

# **SYNTHESIS, CHARACTERIZATION AND AC CONDUCTIVITY STUDIES OF MgO DOPED POLYMER NANO COMPOSITES.**

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**ABSTRACT:** In the present study, a facile, cost effective, synthetic route low temperature solution combustion synthesis was introduced to prepare Magnesium oxide (MgO) nano particles and chemical oxidative polymerization method to synthesize PANi / MgO Nano Composites. Further these nano composites were characterized by PXRD, FESEM and EDAX to investigate their structural and morphological studies. As a part of electrical studies, dielectric constant and AC conductivity measurements were done by AC6500B precision impedance analyser.

**KEYWORDS:** Nano particles, solution combustion XRD, FESEM, EDAX, Dielectric constant, AC conductivity.

## **I. INTRODUCTION**

Among conducting polymers, polyaniline (PANi) has gained much interest due to simple preparation of powders and composites with better environmental stability and suitable conductivity. These features are mainly responsible to utilize PANi for some interesting applications such as sensors, microactuators, polymeric batteries, electronic devices and electrolytic capacitors.[1] Chemical oxidative polymerization has been used for the preparation of PANi, because of its preparation in short duration.[2] The value of electrical conductivity, actually, distinguishes the polymers from metals. For metals, electrical conductivity is of the order of  $10^4 - 10^6$  s/cm where as for polymers, it doesn't exceed  $10^{14}$  s/cm. By simple modification of pure conducting polymer, that is by doping the conducting polymer with nano structured metal oxides such as [ZnO, MgO, CuO, TiO<sub>2</sub>, ZrO<sub>2</sub>, NiO, SnO<sub>2</sub>] the electrical conductivity can be enhanced or modified.[3]

In this work, MgO nano particles (Synthesized by low temperature solution combustion method) were doped to pure PANi with different wt % (0.1, 0.3, 0.5) to prepare PANi/MgO nano composites. Here we present the structural, compositional and electrical properties of synthesized pure PANi as well as PANi/MgO nano composites. These properties were investigated by means of PXRD, FTIR, FESEM and impedance analyzer measurements done by AC 6500 B precision Impedance analyzer.

By using chemical oxidative and electrochemical methods, polyaniline the conducting polymer was synthesized and characterized. The conductivity studies were performed by four-point probe technique by measuring the electrical resistance at room temperature. Magnesium oxide MgO nanoparticles were prepared by sonication method to understand their antibacterial property. By increasing the calcinations time, the Lethal effect of MgO nanoparticles was studied. MgO particles of nano scale were fabricated by solution combustion method and characterized. The relative fuel-to-oxidant ratio ( $\phi_c$ ) is also calculated and concluded that they exhibit larger specific surface area than the other powders. The Electrical conductivity studies of characterized Polyaniline/ZnO nano rods found the decrease in the electrical conductivity of PANI/ZnO nano rods as compared to PANI. By using extract of orange peel as fuel, MgO nano particles were synthesized via green synthesis which is ecofriendly.

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### II. EXPERIMENTAL

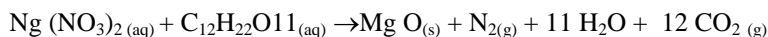
Magnesium Nitrate, Sugar, Aniline (monomer), Ammonium peroxy- disulphate (APS), Hydrochloric acid, Ammonia, Methanol of A.R. Grade were obtained and used as received. PXRD measurements were carried out by an X PERT-PRO Diffractometer using Cu K $\alpha$   $\lambda=0.1540$  nm in a range of  $2\theta$  ( $5^{\circ}\leq 2\theta\leq 85^{\circ}$ ). The scanning electron microscope (SEM) (Cambridge stereoscan S-360) was used for the surface features of the composites. The measurements for dielectric constant and Ac electrical conductivity studies were carried out by precision impedance analyzer Ac 6500-B.

#### SYNTHESIS OF PANI

PAni was synthesized by chemical oxidative polymerization method using aniline as monomer in the presence of hydrochloric acid as catalyst and Ammonium peroxydisulphate (APS) as an Oxidant. 10ml of 0.1 M HCl is mixed with 1ml of Aniline. This mixture was stirred for 1 hour at constant RPM. The solution of 2.5 ml of APS was added drop wise into the mixture. This reaction mixture was continuously stirred in a magnetic stirrer at constant RPM for 24 hrs. under ice cold ( $0^{\circ}\text{C}$ ) temperature. After 24 hrs the Precipitate was separated out by filtering. The obtained final suspension was dried in oven at  $80^{\circ}\text{C}$  for 24 hrs. The final product was grounded into fine powder[4].

#### SYNTHESIS OF MgO NANO PARTICLES

Nano structured Magnesium oxide particles were synthesized by low temperature solution combustion method. Magnesium nitrate  $\text{Mg}(\text{NO}_3)_2$  and sugar were taken in the appropriate stoichiometric ratio. The required amounts of starting materials for synthesis of MgO nano particles were calculated according to the reaction.



5g of  $\text{Mg}(\text{NO}_3)_2$  and 1.4g of sugar were added to 25ml of double distilled water. To get homogeneity the solution is stirred in a magnetic stirrer at constant RPM for 15 min. The Homogeneous solution was then taken in a petridish and kept in a pre heated Muffle furnace maintained at  $400^{\circ}\text{C}$  to carryout combustion. Fig(1)



The solution undergoing spontaneous combustion during the synthesis

Fig.1 : Solution combustion synthesis

$\text{N}_2$  and  $\text{CO}_2$  were evolved as bright pale yellow gas mixture and MgO was left behind as the end residue. This final product was grounded into the fine powder.

#### SYNTHESIS OF PANI/MgO NANO COMPOSITES

0.1 M of 10ml HCl and 1g of polyaniline are mixed at a very low temperature and is mixed drop wise to the main solution of polyaniline. This obtained solution is stirred for a period of 24hr and then filtered. The precipitate was collected on a Buchner funnel and rinsed with water, and then kept in a microwave oven maintained at  $80^{\circ}\text{C}$  for again 24 hr. The final product obtained will be the powder form PANi/ZnO nano composite.

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015

## III.RESULTS AND DISCUSSION

### PXRD ANALYSIS

The PXRD spectrum is a characteristic finger print of a phase and no broad peaks represent 100% crystallinity. The positions of the peaks in a powder pattern determine the size, shape and symmetry of the unit cell and the peak intensities determine the arrangement of atoms within the unit cell .

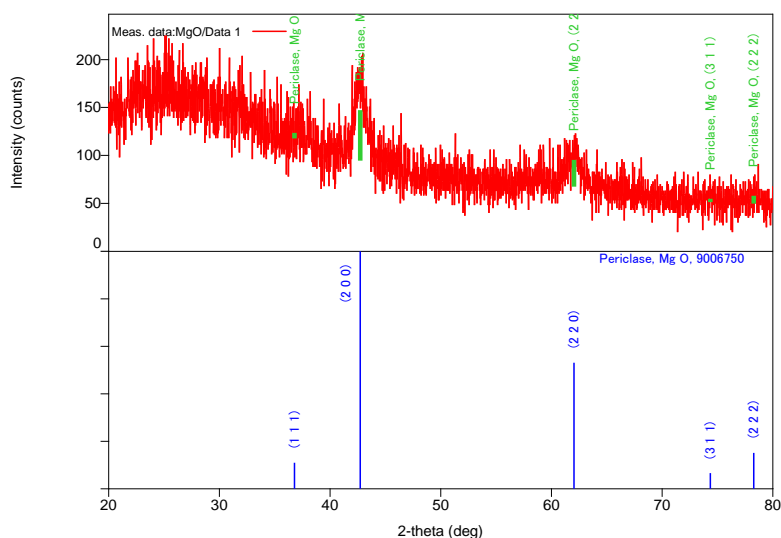


Fig.2 : PXRD spectrum of MgO Nano particles

Fig (2) shows the PXRD spectrum of MgO nano particles. All the diffraction lines are assigned to cubic crystalline phase of Magnesium oxide [JCPDS 4-829] and no other impurity peaks are observed. It confirms the purity of the compound. The crystallite size of the as made MgO nano particles was calculated from the broadening of the X-ray diffraction using the Debye Scherrer’s formula and found in the range 7-10 nm [5].

Debye Sherrer’s formula

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Where D is crystallite size, k is shape factor, which can be taken a value of 0.89 if the shape is unknown,  $\theta$  is the diffraction angle at maximum peak intensity and  $\beta$  is the full width at half maximum of diffraction angle in radians. The peak list is shown in Table (1)

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015

Table 1.

NO	2-theta	d (ang.)	Height (counts)	FWHM (deg)
1	42.64(10)	2.119(5)	49(7)	1.29(8)
2	62.2(2)	1.492(4)	24(5)	1.3(2)

The peaks (111), (200), (220), (311), (222) at (37.5), (42.8), (62.3), confirm the FCC structure of MgO nano particles. The peaks at  $22^{\circ}$ ,  $26^{\circ}$ ,  $72.5^{\circ}$  were attributed to (111), (202), (101). PAni/MgO nano composites.

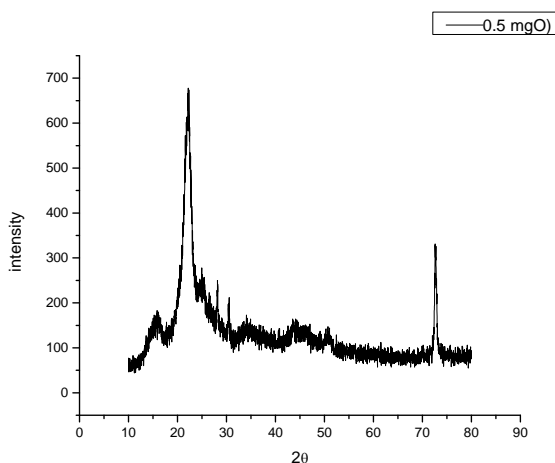


Fig.3. PXRD of PAni/MgO nano composites

### FESEM

The scanning electron microscopy images of MgO nano particles of different magnifications shown in Fig (4).

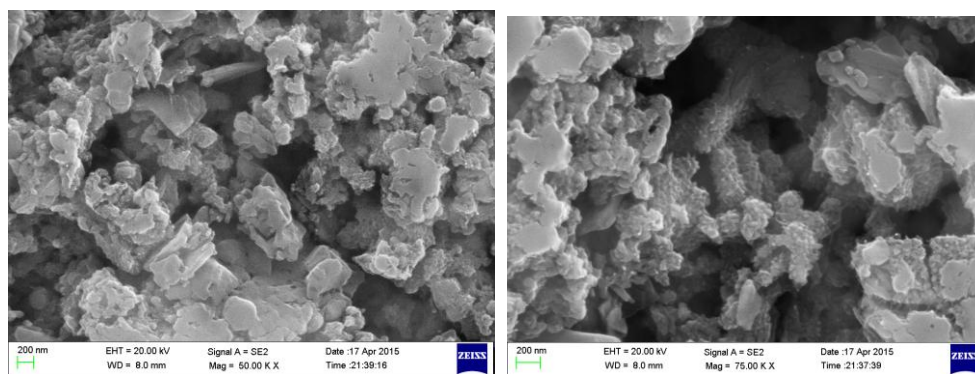


Fig.4 : FESEM micro graphs of MgO

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015

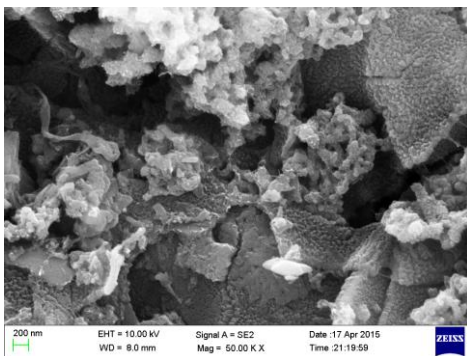


Fig5: FESEM image of PANi

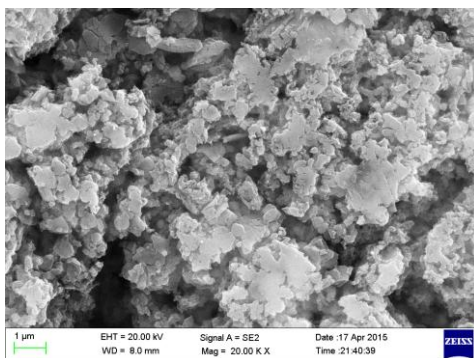


Fig.6.FESEM image of MgO Nano composites

From these images, the average grain size was calculated as 20-30nm. In addition to these micrographs, the SEM images of P Ani as well as its MgO nano composites of different magnifications were also shown in Fig ( 5,6 ). It is confirmed that the MgO nano particles were equally distributed in polymer matrix [6].

## EDAX ANALYSIS

The EDAX spectroscopy image was shown in Fig (7) It confirm the percentage of Magnesium was (60.29 %) and oxide nano particles was ( 39.67 ). No other peaks of impurities were observed [7].

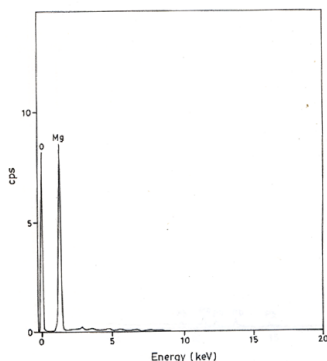


Fig.7 : EDAX of MgO nano composites

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015

## AC ELECTRICAL CONDUCTIVITY MEASUREMENTS

AC frequency has been varied from 100 KHz to 5 MHz to the polyaniline as well as polyaniline / MgO nano composite pellets to conduct two probe method, interfaced to AC 6500 B precession impedance analyzer to study the conductivity. [8]. The table (2) shows that AC electrical studies of polyaniline in its pure form and PANi / MgO nanocomposites.

The capacitance is measured by varying the AC frequency at room temperature to calculate the real dielectric constant  $\epsilon^1 = C_p t / \epsilon_0 A$

Where  $t$  is the thickness of the sample (pellet)

$A$  is the surface area

$\epsilon_0$  is the permittivity of free space.

The imaginary part of dielectric constant is also measured by

$\epsilon^{11} = \epsilon^1 \tan \delta$ , here  $\tan \delta$  is the tangent loss which is equal to  $\tan (90 + \theta) \Pi / 180^\circ$  where  $\theta$  is the phase angle.

The real and imaginary electric moduli were calculated by the formulae

$$M^1 = \frac{\epsilon^1}{(\epsilon^1)^2 + (\epsilon^{11})^2} \quad \text{and} \quad M^{11} = \frac{\epsilon^{11}}{(\epsilon^1)^2 + (\epsilon^{11})^2}$$

By measuring the resistance over the specified frequency AC conductivity ( $\sigma_{Ac}$ ) was determined using

$$\sigma_{Ac} = \frac{1}{\rho} = \frac{RA}{t} \quad \text{Here } \rho = \frac{RA}{t}$$

$\rho$  is the resistivity measured in  $\Omega$  - m. [9-12]

## IV. CONCLUSION

As frequency increases, the AC conductivity was found to be decreased but with increase of doping percentage of MgO nano particles it was found to be increased. This feature can be attributed to the hyper electronic polarization and strong polaron delocalization.

PAni / MgO nano composites were synthesized by low temperature solution combustion and chemical oxidative polymerization methods. Their structural and morphological studies were confirmed by PXRD and FESEM respectively.

AC conductivity measurements confirm that the conductivity of MgO nano composite were slightly greater than that of Pure PANi due to the localized motion of the ions at lower frequencies and due to segmentation motion dipolar relaxations as well as polarization of charge carriers.

Tables (2) (3) (4) and (5) show the estimated values of the parameters  $\sigma$  (Ac conductivity),  $\epsilon^1$  (real dielectric constant),  $\epsilon^{11}$  (imaginary dielectric constant),  $\tan \delta$  (dielectric loss),  $M^1$  (real electric modulus) and  $M^{11}$  (imaginary electric modulus) of PANi and PANi/MgO nano composites.

**Table: 2**

**AC electric conductivity ( $\sigma_{Ac}$ ) of pure PANi and PANi/MgO nano composites are shown below**

$\sigma_{Ac}$	At 0.1 MHz	At 4.9 MHz
PAni	$3.985 \times 10^{-2}$ S/cm	$0.5305 \times 10^{-2}$ S/cm
PAni/0.1 MgO	$4.186 \times 10^{-2}$ S/cm	$0.673 \times 10^{-2}$ S/cm
PAni/0.3 MgO	$7.34 \times 10^{-2}$ S/cm	$0.847 \times 10^{-2}$ S/cm
PAni/0.5 MgO	$9.675 \times 10^{-2}$ S/cm	$0.962 \times 10^{-2}$ S/cm

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015

**Table 3**  
**Dielectric loss (tan  $\delta$ ) tangent loss of pure PAni and PAni/MgO nanocomposites are shown below**

Tan $\delta$	At 0.1 MHz	At 4.9 MHz
Pure PAni	15.2712	1.5831
PAni/0.1 MgO	16.022	2.402
PAni/0.3 MgO	16.462	2.7428
PAni/0.5 MgO	16.712	2.947

**Table :4**  
**The Real electric modulus  $M^1$  variation**

$M^1$	At 0.1 MHz	At 4.9 MHz
PAni	$9.52 \times 10^{-8}$	$2.33 \times 10^{-4}$
PAni/0.1 MgO	$8.66 \times 10^{-8}$	$1.441 \times 10^{-4}$
PAni/0.3 MgO	$8.152 \times 10^{-8}$	$1.367 \times 10^{-4}$
PAni/0.5 MgO	$7.60 \times 10^{-8}$	$1.264 \times 10^{-4}$

**Table :5**  
**The Imaginary electric modulus  $M^{11}$  variation**

$M^1$	At 0.1 MHz	At 4.9 MHz
PAni	$14.56 \times 10^{-8}$	$3.69 \times 10^{-4}$
PAni/0.1 MgO	$13.89 \times 10^{-8}$	$3.479 \times 10^{-4}$
PAni/0.3 MgO	$12.65 \times 10^{-8}$	$1.172 \times 10^{-4}$
PAni/0.5 MgO	$12.152 \times 10^{-8}$	$2.921 \times 10^{-4}$

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