

Structural, Thermal and Electrical properties of prepared polyaniline / Silver Nanocomposites

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Abstract

Conducting Polyaniline/Silver (PANI/Ag) nanocomposite was synthesized by placing nano particle of silver in polymerization mixture of aniline hydrochloride with ammonium peroxydisulfate in acidic medium (2M of HNO₃) by chemical oxidation polymerization. XRD image shows a nanoparticulate structure of silver which is well dispersed in the polyaniline matrix and with that of face-centered-cubic form of metallic silver. DTA results confirmed the weight loss at 70°C. The A.C- conductivities, dielectric permittivity (ϵ') of (PANI/Ag) nanocomposite and pure PANI have been measured in frequency range from (10³-10⁶) kHz. The electrical conductivity of the (PANI/Ag) nanocomposite is higher than pure PANI. The variation of frequency exponents in this blend suggests that AC-conductivity is attributed to correlated barrier hopping mechanism. At all frequencies, the ϵ' value for (PANI/Ag) nanocomposite is higher than that for pure one. The higher dielectric constant of the PANI/Ag nanocomposites indicates their better ability to store electric potential energy under the influence of alternative electric field.

The D.C conductivity of (PANI/Ag) nanocomposites have been measured in the temperature range from (298- 433)K indicated that the Ag nanoparticles increased the electrical conductivity of polyaniline nanocomposites as compared to pure aniline.

Keywords: PANI, Ag nanocomposites A.C D.C , thermal properties

INTRODUCTION

One key property distinguishing classical polymers from metals is their low electrical conductivity. A new class of organic polymers capable of conducting electricity has recently been developed. These polymers become conductive upon partial oxidation or reduction, a process commonly referred to as doping or protonic doping. The electrical properties of conductive polymers can be reversibly changed over the full range of conductivity from insulators to metallic conductors [1]. During the past two decades; conductive polymers have been under intensive research and development in the academic world and also in the chemicals and electronics industry world-wide. Their use as new materials in value added industrial and consumer products is opening up entirely new dimensions for polymeric materials. The major

drawback of existing conductive polymers has been their modest environmental stability and/or intractability, which made it difficult to process them into meaningful end products using conventional processing methods [2]. The unifying characteristic property of this class of polymers is the intrinsic ability of the conjugated polymer backbone to support electrical conduction. Thus the fundamental property of conducting polymers is that electrical conductivity is achieved by charge carrier (electron or hole) through a π conjugated polymer backbone[3,4]. There are many different kinds of polymer systems which can undergo redox doping process other than cis- and trans- polyacetylene, (CH)_x. It has been found that polymers such as polyparaphenylene, poly(phenylenevinylene), polypyrrole, polythiophene, polyfuran, etc., and their ring- and N-substituted derivatives can also undergo redox p-doping and/or ndoping as listed in Figure 1. Moreover, the synthesis of new polymer systems such as poly(heterocycle)vinylenes, where Y=NH, NR, S and O, also attracted considerable attention because of their unique combination of physical properties, solution processibility and environmental stability in the doped form [5,6]

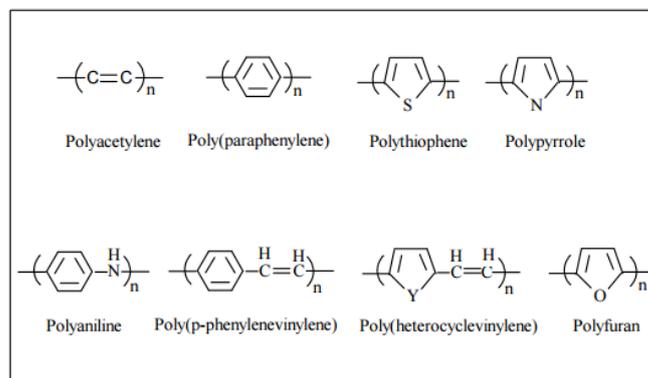


Figure 1: Examples of intrinsically conducting polymers[6]

The interest in polyaniline as an important conducting polymer has increased

Significantly over the past decade, resulting in a number of review article published a few years ago. The polyanilines, probably the earliest known synthetic polymer [7,8], refer to a large class of conducting polymers which have the following general formula (Figure 2):

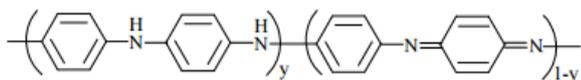


Figure 2: Polyaniline general formula

A large variety of derivatives can be prepared through substitution in the ring or on the N atoms. One of the special properties of polyaniline is that it can be doped by protonic acids. Thus, the properties of the doped polymer can be turned by incorporating different dopant anions. It has been found that polyaniline can exist in three different, isolable oxidation states at the molecular level[9,10]. They are the leucoemeraldine oxidation state $Y=1$, the emeraldine oxidation state $Y=0.5$, and the pernigraniline oxidation state $Y=0$. In this work used Polyaniline because have some advantage like electrical properties can be reversibly controlled by charge-transfer doping and protonation. Polyaniline is environmentally stable and inert (noble) where stainless steel is corroded. Polyaniline is applicable to electrical, electrochemical, and optical applications. Polyaniline is currently used in cell phones and calculators, and other LCD technology etc.[11]

EXPERIMENTAL PART

Materials and Samples Preparation

The preparation of pure (PANI) is based on the oxidation of (0.2M) aniline hydrochloride with (0.25M) ammonium peroxydisulfate in aqueous medium. The pure sample was prepared in distilled water and the doped sample with 2M of HNO_3 aqueous solution and adding (0.05%, 0.1% wt of Ag nano particle). To prepared sample doped with 2M. Aniline hydrochloride was dissolved in (1M) HNO_3 in a volumetric flask to 50ml of solution, ammonium peroxydisulfate was similarly dissolved in (1M) HNO_3 also to 50ml of solution both solutions are mixed at room temperature in a rounder and adding Ag nano in in-situ polymerization, and gentle stirring to polymerize the mixture is left to rest to the next day. The (PANI) precipitate is collected on a filter and for purification the output was washed with 200ml of (0.2M) HCl, and 150ml of ethanol to remove any monomers un polymerized. The washed Polyaniline (emeraldine) hydrochloride powder is dried in air for about one hour then in vacuum oven about (70 °C) for 4 hours the average yield was (2.25)g. The polyaniline powder was thoroughly grounded in a mortar to obtain very fine particles, and then it was compressed under a pressure 5 tone in the form of a pellet. The resulting pellet has a diameter of 1.0cm and thickness of (2mm).

Characterizations

X-ray Diffraction

XRD is based on the elastic scattering of X-rays from structures that have long-range order, and it is an efficient analytical technique used to identify and characterize

crystalline materials. Scattering is a powerful tool to access the bulk structure in a nondestructive way.

Thermal Properties

Differential Thermal Analysis (DTA)

The sample and the reference material (sample) are heated in one furnace. The difference of the sample temperature and the reference material temperature is recorded during programmed heating and cooling cycles.

Electrical properties

A.C. Conductivity

A.C electrical measurements are used to investigate polyaniline samples doped during polymerization with various amount of Ag nano particle. The LCR meter models (HP-4274A and HP-4275A) were used for the A.C measurements. The sample was placed in a holder specially designed to minimize stray capacitance. The range of frequency was 1kHz - 10MHz. For the sample under investigation, the specimen capacitance C, dissipation factor D and resistance R were measured.

The total conductivity σ_{tot} at a certain frequency and temperature is defined as:

$$\sigma_{tot} = \sigma_{a.c}(\omega) + \sigma_{d.c} \quad (1)$$

Where:

$\sigma_{a.c}$ is the A.C. conductivity which is weaker temperature dependence than $\sigma_{d.c}$ and dominate at high frequency; while $\sigma_{d.c}$ is the D.C. conductivity which depends strongly on temperature and dominate at low frequencies, then the empirical relation for the frequency dependence A.C conductivity is given by:

$$\sigma_{a.c}(\omega) = A_1 \omega^s \quad (2)$$

Where:

A_1 is constant parameter, and s is an exponential factor. Its value is $0 < s < 1$, the exponent (s) is a function of frequency and is determined from the slope of a plot $\ln \sigma_{a.c}(\omega)$ versus $\ln(\omega)$ then:

$$S = \frac{\ln \sigma_{a.c}(\omega)}{\ln(\omega)} \quad (3)$$

And the dielectric constant ϵ_1 was calculated from the equation:

$$\epsilon_1 = \frac{dC}{A \epsilon_0} \quad (4)$$

Where ϵ_0 is the permittivity of free space. The dielectric loss, ϵ_2 , was calculated from the equation:

$$\epsilon_2 = \epsilon_1 \tan \delta \quad (5)$$

Where $\delta = 90 - \phi$, ϕ is the phase different angle.

D.C. Conductivity

The electrical resistance has been measured as a function of temperature in the range (298 -433 K) by using the resistivity (ρ) of the films is calculated by using the following equation:

$$\rho = \frac{R.A}{L} \dots \dots \dots (6)$$

Where: R is the sample resistance, A is the cross section area of the film and L is the distance between the electrodes. The conductivity of the films was determined from the relation:

$$\sigma_{dc} = \frac{1}{\rho} \quad (7)$$

The activation energies could be calculated from the plot of $\ln \sigma$ versus $1000/T$.

RESULT AND DISCUSSION:

X-ray Diffraction

Fig (3) shows XRD pattern of pure PANI shows two peaks of 2θ at $\sim 20^\circ$ correspond to (100) and abroad peak at about 26° which is a characteristic peak of PANI correspond to (110) crystal planes .

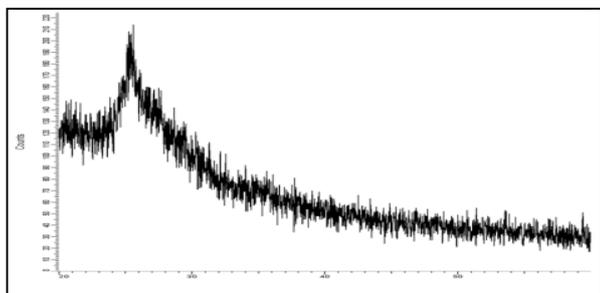


Figure 3: XRD for pure PANI.

Fig (4) shows the XRD for PANI /Ag nano composites for (0.1%wt) peaks corresponding to the cubic structure of silver were also found at $\sim 32^\circ$ (101), $\sim 42^\circ$ (200), $\sim 65^\circ$ (220) and $\sim 78^\circ$ (311) plane , in addition to peaks of pure PANI .

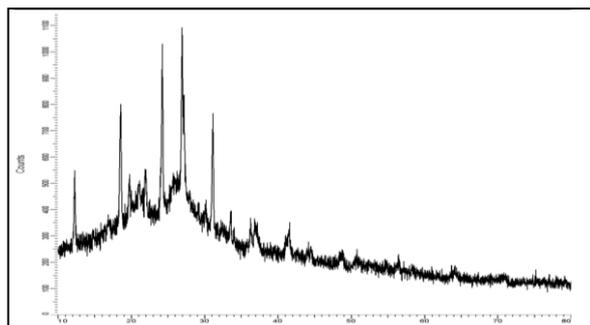


Figure 4: XRD for PANI/Ag nanocomposites (0.1% wt)

Differential Thermal Analysis (DTA)

Fig (5) shows the DTA curves of PANI and ANI/Ag nanocomposites. All curves show weight loss below 70°C is accompanied by a weight loss .This is probably due to the moisture evaporation, which are trapped inside the polymer or bound to the surface of polymer backbone (physisorbed water molecules) . The removing of water is easier in the composite with higher surface area or with increasing the interfaces between their particles[12, 13].

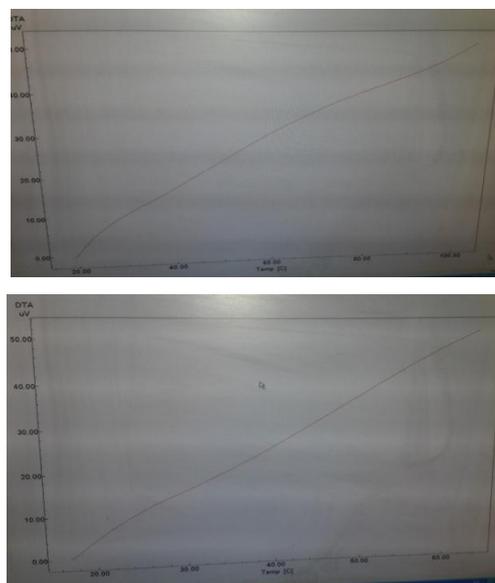


Figure 5: DTA of pure PANI and PANI/Ag nanocomposites at 0.1wt%

A.C. conductivity measurement:

The A.C. conductivity ($\sigma_{A.C.(\omega)}$) was measured for pure PANI, and PANI/Ag nanocomposites to study the mechanism of conductivity. Fig (6) shows the frequency depended of the total conductivity σ_t for pure PANI.

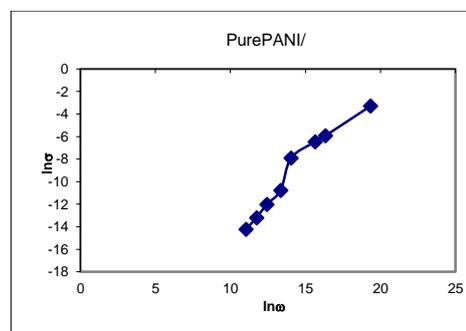


Figure 6: A.C electrical conductivity of pure PANI

The lower conductivity of the pure PANI could be ascribed to low level of protonation of the PANI chains low concentration of polaron in PANI chain. In Fig (7) the AC-electrical conductivity of the PANI/Ag nanocomposites is higher than

that of the pure PANI. The improvement of AC conductivity for PANI/Ag nanocomposite comes from the effective dispersion of Ag nanoparticles in the PANI matrix which favors better electronic transport. This indicates that there may be charge carriers, which can be transported by hopping through the defect sites along the polymer chain [4].

be a result of interface charge polarization (or Maxwell-Wagner-Sillars effect) and intrinsic electric dipole polarization [4]. This phenomenon appears in heterogeneous systems like metal-polymer composites due to the accumulation of mobile charges at the interfaces and the formation of large dipoles on metal particles or clusters. The frequency exponent (s) for pure PANI and PANI/Ag nanocomposites are estimated from the slope of the curves plotted between $\ln \sigma_{ac}(\omega)$ versus $\ln(\omega)$ and listed in table 1. It is found to be less than unity. The doped samples have higher value because higher conductivity which can be related to the hopping of charge carrier over a small barrier between polymer chains.

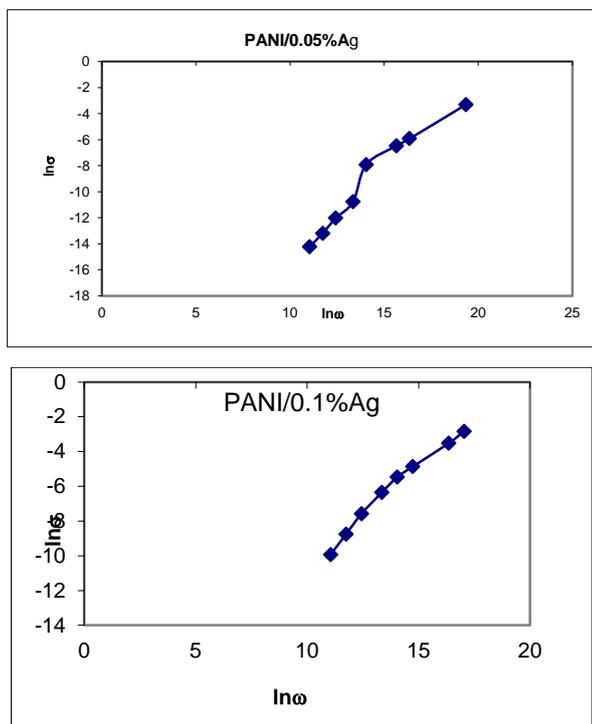


Figure 7: Electrical conductivity of PANI/Ag nanocomposites at 0.05%, 0.1%

It can be seen that the conductivity of PANI/Ag nanocomposite increases as the frequency increases. The frequency dependence of the AC-conductivity is considered to

Table 1: frequency exponent (s) for pure PANI and PANI/Ag nanocomposites

Samples	(S)exponent factor
Pure PANI	0.12
PANI/Ag 0.05%	0.45
PANI/Ag 0.1%	0.33

Fig (8) shows the dielectric constants of PANI/Ag in the frequency range of $10^3 - 10^6$ kHz and at room temperature, higher dielectric constants of PANI/Ag nanocomposite indicates their better ability to store electric potential energy under the influence of alternative electric field. The frequency dependency of dielectric constant is found to be increased in presence of Ag in the nanocomposite. This is thought to be a result of the slow dielectric relaxation of the PANI matrix and the interface of the composite. The dielectric constant is very high due to the AC-conduction loss that dominates over other types of losses present in the polymer e.g. dipole segmental losses and orientation of the polar group [5].

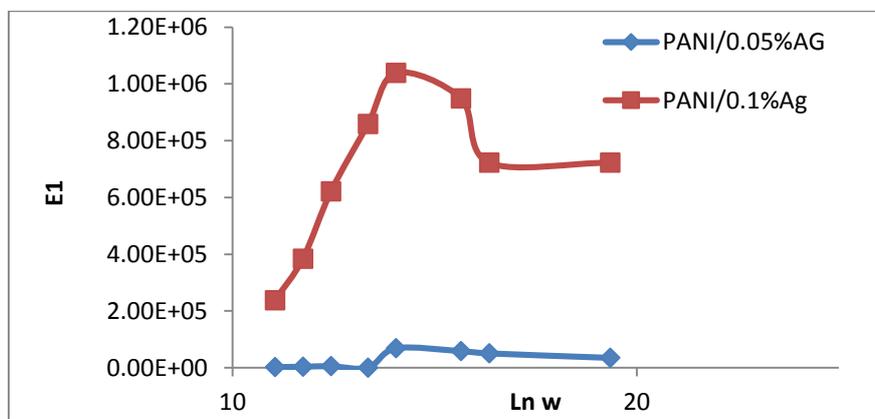


Figure 8: dielectric constant for PANI/Ag nanocomposite

DC-Electrical Conductivity

Fig(9) shows the temperature dependence of DC conductivity in the temperature range (298-433)K for pure PANI and Fig(10) shows DC conductivity of PANI/Ag nanocomposites its higher than that of pure PANI. The plots on the $\ln \sigma_{dc}$ as a function of $1000/T$ are nearly straight lines indicating that the conduction in the samples through an activated process having single activation energy.

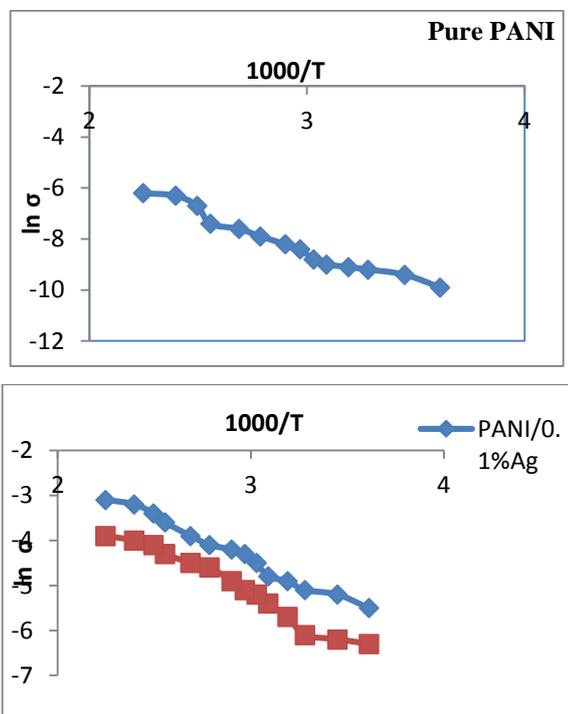


Figure 9 : $\ln \sigma$ vs $1000/T$ of pure PANI and PANI/Ag nanocomposites at (0.05%, 0.1%)wt

The activation energy are measured by Arrhenius equation listed in Table (2) found the E_a for Pure PANI is 0.22eV than higher of Ag nanocomposites. The decrease in E_a is found to be associated with shift of donor level in doped samples. From a single value of activation energy it is clear that the conduction is through the carrier concentration at the Fermi Level.

Table 2: Activation energy data for protonation PANI

sample	Activation Energy(eV)	σ_{dc} ($\Omega^{-1} \cdot \text{cm}^{-1}$)
Pure PANI	0.22	0.098
PANI/0.05% Ag	0.09	0.086
PANI/0.1% Ag	0.06	0.071

CONCLUSIONS

1- PANI/Ag nanocomposites were successfully synthesized by in-situ polymerization at different Ag concentrations.

2- A.C and D.C Conductivity and dielectric constant have been measured and it is suggested that conduction is taking place by the hopping process due to a wide range of localized states present in the sample.

3- The PANI/Ag nanocomposite exhibit remarkable improvement of electrical conductivity and dielectric properties when compared with pure PANI.

REFERENCES

- [1] Cohen, "Corrosion of copper and copper alloys", in ASM Handbook, Corrosion: Materials, Materials Park, OH, Vol. 13B, p. 137, 2005.
- [2] Adrianus.J.Dekker, Solid State Physics, Department Of Electrical Engineering, University Of Groningen, 1962.
- [3] Buttiker and Thomas, "Symmetry of electrical conduction", IBM Journal of Research and Development, vol.32, pp. 317-334, (1988).
- [4] Dyre and B. Schroder, "Universality of a.c. conduction in disordered solids", Review of Modern Physics, vol. 72, pp. 873-892, (2000).
- [5] Gustavsson.J.M. "Corrosion protection using conducting polymers", Ph.D. Thesis, University of Wollongong (2007).
- [6] H Hoffmeister, J Ullrich, "Quantitative effect of transient potentials and temperature on crevice corrosion of Naval Cast CuNiAl Valve bronze in natural sea water" Corrosion, 2000 .
- [7] Jonscher, "Electronic Conduction in Amorphous Semiconductors", Journal of Vacuum Science and Technology, vol. 8, pp. 135-144, (1971).
- [8] Kunigahalli L Vasanth and Richard A Hays. "Corrosion assessment of Nickel Aluminum Bronze (NAB) in sea water", Corrosion paper 04294, 2004.
- [9] Mostafaei A. and Zolriasatein A., "Synthesis and characterization of conducting polyaniline nanocomposites containing ZnO nanorods", Progress in Natural Science: Materials International, vol. 22, no. 4, pp. 273-280, (2012).
- [10] Nestor Perez, "Electrochemistry and Corrosion Science", Kluwer Academic Publishers, 2004.
- [11] M. Khairy and M.E. Gouda, "Electrical and optical properties of nickel ferrite/polyaniline nanocomposite" J Adv Res. 2015 Jul; 6(4): 555-562.
- [12] Mohd Abdul Majeed Khan1, Sushil Kumar , Maqsood Ahamed , Salman A Alrokayan and Mohammad Saleh AlSalhi1, "Structural and thermal studies of silver nanoparticles and electrical transport study of their thin films" Nanoscale Research Letters 2011, 6:434
- [13] R. Winston Revie, Herbert H. Uhlig, "corrosion and corrosion control an introduction to corrosion science and engineering", fourth edition, 2008.