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Synthesis, characterization and conductivity study of polyaniline prepared by chemical oxidative and electrochemical methods

J. Vivekanandan¹, V. Ponnusamy², A. Mahudeswaran¹ and P. S. Vijayanand^{1*}

¹Department of Physical Sciences, Bannari Amman Institute of Technology, Sathyamangalam, Erode - District, India

²Department of Physics, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore, India

ABSTRACT

The present work reports the electrochemical and chemical oxidative synthesis of polyaniline using $K_2Cr_2O_7$ as an oxidant and H_2SO_4 as dopant. The conductivity studies of electro chemical synthesis of PANI doped with H_2SO_4 at various voltages are compared with oxidative synthesized PANI. The confirmation of PANI was done by FT-IR. The crystallinity of the samples was examined by powder X-ray diffraction technique. The various electron transitions present in the PANI were determined by UV-VIS spectroscopy. The electrical conductivity of the synthesized samples was measured by using four probe method at room temperature.

Keywords: Polyaniline, electrochemical and chemical oxidation methods, FT-IR, XRD studies, conducting property.

INTRODUCTION

In recent years alternative renewable energies obtained by solar cells have attracted much attention due to exhaustion of other conventional energy resources especially fossil based fuels and due to global warming they caused [1]. Thus the synthesis of novel conducting polymers and study of their physical properties has been of prime importance. Aqueous electrochemical process in an environmentally friendly and efficient technique used to process conducting polymer. It is widely preferred because of its simplicity and it can be used as a one step method to form polymer. It allows efficient control of the physiochemical properties of the coatings and it can also be easily scaled up for large scale production [2-4]. Conductive polymers had been the topic of the large number of investigations during last decades because of their unique properties such as mechanical strength, electrical conductivity, corrosion, stability and possibility

of both oxidative and electrochemical synthesis. Hence PANI is useful in wide area of application: such as solar energy conversion, rechargeable batteries, electro chromic displays, electrochemical sensors, capacitors and active corrosion protector [5-6]. Due to ease of synthesis, processing environmental stability and low synthetic cost, so polyaniline is probably the most important industrial conducting polymer today [7-8]. The use of conducting polymers for photovoltaic applications has been reported [9]. Since PANI possess high performance of electrical property, easiness to handle, high thermal stability, insolubility and low resistivity it can be used as a material for LEDs organic semiconductors [10-11]. The conductivity of PANI synthesized by electro chemically was dependent on the redox state of the polymer, the solution pH, water content and to a lesser extent [12-14]. The type of dopant anion also affects the stability of the conductivity in PANI at different atmospheres and at temperatures. Changing the nature of the anion also has a significant influence on the kinetics and conversion in the electrochemical polymerization of aniline.

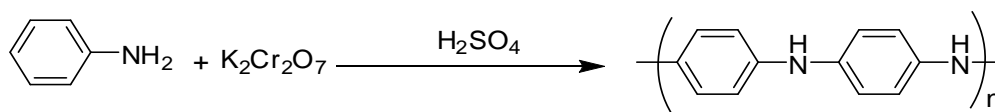
The main aim of this research work is to develop energy efficient materials for the present need by comparing their electrical conductivity properties. In this paper, we report the synthesis, characterization and conductivity studies of polyaniline prepared by electrochemical and chemical oxidation methods. Further, their electrical conductivity was compared with electrochemical, synthesis of PANI doped with H₂SO₄ at various voltages.

MATERIALS AND MATERIALS

All chemicals such as aniline, H₂SO₄ and oxidant (K₂Cr₂O₇) were obtained from Merck chemical company are of high purity (>99%).

2.2. Chemical Polymerization

The chemical polymerization of aniline was carried out in the presence of aqueous sulphuric acid solution. Appropriate amount of aniline (0.1 M) is taken, to which H₂SO₄ acid was added into polymerization vessel and make a total volume of 100 ml. Then the vessel was placed on a magnetic stirrer. 20 ml of aqueous solution of K₂Cr₂O₇ oxidant at appropriate concentration was added slowly to the reaction medium by drop wise fashion for about 20 minutes using a dropping funnel.



At the end of polymerization reaction, final product was filtered, washed with dilute solutions of H₂SO₄ acid and dried at 60°C in vacuum, for 12 hours. The synthesized polyaniline was finally grinded and the product is obtained in the form of fine green powder.

2.3. Electrochemical Polymerization

Aqueous electrochemical polymerization was performed in a single compartment electrochemical cell. A 3cm (b) x 6cm (l) x 2mm (t) stainless steel plate was used as the working electrode (anode). The counter electrode (cathode) in comprised of stainless steel plates. A digital power supply (0-5V) was used as the source.

The electrochemical polymerization of aniline was carried out in the presence of aqueous sulphuric acid. Appropriate amount of aniline (0.1 M) and H₂SO₄ (0.1 M) acid were added to polymerization vessel to make the volume of 500 ml. The different voltages were used for the electrochemical synthesis.

The collected samples was filtered and washed with dilute solution of H₂SO₄ acid and dried at 60°C in vacuum for 12 hours. The synthesized polyaniline was finally grinded and the product is obtained in the form of fine green powder.

2.4. Characterization Techniques

The synthesized polyaniline were characterized by UV-vis spectroscopy and FT-IR spectroscopy. FT-IR spectra were recorded using Thermo Nicolet V-200 FTIR spectrometer by KBr pellet method in the region 400 to 4000 cm⁻¹. Optical absorption spectrum was taken using JASCO V-530 dual beam spectrophotometer in the wavelength region 200 to 800nm with a scanning speed of 400nm/min. X-ray diffraction patterns of the coatings were obtained by employing JEOL JDX Services diffractometer using CuK_α (K_α =1.54056 Å) radiation. The diffractometer was operated at 40Kv and 50mA. A scanning step of 0.1° in 2θ with a dwell time of 10s per step was used. The samples used for x-ray measurements were prepared by using polished steel plates. Powder X-ray diffraction pattern was recorded. The solubility studies were also studied by various polar and non-polar solvents. The electrical conductivity studies were performed by using four probe method.

RESULTS AND DISCUSSION

3.1. Solubility

The solubility of the sulphuric acid doped polyaniline was determined in various solvents. Sulphuric acid doped PANI was soluble in DMSO and insoluble in other solvents like acetone, benzene, chloroform, methanol, m-cresol and water.

3.2. FT-IR Spectra

FT-IR spectra of PANI samples doped with H₂SO₄ acid are shown in Fig 1. In a spectrum the band observed at 3433.75 cm⁻¹ is due to N-H stretching. The polymer shows the absorption bands at 2923.62, 2923.25, 2923.21 and 2825.55 cm⁻¹ are due to asymmetric C-H stretching and symmetric C-H stretching vibrations. The absorption peaks observed at 1654.43, 1637.67 and 1637.68 cm⁻¹ were attributed to C=C stretching in aromatic nuclei. The bands obtained at 1600-1500 cm⁻¹ corresponds to C-H stretching in aromatic compounds. Absorption bands at 1476.12, 1489.67, 1490.77 and 1491.15 cm⁻¹ evidenced to C=N stretching in aromatic compounds. The polymer shows absorption bands at 1300-1200 cm⁻¹ which confirms the C-N stretching of primary aromatic amines. The absorption bands appeared at 1111.76, 1112.28, 1124.11 and 1137.65 cm⁻¹ reveals the C-H bending vibrations. The absorption bands lies below 1000 cm⁻¹ are the characteristics of mono substituted benzene. The same finding has been reported elsewhere [15, 16]. The absorption peaks at 1560 cm⁻¹ assigned to the quinoide structure does not revealed any significant changes for all polymer samples, that concludes that the polymers were prepared using di and tri basic acids. It has been reported that H₂SO₄ may interact with PANI by donating either hydrogen sulfate, HSO₄⁻ or sulfate, SO₄²⁻ anions as dopant anions. Many authors agreed that HSO₄⁻ dopant anions are present in PANI/H₂SO₄ [17, 18]. The Fig.1. (a) shows the oxidative

synthesis of polyaniline. Fig.1. (b), (c) and (d) shows the electrochemical synthesis of polyaniline. The spectrum shows some interesting peaks in electrochemical method due to complete polymerization of regular arrangement. When compared with oxidative method and electrochemical method the intensity of C=N stretching of polyaniline prepared 2V and 2.5V is found to be increased when compared to the samples prepared at 1.5V.

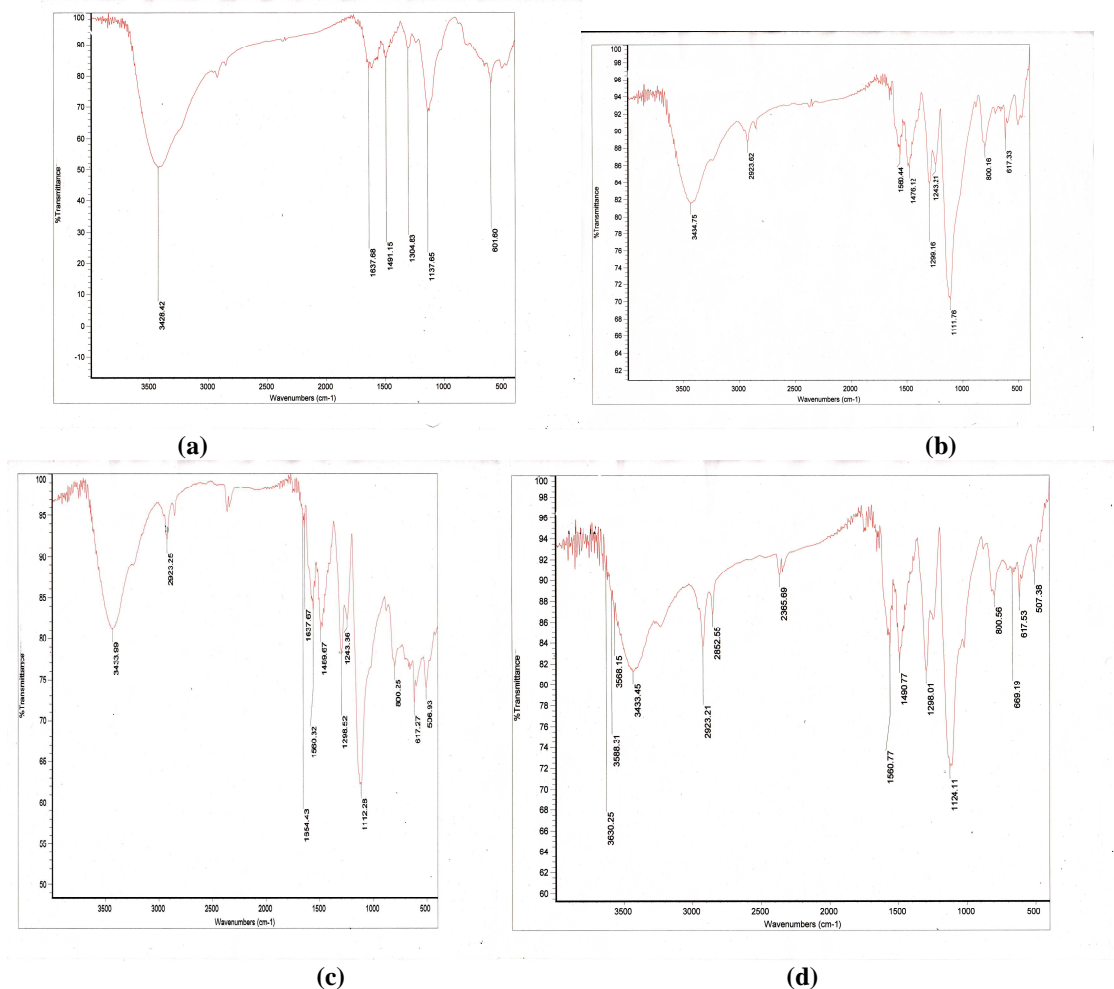


Fig.1. FT-IR Spectrum

3.3. UV-VIS spectroscopy

The UV-VIS spectra of the PANI synthesized with the use of $K_2Cr_2O_7$ in H_2SO_4 media in both oxidative and electrochemical are shown in Fig.2.

The band observed at 327-365 nm for the PANI samples corresponds to $n-\pi^*$ transitions of aniline. The broad bands at 600-620 nm is due to $n-\pi^*$ transitions of quinone-imine groups [19]. The Fig.2. (a) shows the oxidative synthesis of polyaniline. Fig.2. (b), (c) and (d) shows the electrochemical synthesis of polyaniline. When oxidative method compared with electrochemical method high intensity peak was obtained in electrochemical prepared PANI. When increasing the voltage, the absorption peak intensity also increases due to the regular arrangement of monomer units in electrochemical polymerization.

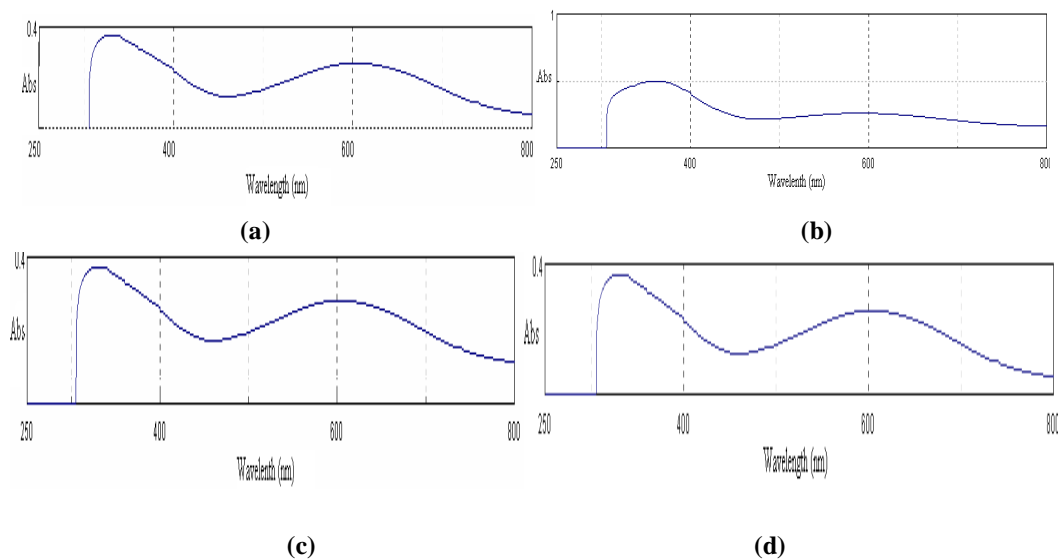
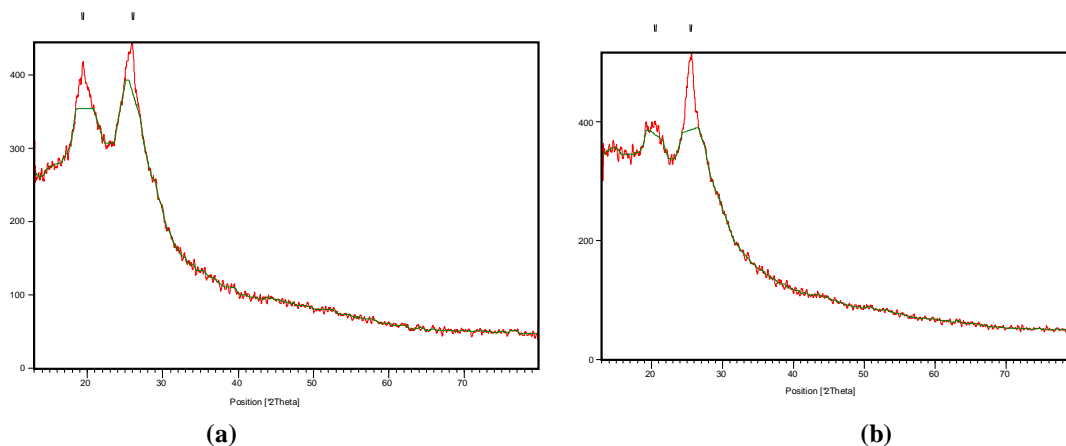


Fig.2.UV-VIS spectrum

3.4. X-ray diffraction

Crystallinity orientation of conducting polymer are of much interest, because more highly ordered systems could display a metallic property such as like conductive state. The X-rd pattern for PANI doped with H_2SO_4 in oxidative and electrochemical synthesis has been assessed are shown in Fig.3. It is clearly indicates that the intensity of observed peaks are better developed on the composites prepared using di and tri basic acid solutions compared with the monobasic acid. The profile of the characteristic peak of PANI at $2\theta \approx 25^\circ$ has the intensity order $H_2SO_4 > H_3PO_4 > HCL > HNO_3$ [20, 21]. Thus the fraction of crystalline phase found to be increased as increasing the voltages. The Fig.3. (a) shows the oxidative synthesis of polyaniline. Fig.3. (b), (c) and (d) shows the electrochemical synthesis of polyaniline. It clearly indicates that the intensity of the peaks is increased while increasing the applied voltage. Obviously, these differences clearly influence the crystalline properties of the prepared polymer by various voltages.



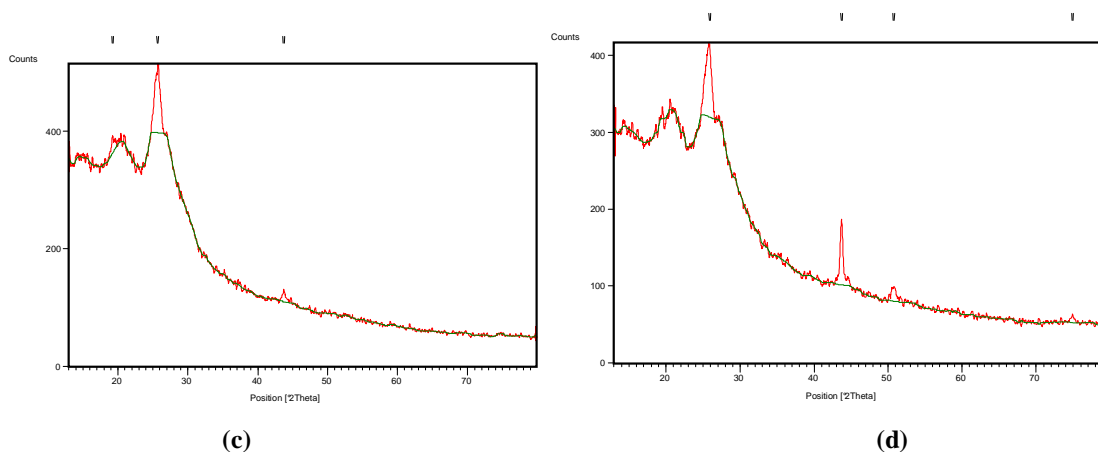


Fig.3. X-ray diffraction pattern

3.5. Electrical conductivity measurement

An electrical resistance R of the pellets was measured at room temperature using the four-point probe technique. The conductivity σ of the pellet can be given by [22].

$\sigma = 1 / (\pi / \ln 2) * R * d$ where $(\pi / \ln 2) R$ is the sheet resistance and d the thickness of the pellet.

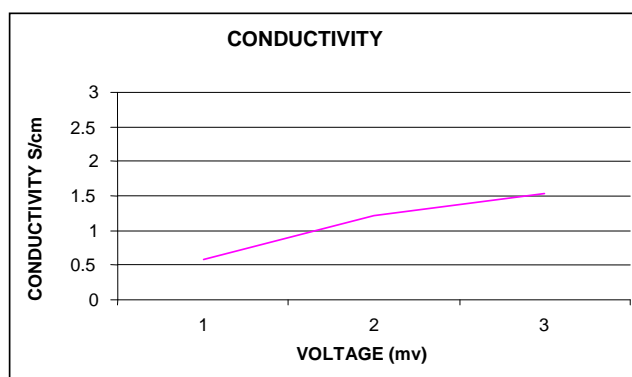


Fig.4. Electrical conductivity

Fig.4 shows the variation of conductivity with different voltages was measured by using the four point probe technique in the voltages 1.5, 2.0 and 2.5 respectively. The conductivity σ of the pellet was calculated by using the above equation. In Oxidative method, the conductivity of the prepared polymer pellets is 0.27 S/cm only, whereas in electrochemical method the conductivity found to be 0.58, 0.94 and 1.23 S/cm respectively. When increasing the voltages the conductivity was also increases. Thus compared to the oxidative method the electrochemical method has high conductivity because the regular arrangement of monomer units.

CONCLUSION

Our result shows the synthesized H_2SO_4 polyaniline is soluble in DMSO. The conclusions arrived from the studies are as follows. The synthesized polymers were characterized by UV-visible, FTIR and XRD spectroscopic techniques. The π - π^* transitions of aniline and/or anilium

radicals and $\pi - \pi^*$ transitions of quinone- imine groups were confirmed from the UV spectral studies. The FTIR analysis confirms the chemical structure of polyaniline. From the X-ray diffraction pattern, we can observe that the crystallinity gradually increases with increase in applied voltage. The conductivity of the electro chemical method at 1.5V is 0.58 S/cm and in oxidative method, the conductivity is 0.27 S/cm. This indicates when compared to oxidative method the electro chemical method of synthesis is more suitable. On increasing the applied voltage, the conductivity also increases. These results reveal that they are ideally suited for the manufacture of opto- electronic devices in the visible wavelength and could be used to photo voltaic applications. Further work in this direction will be highly useful for solar cell fabrication technology.

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