate and as we increase the composition from 5% to 50% it shows that increasing crystallinity of the PANI. Figure-1 shows the prominent peak of pure polyaniline is in the range of 25-27°, which is characteristic peak of PANI. It is observed that, two broad peaks are observed at 2θ values ranging from 5-20° of MgO/PANI. The average crystalline size of the PANI was calculated from the broadening of the X-ray diffraction using the Debye Scherrer's formula and found approximately in the range 12-30 nm. It is also observed from pattern that, the intensity of the peak decreasing as doping increased, suggests that MgO are dispersed in the PANI matrix.

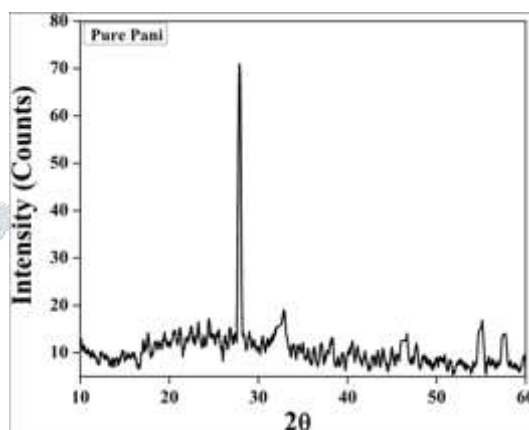


Figure-1: X-ray diffraction patterns of Pure Polyaniline

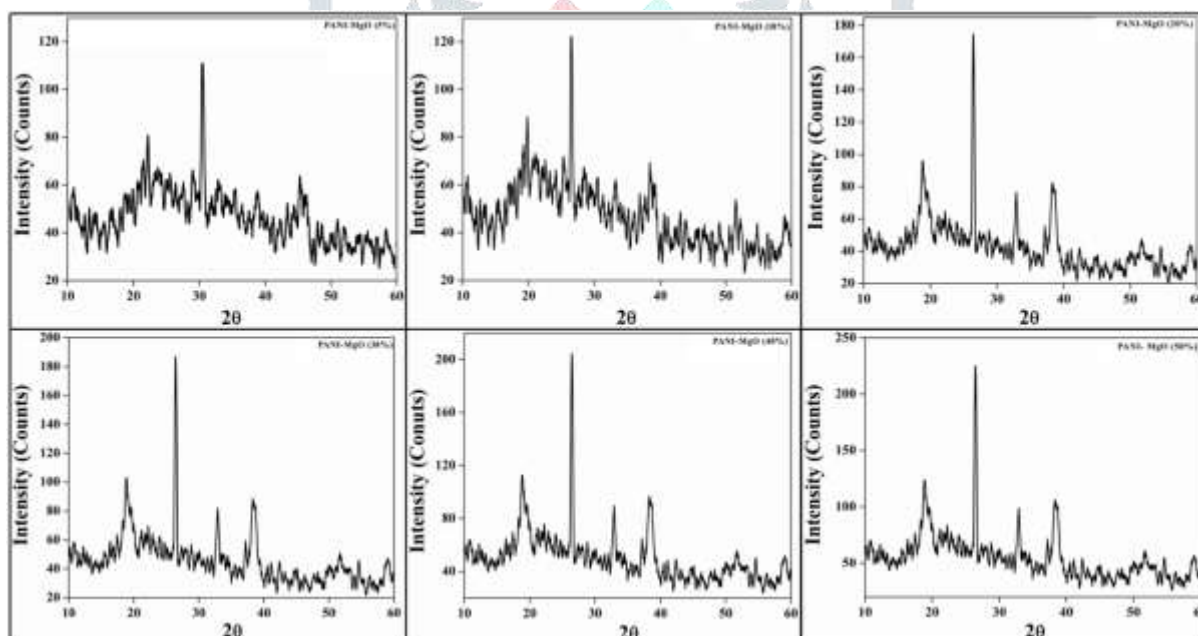


Figure-2: X-ray diffraction patterns of (a) MgO (5%)/PANI, (b) MgO (10%)/PANI, (c) MgO (20%)/PANI, (d) MgO (30%)/PANI, (e) MgO (40%)/PANI, (f) MgO (50%)/PANI.

#### ii. Morphological Study:

Figure-3 illustrates the surface morphology of pure polyaniline and Figure-4 (a-f) are the surface morphology of MgO/PANI (5%, 10%, 20%, 30%, 40% & 50%) respectively. SEM micrographs exhibit agglomeration of particles having irregular shape and it is confirmed that the MgO particles were equally distributed in the polymer matrix. Chemical composition is confirmed the percentage of magnesium and PANI. High magnification of SEM image suggest the composition of MgO affects morphological image considerably and reveals the presence of MgO particles along with variation in the particle dimension of MgO which is uniformly distributed in the sample.

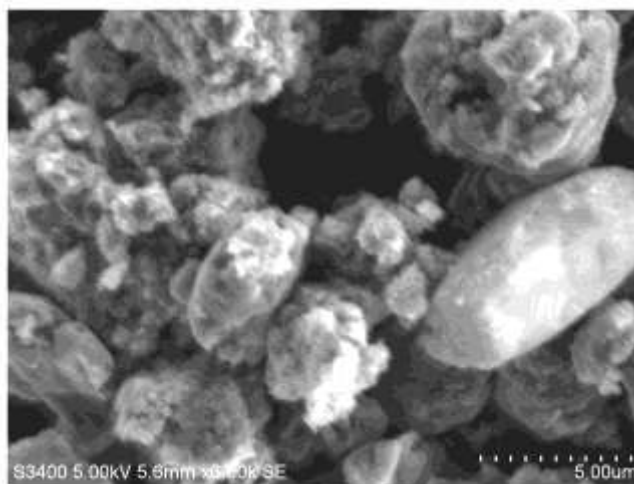
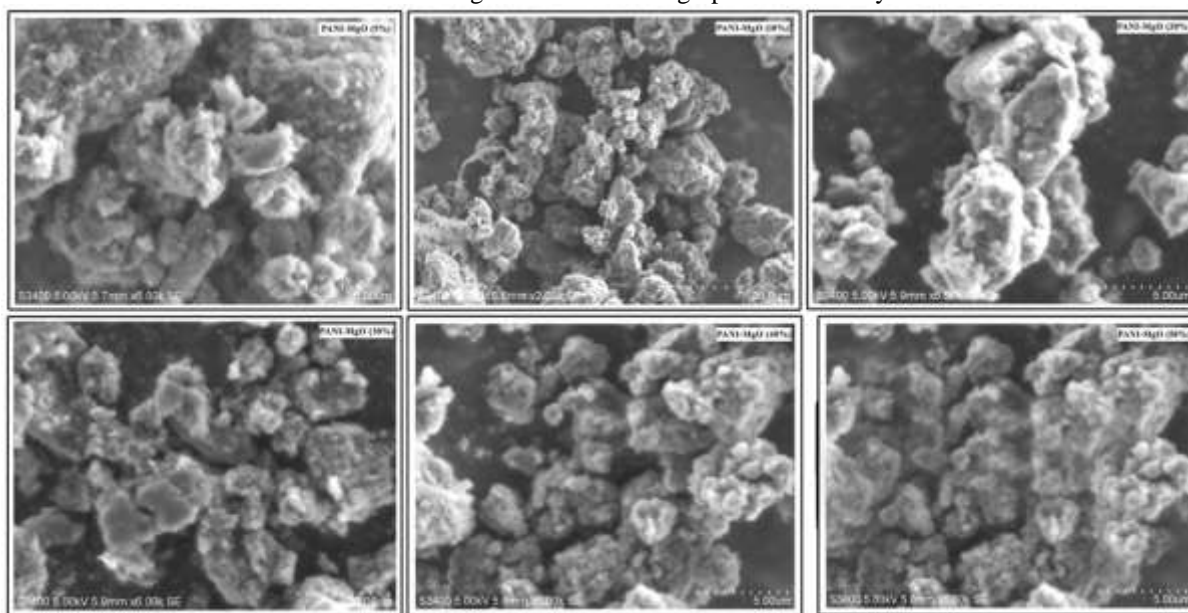


Figure-3: SEM micrographs of Pure Polyaniline

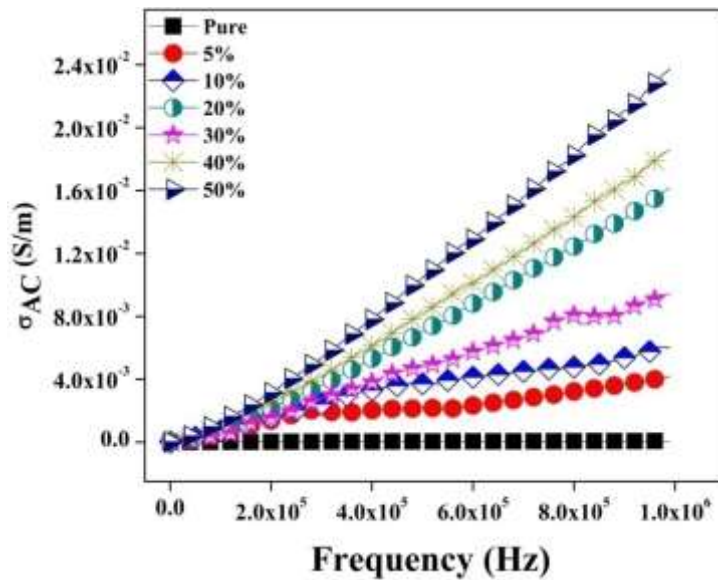


**Figure-4:** SEM micrographs of (a) MgO (5%)/PANI, (b) MgO (10%)/PANI, (c) MgO (20%)/PANI, (d) MgO (30%)/PANI, (e) MgO (40%)/PANI, (f) MgO (50%)/PANI.

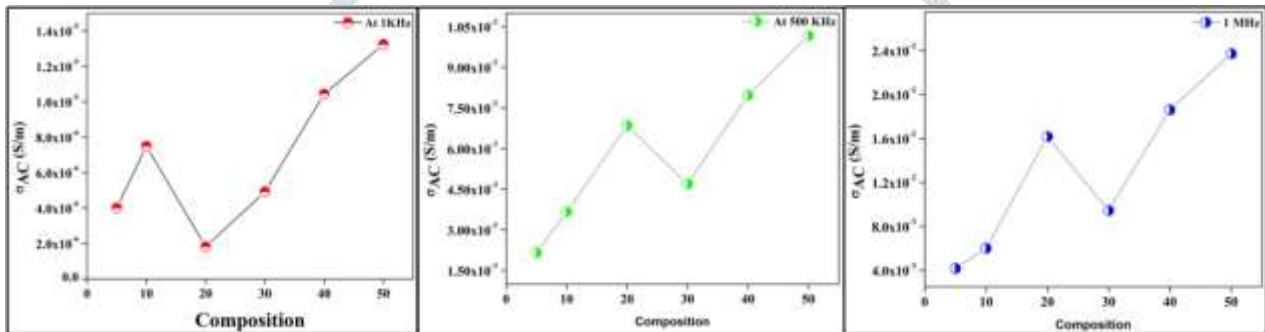
#### iv. Electrical Conductivity:

##### a. AC Electrical Conductivity:

Figure-5 shows the variation of ac conductivity as a function of frequency for pure polyaniline and MgO/PANI (5%, 10%, 20%, 30%, 40% & 50%) was carried out at 1KHz–1MHz frequency in room temperature. Pure polyaniline shows constant variation of ac conductivity in single phase and it increases from the order  $2.88 \times 10^{-6}$  to  $1.32 \times 10^{-5}$  S/m as frequency increased from 1KHz–1MHz. It is observed that in all the cases, ac conductivity increases as frequency increased from 1KHz–1MHz in single phase and also it increases as doping increases. The conductivity of all the composites are higher than that of the polyaniline, the increase in the ac conductivity of the polyaniline composites may due to the distribution of MgO in polyaniline. Increase of  $\sigma_{ac}$  at higher frequencies is due to the charge motion in the amorphous region and this supports the presence of isolated polarons in this region. Figure-6 shows the variation in the ac conductivity of polyaniline and polyaniline composites as function of composition at 1KHz, 500KHz and 1MHz frequency. In all cases (1KHz, 500KHz and 1MHz) and among all the composites, the composite 50% was found to be higher value of ac conductivity which of the order  $1.02 \times 10^{-2}$  S/m.



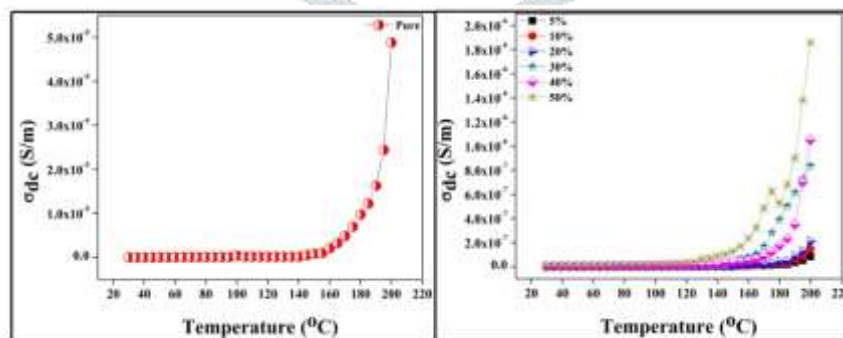
**Figure-5:** AC conductivity of pure polyaniline, MgO (5%)/PANI, MgO (10%)/PANI, (MgO (20%)/PANI, MgO (30%)/PANI, MgO (40%)/PANI & MgO (50%)/PANI as a function of frequency.



**Figure-6:** Variation of AC conductivity of PANI & Composites at 1 KHz, 500KHz & 1 MHz Frequency

**b. DC conductivity:**

Figure-7(a) shows the dc conductivity of the pure polyaniline as a function of the temperature. The temperature dependence of conductivity of PANI was measured in the temperature range 30° C to 200° and it is found that there is increase in the conductivity of the PANI for the increase in temperature exhibiting semiconducting behaviour and it is the characteristic property of materials [18]. It is observed from figure that, conductivity of PANI showing in two phase i.e., the conductivity in the range 30° C - 140° C & 150° C - 200° C. The first phase conductivity is almost constant may be due to inter-chain transport of charge carriers, i.e., hopping of charge carriers between the polymer chains and is usually observed at intermediate temperature. But, at high temperature region, (phase two) there is an sudden increase in the conductivity with increase in temperature due to intra-chain transport of charge carriers which can be described by the band conduction mechanism and is usually it is observed at high temperatures as reported by authors in their previous work [19, 20, 21].



**Figure-7:** dc conductivity of (a) pure polyaniline, (b) MgO/PANI (5%, 10%, 20%, 30%, 40% & 50%) as a function of the temperature

Figure-7(b) is the dc conductivity of MgO/PANI (5%, 10%, 20%, 30%, 40% & 50%) as a function of the temperature in the range 30° C to 200° and found that there is increase in the conductivity of the all samples for the increase in temperature exhibiting semiconducting behaviour. Compared to the conductivity of PANI, the conductivity of MgO/PANI composites increased. This increase in the dc conductivity may due to the presence of MgO in polyaniline.

**v. Dielectric properties:**

**a. Variation of real dielectric constant ( $\epsilon'$ ):**

Figure-8 show the variation of real dielectric constant ( $\epsilon'$ ) as a function of frequency for polyaniline and polyaniline composites at room temperature (RT) in the frequency range of 10K Hz to 1MHz. It is observed that, obtaining higher value of dielectric constant at low frequency range. Debye type relaxation mechanism may be responsible for higher value of dielectric constant at low frequency. Dielectric constant of polyaniline and polyaniline composites decreases as frequency increases over the measured frequency range 1KHz to 1 MHz, which is a typical characteristic of disordered conducting polymer. Figure-9 shows the variation of dielectric constant ( $\epsilon'$ ) as a function of composition at 1 KHz 500KHz & 1MHz frequency. Among all the composites, 50 wt% found to be higher in value of dielectric constant ( $\epsilon'$ ) which is of the order 11659.02. The degree of polarization inside the nanocomposite system is thought to be increased with increasing MgO concentration for 50%, which in turn enhances the dielectric constant of the composite. The  $\epsilon'$  values matches to previously reported values i.e., the dielectric constant of polyaniline found to be 122.83 at room temperature for 1 KHz and 85.68 for 500 KHz [22]. Also reported that, the  $\epsilon'$  values for composite (wt.2% of EGf) found to be  $7.92 \times 10^6$  at 1 KHz [23].

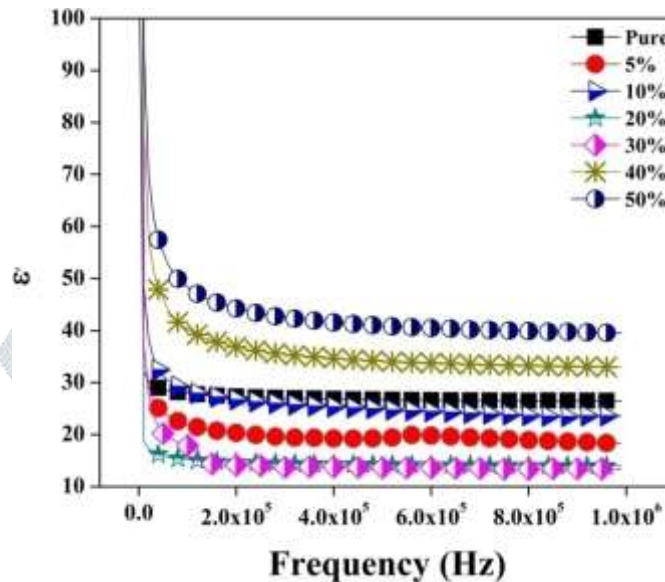


Figure-8: Real part of dielectric constant of polyaniline and MgO/PANI (5%, 10%, 20%, 30%, 40% & 50%) as a function of frequency.

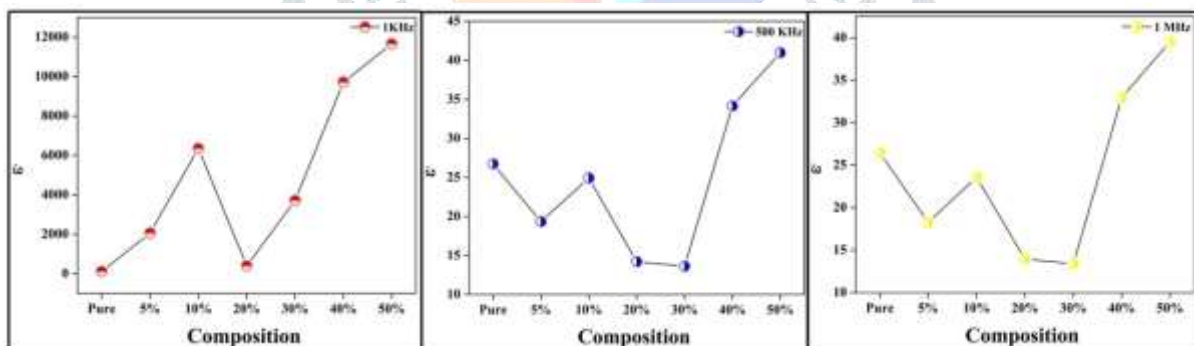


Figure-9: Variation of Dielectric constant ( $\epsilon'$ ) of PANI & composites at 1 KHz 500KHz & 1 MHz Frequency

**b. Variation of imaginary dielectric constant ( $\epsilon''$ ):**

Figure-10 shows the variation of imaginary part of the dielectric constant ( $\epsilon''$ ) as function of frequency for polyaniline and polyaniline composites. For polyaniline, the imaginary part of the dielectric constant has value of about 472.40 at 1KHz and decreases with increasing frequency, reaching the value of about 1.29 at 1MHz. It is observed that, imaginary part of dielectric constant is dependent of composition i.e, the value of  $\epsilon''$  is high for composites as compared to polyaniline in low frequency & higher frequency range. The increase in the value of imaginary part of dielectric constant at low frequency & higher frequency range in composites compared to polyaniline may responsible for distribution of MgO in polyaniline. The variation of imaginary part of the dielectric constant ( $\epsilon''$ ) as function of composition at 1KHz, 500KHz and 1MHz frequency shown in figure-11.

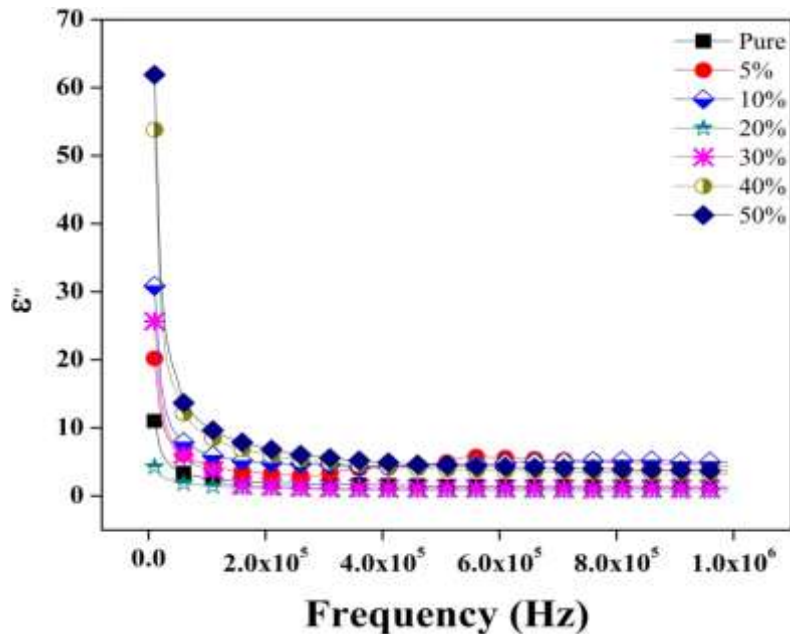


Figure-10: Imaginary part of dielectric constant of polyaniline and MgO/PANI (5%, 10%, 20%, 30%, 40% & 50%) as a function of frequency.

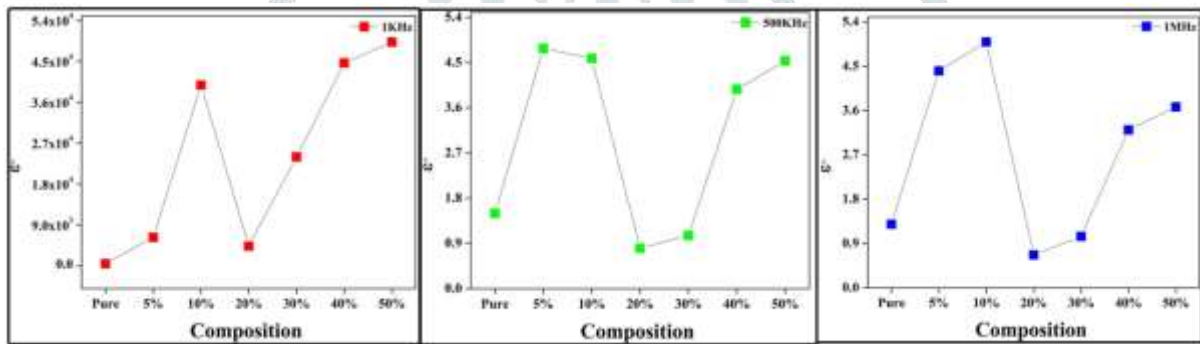


Figure-11: Dielectric constant ( $\epsilon'$ ) of PANI & Composites at 1 KHz 500KHz & 1 MHz Frequency

**c. Variation of Dielectric loss tangent ( $\tan\delta$ ):**

Figure-12 shows the variation of dielectric loss tangent ( $\tan\delta$ ) as a function of frequency for polyaniline and polyaniline composites. The loss tangent for polyaniline has a value of 3.21 at 1KHz, which decreases with increasing frequency, reaching a value of 0.04 at 1 MHz. It is observed from the figure that, high dielectric loss at low frequency in all the composites may be attributed to the high resistivity caused by grain boundary. Figure-13 shows the variation of dielectric loss tangent ( $\tan\delta$ ) as a function of composition at 1 KHz 500KHz & 1 MHz frequency. It is observed from plots that, the value of  $\tan\delta$  decreases as frequency increased and compared to polyaniline, the composites 10%, 20%, 30%, 40% & 50% have higher value of  $\tan\delta$ . The higher value of  $\tan\delta$  responsible for distribution of MgO in polyaniline. The dependence of  $\tan\delta$  with frequency can be classified into two stages. In first stage, the value of  $\tan\delta$  decreases with increasing frequency within the frequency range 10 KHz to 200 KHz. In second stage, from 300 KHz to 1 MHz frequency, the value of  $\tan\delta$  is almost constant in the order  $10^{-1}$ . Previously reported that i.e., the values of  $\tan\delta$  of polyaniline found to be 0.24 at room temperature for 1 KHz and 0.0305 for 500 KHz [24].

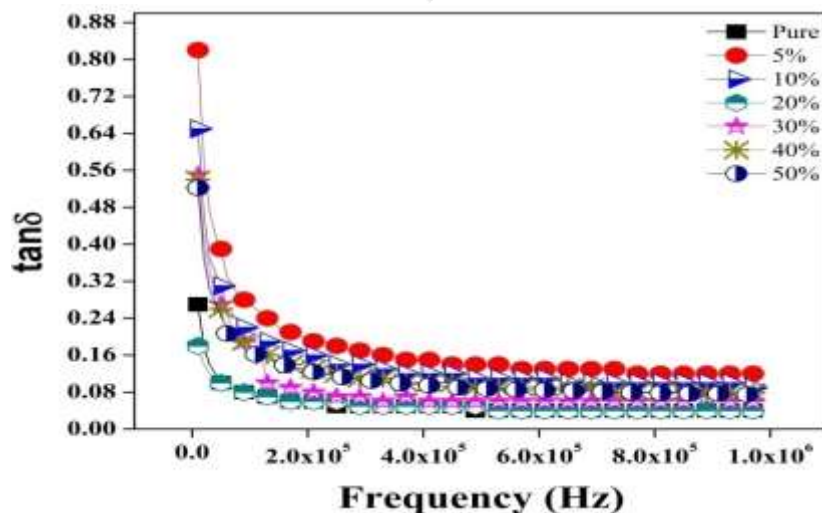


Figure-12: Dielectric loss tangent ( $\tan\delta$ ) of polyaniline and MgO/PANI (5%, 10%, 20%, 30%, 40% & 50%) as a function of frequency.

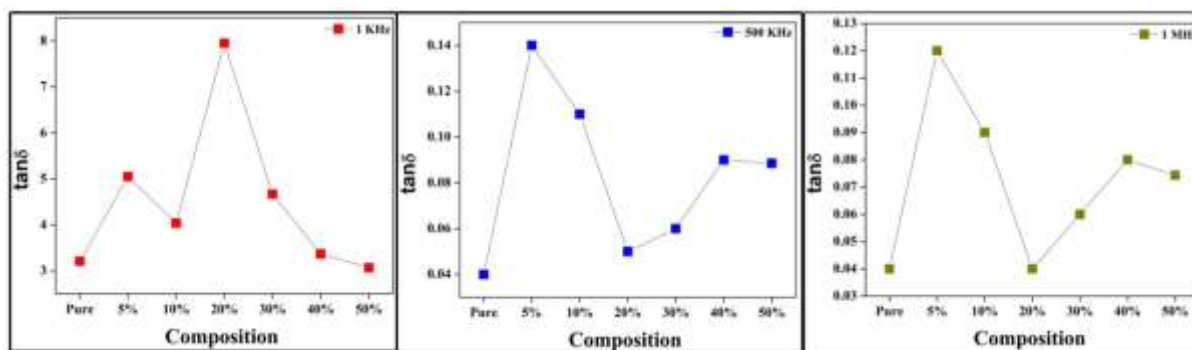


Figure-13: Variation of Dielectric loss tangent ( $\tan\delta$ ) of PANI & Composites at 1 KHz 500KHz & 1 MHz Frequency.

#### 4. Conclusion:

We have successfully synthesized MgO/PANI composite by employing chemical oxidative polymerization method. The structural and morphological properties of the resulting composites were investigated in detail by X-ray diffraction (XRD), Scanning Electron Microscope (SEM) technique. Pure polyaniline shows constant variation of ac conductivity in single phase and it increases from the order  $2.88 \times 10^{-6}$  to  $1.32 \times 10^{-5}$  S/m as frequency increased from 1KHz–1MHz. It is observed that in all the cases, ac conductivity increases as frequency increased from 1KHz–1MHz in single phase. Also ac conductivity increases as doping increases, the maximum conductivity found to be  $1.02 \times 10^{-2}$  S/m for MgO/PANI (50%). It is found that there is increase in the dc conductivity of the PANI and polyaniline composites for the increase in temperature exhibiting semiconducting behaviour. Higher value of dc conductivity were achieved for polyaniline composites compared to polyaniline due to the presence of MgO in polyaniline. Dielectric constant of polyaniline and polyaniline composites decreases as frequency increases over the measured frequency range 1KHz to 1MHz, which is a typical characteristic of disordered conducting polymer. It is also observed that, composite 50% is found to be high value in dielectric constant among the composites in all the frequency range. The imaginary part of the dielectric constant decreases from 472.40 at 1KHz to 1.29 at 1MHz frequency and it is dependent of composition. The value  $\tan\delta$  also decreases as frequency increased.

#### Acknowledgment:

The authors gratefully acknowledge and this work was supported by (Vision Group on Science and Technology) VGST of Department of Physics, Bheemanna Khandre Institute of Technology, Bhalki, Bidar.

#### 5. References:

- [1]. Debarnot, D. N. And F. P. Epailard, Anal. Chim. Acta 475, 1–15 (2003).
- [2]. D. L. Wise, G. E. Wnek, D. J. Trantolo, T. M. Cooper, and J. D. Gresser, Marcel Dekker, Inc., New York, 1996.
- [3]. J. STEJSKAL, R.G. GILBERT Pure Appl.Chem., Vol. 74, No. 5, pp. 857-867, (2002).
- [4]. A. Malinauskas, Polymer, 42 (2001)3957.
- [5]. G. Duan, X. Yang, J. Chen, G. Huang, L. Lu, X. Wang, Powder Technol. 172, 2007, 27-29.
- [6]. H. Niu, Q. Yang, K. Tang, Y. Xie, Scr. Mater. 54, 2006, 1791-1796.
- [7]. M.A. Shah, A. Qurashi, J. Alloys Comps. 482, 2009, 548-551.
- [8]. T. Qiu, X.L. Wu, F.Y. Jin, A.P. Huang, Paul K. Chu, Appl. Surf. Sci. 253, 2007, 3987-3990.
- [9]. Q. Yang, J. Sha, L. Wang, J. Wang, D. Yang, Mater. Sci. Eng., C 26, 2006, 1097 - 1101.
- [10]. Xie Yi, Wang Wenzhong, Qian Yitai, Yang Li, Chen Zhiwen, Surf. Coat. Technol. 82, 1996, 291-293.
- [11]. J.J. Helble, J. Aerosol Sci. 29, 1998, 721- 736.
- [12]. Y. Li, Y. Bando, T. Sato, Chem. Phys. Lett. 359, 2002, 141-145.
- [13]. L. Kumari, W.Z. Li, C.H. Vannoy, R.M. Leblanc, D.Z. Wang, Ceram. Int. 35, 2009, 3355–3364.
- [14]. P. Ouraipryvan, T. Sreethawong, S Chavadej, Mater. Lett. 63, 2009, 1862-1865.
- [15]. S. D. Thakre, U. B. Mahatme, A. A. Dani, "Preparation and Characterization of Polyaniline/Zinc Oxide Composites via Oxidative Polymerization", ijcm, 2014, 4(1): 14-20.
- [16]. N.Chandrankanth and M. A. Careem, Polymer Bulletin, 44 (2000) 101.
- [17]. M. Ghosh, A. Barman, A.K. Meikap, S.K. De, S. Chattejee, Phys. Lett. A, 260 (1999) 138.
- [18]. Thesis "Synthesis and characterization of polyaniline doped with some nanoferrites, Prasanna, G D, <http://hdl.handle.net/10603/80975>, Shodhganga@ INFLIBNET.
- [19]. Saxena Dinesh, Dwivedi Vivek and Mishra Pankaj Kumar, " Dielectric Study of Polyaniline in Frequency Range 100Hz to 500 KHz at Temperature 200C and 300C", Research Journal of Chemical Sciences, Vol. 3(2), 16-19, February (2013), ISSN 2231-606X.
- [20]. Prasanna B P, Avadhani D N, Muralidhara H B, Revanasiddappa M, " Synthesis, Characterization and Enhanced Dielectric Constant of Polyaniline-Exfoliated Graphite Flakes Composites", IJLTEMAS, Volume III, Issue V, May 2014, ISSN 2278 – 2540.
- [21]. Saxena Dinesh, Dwivedi Vivek and Mishra Pankaj Kumar, " Dielectric Study of Polyaniline in Frequency Range 100Hz to 500 KHz at Temperature 200C and 300C", Research Journal of Chemical Sciences, Vol. 3(2), 16-19, February (2013), ISSN 2231-606X.
- [22]. Saxena Dinesh, Dwivedi Vivek and Mishra Pankaj Kumar, " Dielectric Study of Polyaniline in Frequency Range 100Hz to 500 KHz at Temperature 200C and 300C", Research Journal of Chemical Sciences, Vol. 3(2), 16-19, February (2013), ISSN 2231-606X.

- [23]. Prasanna B P, Avadhani D N, Muralidhara H B, Revanasiddappa M, “ Synthesis, Characterization and Enhanced Dielectric Constant of Polyaniline-Exfoliated Graphite Flakes Composites”, IJLTEMAS, Volume III, Issue V, May 2014, ISSN 2278 – 2540.
- [24]. Saxena Dinesh, Dwivedi Vivek and Mishra Pankaj Kumar, “ Dielectric Study of Polyaniline in Frequency Range 100Hz to 500 KHz at Temperature 200C and 300C”, *Research Journal of Chemical Sciences*, Vol. 3(2), 16-19, February (2013), ISSN 2231-606X.

