Synthesis of Silver chloride doped in polyaniline and its characterization

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Abstract : In this present work, the doping effect of transition metal ion (Ag) in polyaniline thin film investigated. Polyaniline (PANI) composites containing Silver chloride (AgCl) were prepared by HCl and ammonium persulphate. The chemical polymerization of aniline hydrochloride using ammonium persulfate as an oxidant in the presence of Silver chloride. Polyaniline-Silver (PANI-Ag) composite was prepared by the chemical oxidative polymerization method. The formation of Polyaniline-Silver (PANI-Ag) composited was characterized by various methods like UV–Vis spectroscopy; Fourier transforms infrared (FT-IR) spectroscopy, X-ray diffraction, Transmission electron microscopy (TEM), and DC electrical resistivity.

I. INTRODUCTION

During the last thirty years, the conducting polymer like polyaniline, polythiophene, polypyrrole polyacetylene, etc. was extensively studied by polymer researchers. Due to its electrical conducting capacity, a high degree of stability   is used in the laboratory instead of the metal conductor all over the world.[1] It belongs to the class of conjugated conducting polymer. This feature polyaniline (PANI) originates from π-electron. polyaniline has a π-conjugated backbone structure with imine groups by this structure and group, it can stabilize the metal ion in an aqueous medium as well as polymer by π-π interactions, steric effects, and hydrophilic interaction. polyaniline has received much attraction in the last ten years due to its properties like intrinsic electrical conductivity, simple and easy synthesis method, excellent environmental stability, cheap and easy availability of monomer, and behavior redox properties. It remains stable at a long time in the presence of a large range of humidity, hot and cold air. [2-4] Besides these properties, polyaniline (PANI) has much practical application such as chemical sensor device,[5] light-emitting devices,[6-7] electromagnetic interference shielding materials,[8-9] electrode, [10-12] molecular sensors, lightweight batteries, and surgical instrument,[13] for making important constituent of solar cells, electrochromic displays [14] and as corrosion protecting agent in the paint industry, [15] polyaniline exists in various oxidation states fully oxidized pernigraniline , fully reduced leucoemeraldine and half oxidized emeraldine base. The main aim of this research work is to develop high-performance and high conductive silver doped polyaniline for the to improve the electronic conductivity of polyaniline thin films and comparing their properties. The physical properties of polyaniline (PANI) depend on the choice of the counter metal ion called dopants. In this research paper, we report the synthesis, the characterization of silver doped polyaniline prepared by chemical methods.

2   Experimental Details

2.1   Materials

All chemical were supplied by Merck (Extra Pure) and were used without further purification.

2.2.Chemical Polymerization

The monomer Aniline, oxidizing agent Ammonium persulphate (APS) and Hydrochloric acid used as received without further treatment. Polyaniline was synthesized by the chemical oxidation method at lower temperatures (0-2°) C. Ammonium persulphate (APS) (Merck, Germany) was used as an oxidant. Five ml aniline was first dissolved in 1.5 M, 70ml HCl (Merck, Germany). After this process, this solution was kept in an ice bath maintaining the temperature below 5° C. Ten gram ammonium persulphate (APS) dissolved double-distilled deionized water. The solution of APS was added drop by drop into monomer solution and stirred at a constant speed. The polymerization process was performed for four to five hours. At the end of the polymerization reaction, final green color polyaniline was formed, washed with dilute hydrochloric acid solution and dried at 70°C in a hot air oven, for 10-12 hours. After forming polyaniline, an appropriate amount of Silver chloride solution 0.2 M was dissolved in the Polyaniline solution. Doping of Ag in polyaniline was done by the chemical doping method. In order to obtain the uniform distribution of Ag ion in the polyaniline solution, the mixture was stirred for 1 hour. The surface morphology of the doped polyaniline film was examined by FTIR, SEM, TEM methods, UV/VIS spectroscopy, X-ray diffraction, and DC electrical resistivity
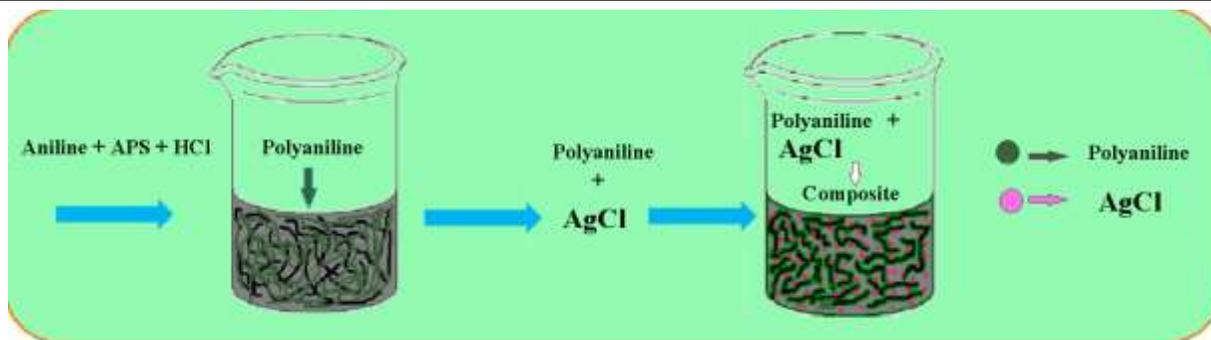
Schematic representation of the polyaniline-AgCl composite synthesis process.
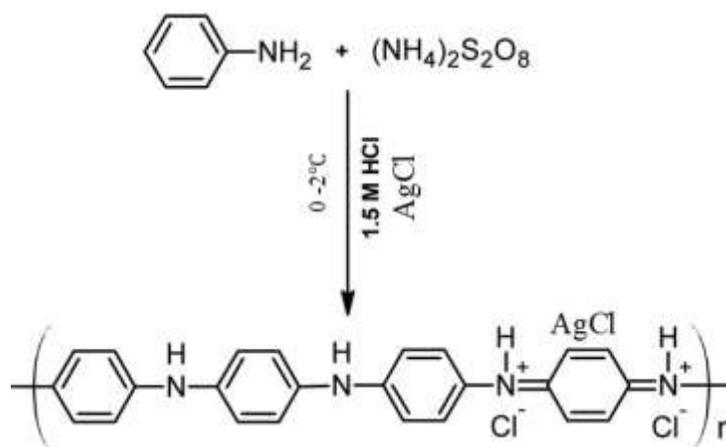
The reaction mechanism of AgCl doped in PANI.

Results And Discussion

The sample of the deposition was characterized by the structural, morphological, optical characterization

3.1 UV-Vis. Spectroscopy

Figure 1 shows the UV-Vis absorption spectra of the powder samples. UV-Vis Spectroscopy was studied by Perkin - Elmer-spectrophotometer (Lambda 35). Figure 1 shows the UV-Vis spectra for (polyaniline) PANI-AgCl composites. It shows two absorption peaks between 250-350 and 575 - 725 nm for Silver chloride (AgCl) doped in polyaniline. The polaron-π transition located between 250–320 nm and $\pi\rightarrow\pi^*$ transition located between 200–300 nm. The presence of AgCl silver chloride influences the absorption spectra of (PANI) polyaniline which appears between 250–560 nm and therefore we can suggest the presence of (AgCl) silver chloride nanoparticles in polyaniline. The figure also shows a peak at 575-725 nm corresponding to the formation of an intermolecular charge-transfer exciton.
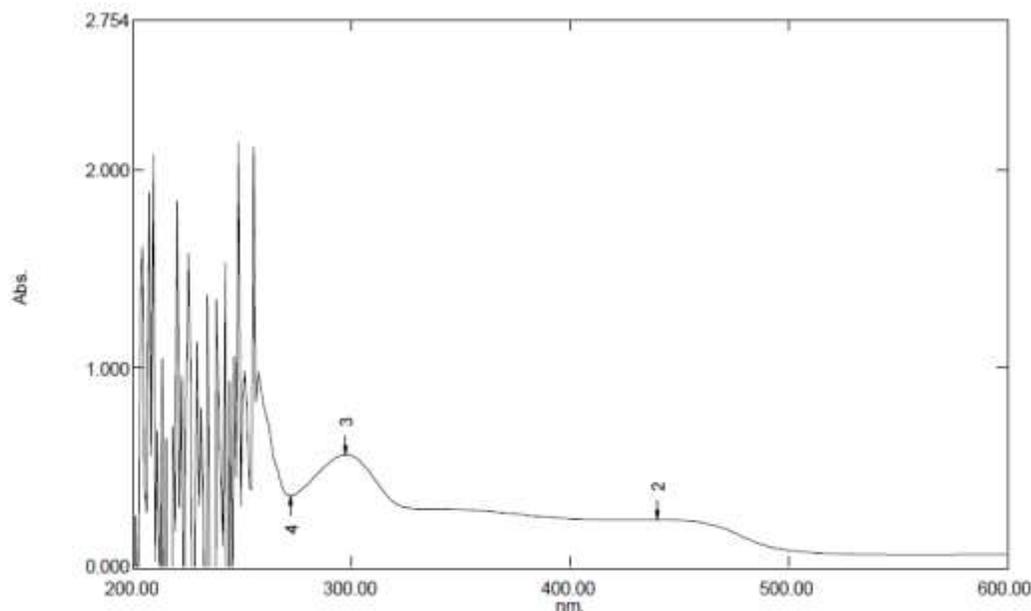
3.2 Fourier Transform Infra-Red (FT-IR)

The samples were characterized by Fourier Transform Infra-Red (FT-IR) spectroscopy using Shimadzu FTIR 8201 spectrophotometer in the range of 4000-500 cm^{-1}. FTIR spectroscopy is used to identify certain functional groups in a molecule and it also used to confirm the pure compound and as well as the impurities in the molecule. It shows peaks at 421, 423, 853, 1247, 1304, 1485, 1497, 2974 and 3280 cm^{-1}. It shows the band at 421 and 423 cm^{-1} represents the Ag-O bond. And band 853, 1247 and 1304 cm^{-1} represent vibration modes of N-H. The peaks at 1485 cm^{-1} and 1497 cm^{-1} are the related presence of benzenoid and quinoid rings respectively. The band 2974 cm^{-1} is related to C-H stretching vibration and N-H stretching at 3280 cm^{-1}.
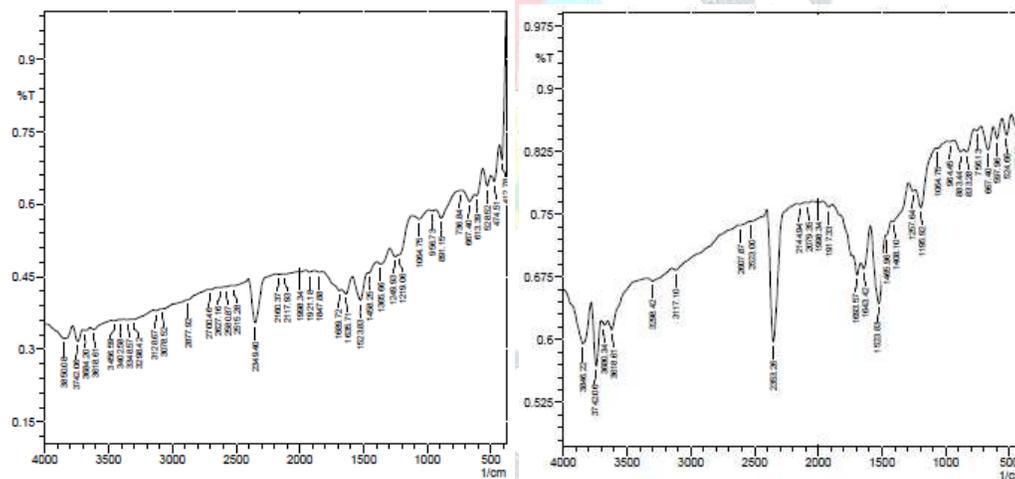

Figure 2 (Left) FTIR Spectra for Pure PANI and (Right) FTIR Spectra for Ag- doped PANI

3.3 XRD

In general, XRD characterization indicates the crystalline material structure with crystallite size, an atomic arrangement in the molecule, and imperfections in the molecule. It is also used to determine the prepared composite is amorphous or crystalline. In this case, it observed that undoped polyaniline and the composite has an amorphous form in nature. The X-ray diffractograms for Ag ion-doped polyaniline has been found to display at 2θ values of 17.79°, 19.00°, 20.23°, 26.16°, 32.18°, 35.57°, 46.43°, 57.46°, 74.32°, and 76.65°. The strongest peak is obviously for 2θ at 32.18°, 35.57°, 46.43°, 57.46°, 74.32°, and 76.65°. This entire strongest peak related to a pure silver metal with face-centered cubic symmetry. Bragg's equation is used for the calculation of inter-chain distance. This strongest peak corresponding to the crystalline order of protonated Ag ion-doped polyaniline. The 2θ values of 32.18°, 35.57°, 46.43°, 57.46°, 74.32°, and 76.65° correspond to crystalline order in other ordered arrangements of oligomers.
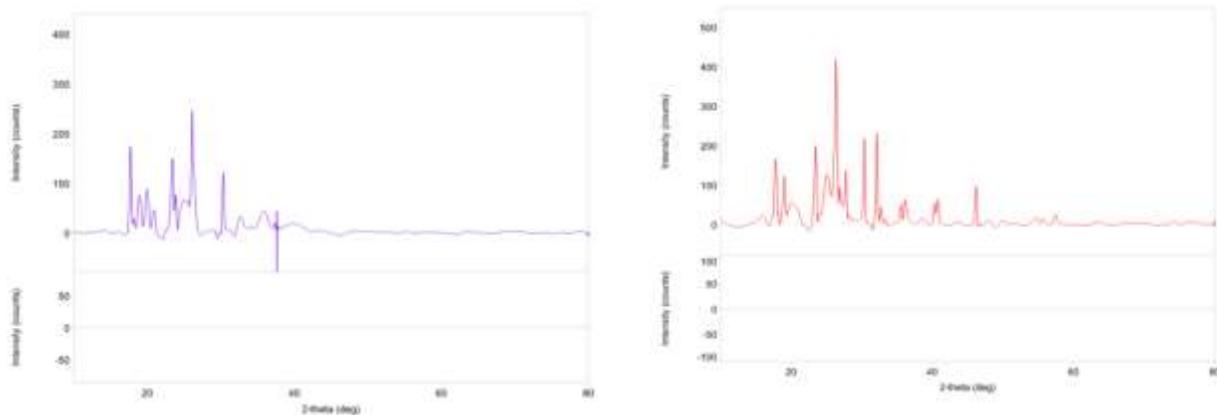
Figure 3a (left)   XRD of Pure PANI and 3b (Right) XRD for Ag- doped PANI

3.4   SEM

The SEM images of PANI and PANI-Ag are shown in Figures 4a and 4b respectively. The nanofiber's perfect structure is observed in the polyaniline (PANI) sample. Figure 4a shown an uneven irregular morphology. But in figure 4b of polyaniline Ag (AgCl) composite the irregularity increase than the figure of pure polyaniline. And the pore size in polyaniline-Ag (AgCl) composite is larger and uneven than polyaniline. The surface morphology of the mixed Polyaniline-Ag (AgCl) does not differ from the pure Polyaniline. When AgCl is added in polyaniline, the pore size of the mixture or composite becomes larger, which leads to the change in the morphological structure of polyaniline and Ag bind to various sites of polyaniline to form interchain linkage among several adjacent polyaniline chains by coordination bond. This porous structure and nanofiber are beneficial for supercapacitor because it decreases the diffusion resistance of the electrolyte into the electrode matrix.
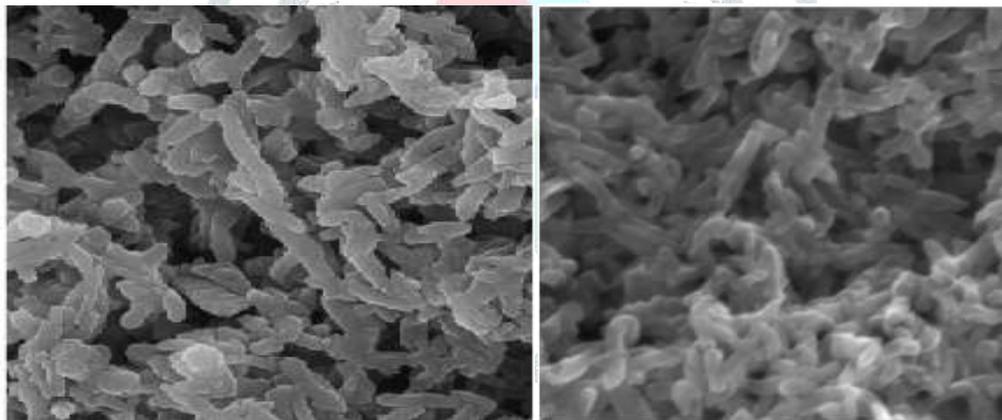

Figure 4a (left) SEM Image for Pure PANI and (Right) 4b SEM Image for AgCl- doped PANI

3.5 TEM

Figure 5a and 5b shows the TEM image of pure polyaniline (PANI) and silver chloride- polyaniline (PANI) composite obtained at 500 nm. Figure 5a shows AgCl attached to the PANI composite. It also shows spherical-particle like structures with dark and gray regions but in pure polyaniline it does not show any spherical-particle. The diameters of these granular black and gray spherical structures are between 10–20 nm. The morphological characteristics of AgCl doped in polyaniline (PANI) were investigated by TEM and images are shown in figure 5b. It represents AgCl doped in polyaniline (PANI). However, uniform doping of polyaniline (PANI) by AgCl is observed in figure 5b. So, we can expect that due to uniform doping, composite polyaniline show more electrical conductivity and low resistivity.
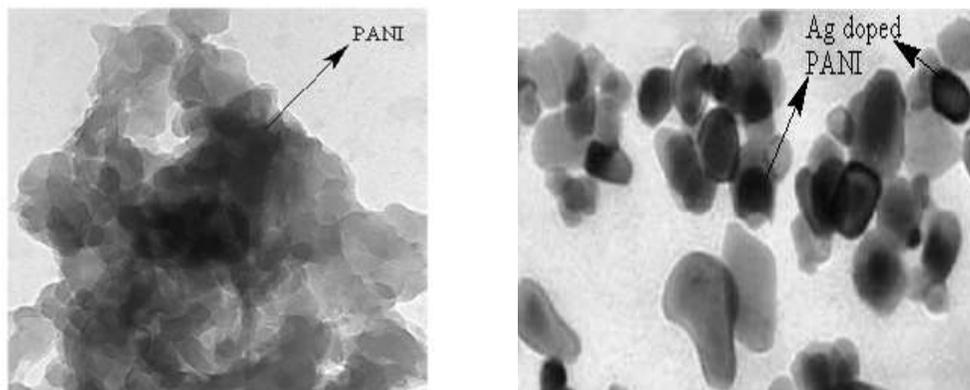
Figure 5a (left) TEM Image for Pure PANI and (Right) 5b TEM Image for AgCl- doped PANI

3.6. Thermo gravimetric analysis (TGA)

The thermogravimetric analysis (TGA) was performed on polyaniline samples at a temperature range from 0°C to 650°C by using Diamond TGA/DTA Perkin Elmer, United States of America. The thermal stability of prepared Polyaniline and silver doped polyaniline was tested by using the thermogravimetric analysis (TGA) technique. The polyaniline samples were kept for one minute at 30°C and then heated from 30 to 650°C at a rate of 10°C/min. The loss in weight for polyaniline and silver doped polyaniline upon heating under an inert gas atmosphere is shown in figure 6 graph (a) and (b) respectively. Figure 6 graph (a) polyaniline and (b) silver doped polyaniline shows a steady mass decrease is found at the range 280°C to 295°C. It also shows a rapid change at range from 270°C to 400 °C. The figure indicates polyaniline weight% is less than composite polyaniline. The weight loss of Polyaniline and Polyaniline-silver composite at 650°C was 62.05% and 92.00% respectively. Thermal stability of silver chloride have less stability than other 3d block and some 4d block element. Silver chloride loosely attached to polyaniline chain. But it conductivity is more than other metal chloride. Temperature plays an important role for conductivity. Thermogravimetric analysis (TGA) indicates polyaniline-silver composite has less thermal stability because of the silver particle as dopant at the nitrogen sites of polyaniline.
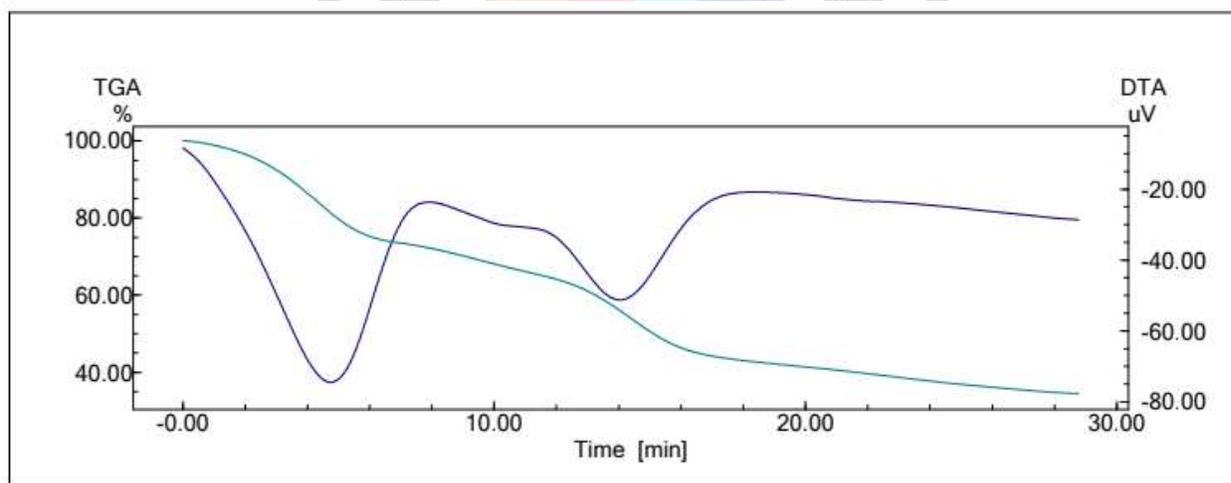
3.7 Conductivity measurement

The DC electrical resistivity (ρ) of the synthesized pure polyaniline and AgCl Ag ion-polyaniline composite materials was measured by the four-point probe method at change temperature with the change in current. The temperature variation of voltage was determined. The DC electrical resistivity (ρ) of the pure polyaniline and (AgCl) Ag-polyaniline sample was determined from the range room temp. to 100°C temperature. It was observed that the resistance of Ag ion-doped polyaniline and pure polyaniline is different from each other. It depends on the dopant agent as well as the temperature of the sample. The DC electrical resistivity (ρ) of the (AgCl) Ag-polyaniline was calculated by using the following equations.

$$\text{Resistivity (r, V cm)} = \rho \, t/In2 \ (V/I) \qquad (1)$$
$$\text{Conductivity (s, S cm}^{-2}) = 1/r \qquad (2)$$

Where I is the applied current, and V is the measured voltage and t is the thickness of pure polyaniline and (AgCl) Ag-doped polyaniline. Maximum ten tests were performed for pure polyaniline as well as (AgCl) Ag-doped polyaniline and finally, data were averaged. All the data was used for the calculation and graph. Knowing DC resistivity (ρ) of the sample platinum probe was used. The frequency-dependent AC conductivity and dielectric permittivity of the pure polyaniline a flat, square shape thickness 0.46 and area 1.9 x10^{-1}cm^2 (AgCl) Ag ion-doped polyaniline flat, square shape thickness 0.47 and area 1.9 x10^{-1}cm^2 were obtained by using a computerized impedance analyzer and using an alternating electric field amplitude 1.000 V across the pure polyaniline and Ag-doped polyaniline in the frequency region of 50 HZ to 10 MHZ. By using the formula and data plots is observed that conductivity increases with an increase in temperature. As the temperature increases, the mobility of electrons or ions also increases which results in a rise in

conductivity in pure polyaniline availability of free electrons or ions is low but in (AgCl) Ag ion-doped polyaniline composite availability of free electrons or ions is more than pure polyaniline. The curve is linear. The slope of the curve shows activation energy. DC electrical resistivity (ρ) decreases with an increase in Ag-polyaniline samples. The decrease in resistivity and an increase in the conductivity of (AgCl) Ag ion-doped polyaniline increased due to the mobility of electrons or ions. As the crystallinity increases and hydrogen bonding from FTIR confirmed which also shows increased conductivity. Ea value of Ag-polyaniline shows a low potential barrier than pure polyaniline. (AgCl) Ag ion concentration increases the conductivity. The conductivities of the (AgCl) Ag-polyaniline composites increased with increased temperature. At room temperature, DC electrical resistivity (ρ) for pure PANI film observed at 0.025 S/m and it decreases with the presence of Ag. And resistivity of pure polyaniline is 40 Ω m and Ag-doped polyaniline is 04.60 Ω m.
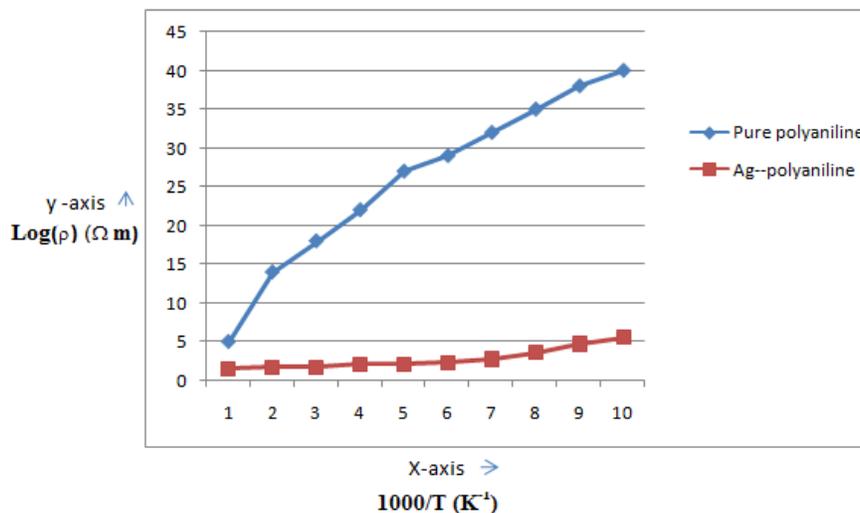

Figure 7 Electrical resistivity of the a) pure polyaniline, (b) Polyaniline- AgCl composite

1. **Conclusions**

The SEM image shows the pore size in polyaniline- AgCl is larger and spherical and uneven than polyaniline. TEM analysis shows uniform dispersion of the silver nanoparticles in the polyaniline. XRD which suggests that the polyaniline sample is more crystalline than Ag-doped polyaniline that's mean doped polyaniline has less crystallinity. Although the polyaniline-Ag composite is more conductive than pure undoped polyaniline.

II. **ACKNOWLEDGMENT**

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