STUDIES ON EFFECT OF SILVER OXIDE ON STRUCTURAL, MORPHOLOGICAL AND ELECTRICAL PROPERTIES OF POLYANILINE [PANI]

Shabana Begum[1], Sangshetty Kalyane[2*]

[1]*Department of Physics, B.B.Roza College of Womens, Kalaburagi, Karanataka, India*

[2]*Bheemanna Khandre Institute of Technology, Bhalki, Bidar, Karanataka, India*

ABSTRACT:

We have prepared Polyaniline (PANI) and metal oxide doped polyaniline (AgO/PANI) composites by incorporating silver oxide with conducting polymer (PANI) with 5%, 10%, 15%, 20% & 25% wt% of AgO via chemical oxidative polymerization method with APS as oxidant. X-ray diffraction & scanning electron microscopy (SEM) technique are used to investigate structural analysis and surface morphology of the prepared sample. The effect of silver oxide on PANI and the electrical properties (AC & DC). The AC conductivity all the composites were studied as a function of frequency at room temperature and DC conductivity were analysed as function of temperature.

KEY WORDS: Polyaniline, AC & DC Conductivity.

***Corresponding Author**
Dr. Sangshetty Kalyane
Department of Physics,
Bheemanna Kahndre Institute of Technology,
Bhalki, Bidar, Karnataka India
E-mail: sangshetty_2007@rediffmail.com. Mob: 9449274532

1. INTRODUCTION:

Conducting polymer composites are the future materials for emerging technologies as they possess a combination of unique properties of their constituents. The properties become more interesting when one of the components is in the nano range. Due to the synergistic effect of the polymer and the nano filler, the resulting materials are expected to display desirable properties with enhanced performance.[1]Polyaniline (PANI) was discovered over 150 years ago, it has only recently captured the attention of the scientific community due to its high electrical conductivity on treatment with protonic acids and became the most investigated conducting polymer since its discovery about three decades ago. It was first prepared in 1834 and has been the subject of mild research ever since.[2] However, the conducting properties of PANI were recognized and the number of research articles dealing with this conducting polymer grew rapidly since 1980s. Among all conducting polymers, PANI has a special representation due to its unique properties such as low cost of its monomers, ease of synthesis by chemical or electrochemical routes and high environmental stability. The specific advantages of PANI include the ability to tune its electrical properties easily by proton doping or simple versatile redox reactions. These features made PANI an attractive replacement material in many areas of applications such as electrodes, charge transfer and active layers, electrochromic displays, electromagnetic shielding as well as a growth template for neurons.[3-4]

The properties of these conducting polymers can be modified by the addition of inorganic particles. Nano scale particles are more attractive due to intriguing properties arising from the nano size and large surface area. The insertion of nano

scale fillers may improve the electrical and sensing properties of the polymers.[5]In recent years, nano-sized metal particles have got much attention due to its unique optical, electrical and magnetic properties, which depends on the size and shape of the particle. Silver oxide (AgO) nano particles is a well-known material having vast applications in the field of oxidation catalysis [6-7], sensors[8], fuel cells[9], photovoltaic cells[10], all-optical switching devices, optical data storage systems[11]and as a diagnostic biological probes.[12] Many physical and chemical properties including luminescence, conductivity, and catalytic activity depend upon the size of nano scale materials.

2. METHOD OF PREPARATION

a. Preparation of Polyaniline and AgO/PANI composite

In the first step, 0.1M of aniline solution and 1N of hydrochloric acid is taken in first beaker and stirred by magnetic stirrer for 2hrs at room for completion of the mixer. In second step, the solution of 0.25M of ammonium persulfate is taken in second beaker and it was added drop wise into the first beaker and continued the stirring for 8 hrs. In third step, continuous stirring of solution was filtered by Buchner funnel and washed with deionised water with acetone. In fourth step, final obtained product was dried in oven at 50 °C for 24 hrs. The dried sample was grinded into fine powder for further characterization. For preparation of AgO/PANI composite, continuation to the second step, silver oxide powder for different additive weight percentage (5%, 10%, 15%, 20% & 25%) is dissolved in the mass fraction to the above solution with vigorous stirring in order to keep the AgO homogeneously suspended in the solution and stirring of final solution was continued for another 8 hours at room temperature. Then step four continued to obtain grinded powder.

b. Flow chart:

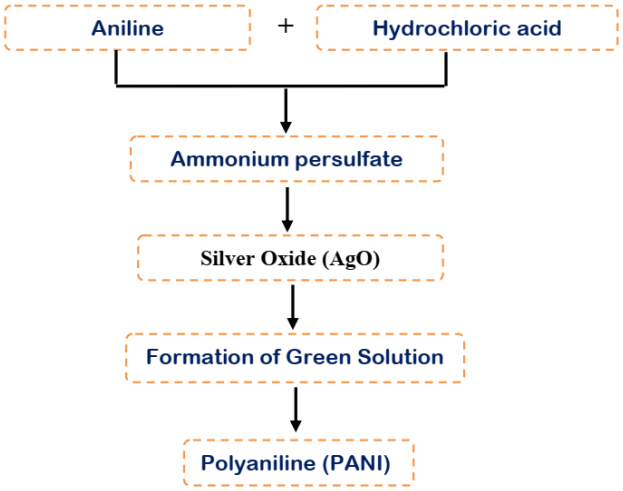

Figure-1: Flow chart of preparation of PANI/AgO composite

3. RESULT AND DISCUSSIONS

i. Structural Analysis:

The structural analysis of the sample was studied by X-ray diffraction technique. Figure-2 shows the XRD pattern of the Pure PANI and AgO/PANI for different additive weight percentage (5%, 10%, 15%, 20% & 25%) respectively. Generally polyaniline is the amorphous in nature. From pattern it reveals that, the broad peak of the pure polyaniline indicates the amorphous nature of the sample. The sample shows crystalline in nature when it is doped with AgO and crystallinity increases when doping concentration increased from 5% to 25%. Figure-1a shows the prominent peak of pure polyaniline is in the range of 25-27°, which is characteristics peak of polyaniline. Figure-2(b-f) shows sharp peak of maximum intensity at 2θ values 32.7 degree and other weak peaks are 2θ values 54.7 & 58.9 degree and as doping concentration increases, the enhancement in the sharpness of the peaks and intensity of (111) reflection indicated the increase in the crystallinity of the PANI. The diffractions (111), (220) and (222) reflections related to the cubic structure of AgO (ICCD Card No: 00-41-1104). Along with (111) reflection at 2θ values 32.7 degree, an additional two diffraction peaks at 2θ values 44.1 and 54.8 degree are correspond to the (200) and (220) reflections of metallic silver (ICCD Card No: 00-004-0783). It is also observed that, the intensity of the peaks is increasing from 45 counts to approximately 230 counts as

doping concentration increased from 5% to 25%. This increase in the intensity of the XRD peak may suggest that, silver oxide dispersed in the polyaniline matrix.

The average crystalline size of the PANI are estimated to be approximately 10 nm are calculated by using Debye - Scherrer formula,

$$D = K\lambda/(\beta \cos\theta)$$

Where D is average crystalline size, λ is wavelength of the X-ray, K is crystallite shape factor a good approximation is 0.9, **β** is the full width at half the maximum (FWHM) of the X-ray diffraction peak and 2θ is the Braggs' angle (deg.).

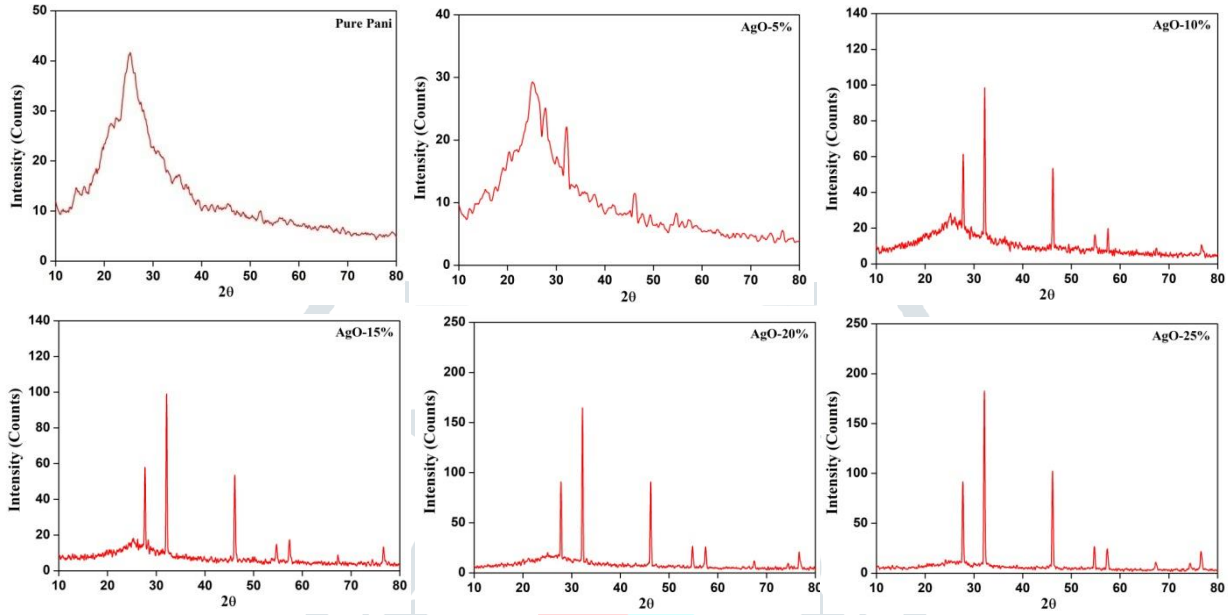

Figure-2: X-ray diffraction patterns of PANI and PANI/AgO Composite (5%, 10%, 15%, 20% & 25%)

ii. Morphological Study:

Figure-3 illustrates the surface morphology of pure polyaniline AgO/PANI (5%, 10%, 15%, 20% & 25%) respectively. The SEM image of PANI shows uniform morphology with semi-crystalline like structure. The SEM image of AgO/PANI reveals that the dopant metal oxide particles are dispersed in PANI which also justifies the successful composite formation and mainly composed of irregularly arranged granular, nonporous, aggregated surface morphologies with diverse sizes. Also observed that, percentage of composites doesn't affect the morphological image considerably**.** The average grain size was calculated as 30-40nm**.**The average grain size was determined by the linear intercept technique. A number of lines were drawn on a photograph and number of intercepts between the test line and grain boundaries were counted. The average grain size was calculated by using

$$D = \frac{1.56 \times C}{M \times N}$$

Where, D- Average grain size, N- Number of intercepts and M- Magnification of the photograph.

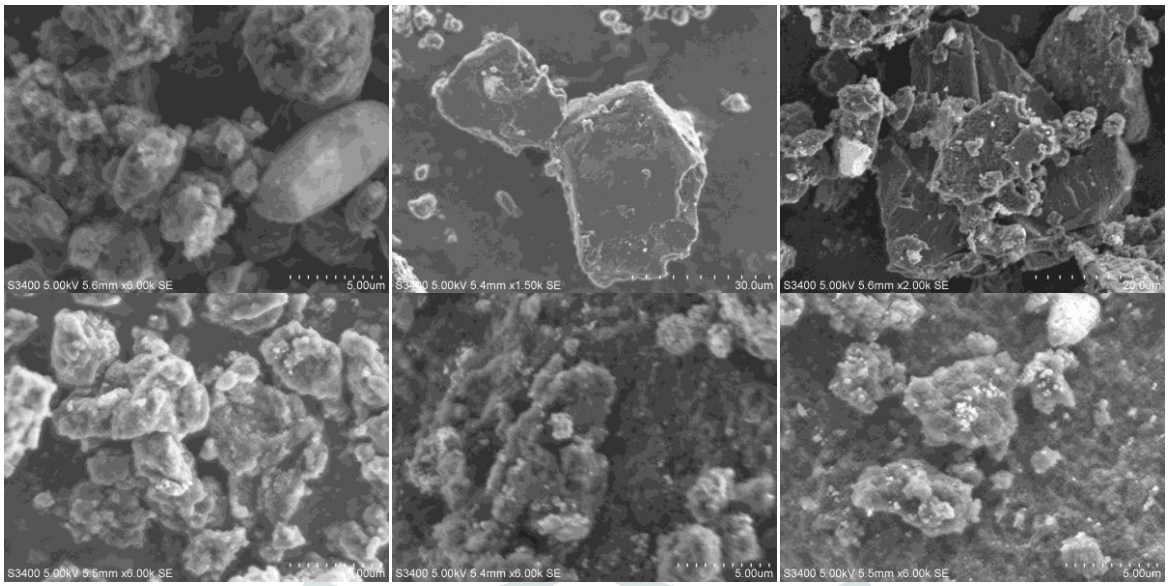

Figure-3: SEM micrographs of PANI and PANI/AgO Composite (5%, 10%, 15%, 20% & 25%)

iii. Electrical conductivity

a. AC Conductivity

The frequency dependent conductivity for disordered materials such as polymers can be due to interfacial polarization at contacts and grain boundaries of the sample.[13] Figure-4 shows the frequency dependence of σ_{AC} conductivity as a function of frequency for pure PANI and AgO/PANI composites with different wt%. The conductivity of all the studied samples is observed at room temperature. In all cases it observed that, the σ_{AC} conductivity increases as frequency increased from 1KHz to 1MHz. It is reported previously that, polyaniline has electrical conductivity ranges between 10^{-10} and 10^{3} S/cm depending on the acid dopant and fillers[14]. From plots it is observed that, the conductivity of all composites are higher than that of pure polyaniline. This observed high conductivity of the composites may due to the distribution of silver oxide in the polyaniline matrix. Previously reported that, the ac conductivity of pure polyaniline was found to be approximately $3x10^{-7}$ S/m at 1 KHz and it increases to $6.5x\ 10^{-6}$ S/m at 1 MHz.[15] Compared to previously reported, the conductivity was found to be higher for polyaniline at both the frequency 1KHz and 1MHz may be due to the variation aniline, oxidant and HCL in synthesis process.

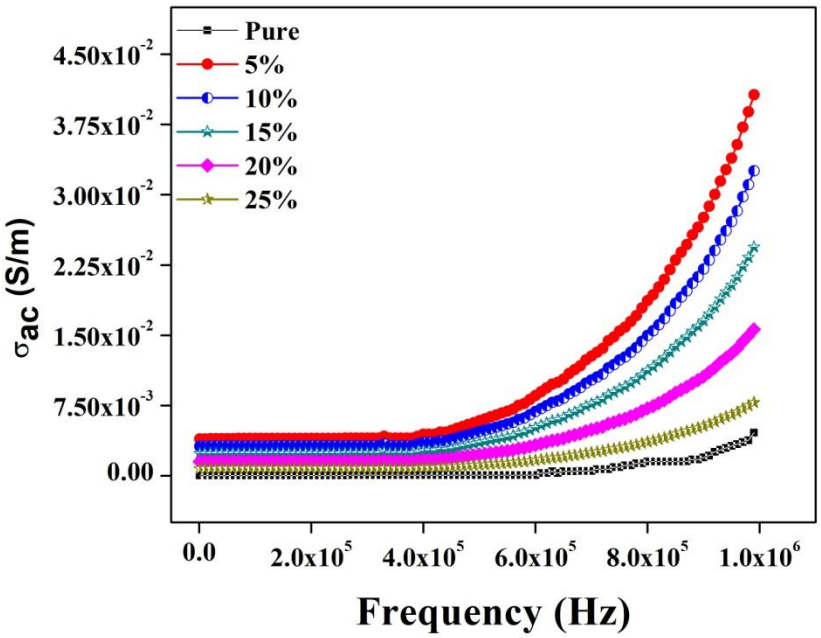

Figure-4: AC conductivity of PANI and PANI/AgO Composite (5%, 10%, 15%, 20% & 25%)

b. DC Conductivity

To illustrate the effect of AgO on the DC- conductivity of polyaniline material, a comparison of pure PANI and PANI/AgO composite was made. The temperature dependence DC electrical conductivity of pure PANI & AgO/PANI composites was carried out from 40°C temperature to 200°C on silver paste coated pellets with thickness ranging from 1-2mm. Figure-4 shows the variation of dc electrical conductivity as a function of temperature for pure polyaniline & polyaniline composites. It is observed that in all cases, dc conductivity of the PANI increases with increase in the temperature indicates semiconductor behavior of PANI sample. As is known the most common green polyaniline emeraldine salt has conductivity on a semiconductor level of the order of $10^0 Scm^{-1}$.[16]

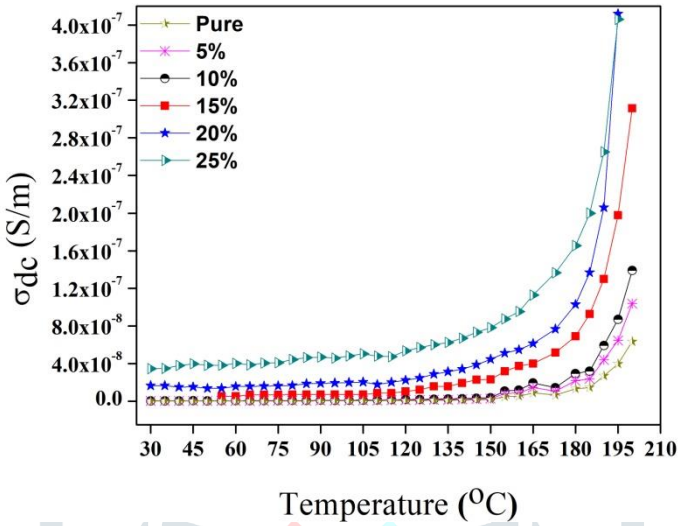

Figure-4: DC conductivity of PANI and PANI/AgO Composite (5%, 10%, 15%, 20% & 25%)

4. CONCLUSION:

Polyaniline and Ago/PANI were successfully synthesized by the chemical oxidative method. The result of XRD and SEM shows the formation of the composites and indicates the interaction between PANI and AgO. The average crystalline size of the PANI is estimated to be approximately 10 nm by XRD technique. The SEM image of PANI shows uniform morphology with semi-crystalline like structure. The SEM image of AgO/PANI reveals that the dopant metal oxide particles are dispersed in PANI which also justifies the successful composite formation and mainly composed of irregularly arranged granular, nonporous, aggregated surface morphologies with diverse sizes. AC conductivity increases as frequency increased but decreases as content of AgO is increased in the PANI matrix. AC conductivity of the composites are found to be higher in value compared to the conductivity of the pure PANI. DC conductivity of the PANI increases with increase in the temperature indicates semiconductor behaviour of PANI sample.

5. REFERENCES:

[1]. Mohd Omaish A, Faiz Mohammad, "Thermal stability of HCl-dopedpolyaniline and TiO_2 nanoparticles based nanocomposites", Journal of Applied Polymer Science, 2011, Volume 24, Issue 06, Page No-4433-4442.

[2]. H Letheby, "On the production of a blue substance by the electrolysis of sulphate of aniline" Journal of the Chemical Society, 1862, Volume 15, Page No-161.

[3]. P. Anilkumar and M. Jayakannan. A Novel Supramolecular Organogel Nanotubular Template Approach for Conducting Nonmaterial's. The Journal of Physical Chemistry B**2010,***114* (2) , 728-736.

[4]. G Cui, JS Lee, SJ Kim, H Nam, GS Cha, HD Kim, Analyst, 1998, 123, 1855.

[5]. Mohd Omaish Ansari and Faiz Mohammad; Thermal stability, electrical conductivity and ammonia sensing studies on p-toluenesulfonic acid doped polyaniline/titanium dioxide (pTSA/Pani/TiO2) nanocomposites, Sensors and Actuators B 157 (2011) 122- 129.

[6]. F. Derikvand, F. Bigi, R. Maggi, C.G. Piscopo, G. Sartori, "Oxidation of hydroquinones to benzoquinones with hydrogen peroxide using catalytic amount of silver oxide under batch and continuous-flow conditions"Journal of Catalysis 271 (2010) 99.

[7]. Wang W, Zhao Q, Dong J, Li J. A novel silver oxides oxygen evolving catalyst for water splitting. International Journal of Hydrogen Energy. 2011, 36, 7374–7380.

[8]. V.V. Petrov, T.N. Nazarova, A.N.Korolev, N.F. Kopilova, "Thin sol–gel SiO2–SnOx–AgOy films for low temperature ammonia gas sensor", Sensors and Actuators B: Chemical, 2008, 133(1), 291-295.

[9]. E. Sanli, B.Z. Uysal, M.L. Aksu, "The oxidation of NaBH4 on electrochemicaly treated silver electrodes", International Journal of Hydrogen Energy,2008, 33, 2097.

[10]. Y. Ida, S. Watase, T. Shinagawa, M. Watanabe, M. Chigane, M. Inaba, A. Tasaka, M. Izaki, "Direct electrodeposition of 1.46 eV bandgap silver (I) oxide semiconductor films by electrogenerated acid", Chemistry of Materials, 2008, 20(4), 1254-1256.

[11]. W.-X. Li, C. Stampfl, M. Scheffler, "Subsurface oxygen and surface oxide formation at Ag(111): A density-functional theory investigation", Physical Review B, 2003, 67(4), p.165412.

[12]. Saxena D, Dwivedi V, Mishra P, Dielectric Study of Polyaniline in Frequency Range 100Hz to 500 KHz at Temperature 200C and 300C, *Research Journal of Chemical Sciences*,*2013*, Vol. 3(2), 16-19.

[13]. R. Patil, A.S. Roy, K.R. Anilkumar, K.M. Jadhav, S. Ekhelikar, "Dielectric relaxation and ac conductivity of polyaniline–zinc ferrite composite"Composites: Part B, 2012, 43, 3406.

[14]. Y. Long, Z. Chen, N. Wang, J. Li, M. Wan, **"**Electrical transport in Polyaniline –CSA/Polyaniline – DBSA polyblends**"**, Physica B:Condensed Matter, 2004, 344, pp. 82-87.

[15]. Sangshetty Kalyane, "Synthesis, characterization and ac conductivity Study of Polyaniline/ $MgSnO_3$composites", International Journal of Materials Science, 2017, volume 12, issue 2, pp. 175-180.

[16]. Stejskal J, Gilbert RG, "Polyaniline, preparation of a conducting polymer", Pure Appl Chem, 2002, Volume 74, Page No- 857-867.