Journal of Applied Science and Engineering Methodologies
Volume.2, No.3, (2016): Page.317-321
www.scientistlink.com/jasem

Synthesis, Electro Chemical and Optical Performance of Organic Acids Doped Polyaniline (PANI)

M. REKA DEVI [a], A. SARANYA [b], J. PANDIARAJAN [b], J. DHARMARAJA [c], N. PRITHIVIKUMARAN [b], and N. JEYAKUMARAN [b*]

[A] DIVISION OF PHYSICS, FACULTY OF SCIENCE AND HUMANITIES, SREE SOWDAMBIKA COLLEGE OF ENGINEERING, CHETTIKURICHI, ARUPPUKOTTAI – 626 134, TAMIL NADU, INDIA.
*[B, *] NANOSCIENCE RESEARCH LAB, DEPARTMENT OF PHYSICS, VHNSN COLLEGE (AUTONOMOUS), VIRUDHUNAGAR – 626 001, TAMIL NADU, INDIA.*
[C] DIVISION OF CHEMISTRY, FACULTY OF SCIENCE AND HUMANITIES, SREE SOWDAMBIKA COLLEGE OF ENGINEERING, CHETTIKURICHI, ARUPPUKOTTAI – 626 134, TAMIL NADU, INDIA.
E–MAIL ID: bhavesh_2j2@yahoo.com

ABSTRACT

Conducting polymers have received much attention due to their unique thermal, electrical, optical, conducting, magnetic properties, easy to synthesis process and significant environmental stability. The wide range of electrochemical and optical properties of polyaniline (PANI) along with its excellent stability makes it useful for various applications like super capacitors, sensors, light emitting diodes, solar cells and rechargeable battery etc. In the present study, Its mainly focused to synthesis the conducting polymers of PANI by suitable chemical oxidation method i.e., the oxidation of aniline monomer using ammonium peroxy disulphide (oxidizing agent) along with three different organic acids dopant namely salicylic acid, benzoic acid and oxalic acid respectively. The synthesized PANI doped organic acids compound were structurally characterized by electrochemical and optical studies. The electrochemical characterization was performed by cyclic voltammetry and the optical properties were investigated by UV–vis., spectroscopy analysis. From the cyclic voltammetry analysis, the PANI compounds show well resolved oxidation and reduction peaks which indicate that the synthesized PANI was emeraldine salt form in nature. Moreover the UV–vis., absorption spectra show that the well defined absorption bands in three different organic acids doped PANI samples. Moreover, the obtained spectral studies indicate that the PANI compounds show significant applications in the field of electronic device fabrication.

KEYWORDS**:** *Conducting Polymer, PANI, Organic acids, Optical and Electro chemical studies.*

1. INTRODUCTION

For recent years, the conducting polymer have been widely employed in multidisciplinary areas like solar cells, batteries, electromechanical actuators, manufacture of sensors, nanowires, nanofibers, indicators and electrodes, diode and FET fabrications, Drug delivery in medicine, super capacitors, anti–noise devices, biocompatible wires, gas separation membranes, photodiodes [1-3] *etc*., due to its unique properties such as corrosion, stability, mechanical strength and high electrical conductivity. Among these, polyaniline (PANI) have been considered as one of the best conducting polymer because PANI possesses high electrical conductivity, mechanical and thermal stability, ease of synthesis process and better environmental stability, low cost synthesis and better productive coating against corrosions [4–6]. Also, PANI shows the wide range of electrical and electrochemical properties which makes it useful for electronic material for various applications like organic light emitting diodes, low power rechargeable batteries, fabricate integrated circuit, electromagnetic interference (EMI) shielding, smart window, conductive adhesives, electrochromic devices, gas sensors, supercapacitors, photovoltaic cells, liquid crystal displays and Schottky devices [7–13]. Generally PANI shows potential dependent changeable oxidation states namely pernigraniline (violet color, fully oxidized form), leucoemeraldine (white color, fully reduced form) and emeraldine (dark green or blue color, half oxidized form) [14]. Ammonium peroxy disulphide (APS) has been used as the oxidizing agent for the polymerization of polymer. For the synthesis of conducting PANI polymer, the chemical polymerization method is widely employed because it gives high yields and the obtained product is more stable than any other methods. In the synthesis process, the surface morphology, electrical as well as physical properties of conducting polymer are mainly depends on the type of acid dopant used in it. In this work, the three different organic acid dopants were used namely salicylic acid, benzoic acid and oxalic acid respectively because it shows more conductive and uniform adherent nature than inorganic acids [15]. However, the literature studies shows that little amount of attention has been paid to synthesis and applications of organic acids doped PANI compounds in various fields. In the present work, the synthesized Emeraldine salt form of PANI compounds by chemical oxidation method doped with different organic acid dopants (oxalic acid, Benzoic acid, and salicylic acid) and it was structurally characterized by electrochemical and optical studies and the results were also discussed.

2. EXPERIMENTAL METHODS

2.1 Materials and Analytical Measurements

The aniline and organic acids (oxalic, benzoic acid and salicylic acids) used in this work were extra pure analytical grade and purchased from Sigma–Aldrich and Fluka (Puriss) products without further purification. Triply distilled CO_2–free water with specific conductance equal to ($1.80 \pm 0.1\ \Lambda^{-1}\ cm^{-1}$) was used for the preparation of all solutions. The synthesized organic acids doped PANI compounds were structurally characterized by various spectral analyses. The electronic (UV–visible) spectra were measured on a Schimadzu 1800 UV – VIS – NIR spectrophotometer (cell length, 1 cm) in the range of 200–1100 nm at 310 K in DMF solvent. Cyclic voltammetric studies of organic acids doped PANI compounds were carried out at room temperature with a AUT 85670 electrochemical analyzer in DMF and NMP (N–methyl–2–pyrrolidone) solutions containing 0.1M $NaClO_4$ using a glassy carbon electrode at 100 mVs^{-1} scan rate. A Pt wire and saturated Hg_2Cl_2 electrode were used as counter and reference electrodes, respectively. Before each investigation, the electrolyte was purged with nitrogen for 8 min. Before each experiment the working electrode was cleaned perfectly by polishing with alumina and rinsed thoroughly with distilled water and acetone.

2.2 Polymerization Process

In the chemical oxidative synthesis route, 0.30 g of organic acids (salicylic, benzoic and oxalic acids in 50 ml water) was thoroughly mixed with 0.30 g of aniline (dissolved in 190 ml deionized water) and the resulting solution was stirred continuously at room temperature for 30 min. Afterword's, 10 ml of aqueous ammonium peroxy disulphate (1 mol / L) solution was added to the above mixed solution and the resulting solution was stirred for another 10–20 min for complete mixing. During this process, the solution color was noted, initially a golden color was observed and then dark brown color was observed after five min and finally the solution became as deep green in color. The reaction was then allowed to proceed without agitation for 24 hour at room temperature. Finally, the products were washed with deionized water and ethanol until the filtrate became colorless and then dried in air at room temperature. The compounds were obtained as powders, dried in air, and stored in *vacuo* over anhydrous $CaCl_2$ at room temperature (Yield: 70–85 %).

3. RESULTS AND DISCUSSIONS

3.1. Cyclic Voltammetry Analysis

The cyclic voltammetric studies were carried out for the organic acids doped PANI compounds at room temperature in DMF and NMP solutions containing 0.1 M $NaClO_4$ using a glassy carbon electrode in the potential range –3.5 to 3.5 V with a scan rate of 100 mv/s and its graphical representation is given in the Figure 1. From the figure 1, all the compounds show well defined oxidation–reduction responses which indicate that the organic acids doped PANI have electro active in nature [16]. The oxidation peak (Ep_a) for PANI doped with salicylic acid compound (Fig. 1a) shows at 0.1 V and the reduction peak (Ep_c) at 1.2 V which indicate that the appearance of conducting form of PANI (Emeraldine salt form) and also confirms the formation of fully doped form of PANI. Fig. 1b shows that the PANI doped with benzoic acid compound, the oxidation peak (Ep_a) was observed at 0.1 V and the reduction peak (Ep_c) at 1.5 V which indicate that the synthesised conducting PANI polymer compound behave as electro active in nature [17]. The PANI doped with oxalic acid compound (Fig. 1c) exhibits the anodic oxidation peak (Ep_a) at 0.3 V and the cathodic reduction peak (Ep_c) at 1.5 V which indicate that the formation of conducting PANI as Emeraldine salt form and also the obtained values are very similar to other reported values [18,19]. The oxalic acid doped PANI polymer show the low current and high voltage peak value which causes the decreasing resistance value and increasing conductivity than other compounds. The studies indicate that oxalic acid doped PANI Emeraldine salt compounds show appreciable electrochemical behavior in nature.

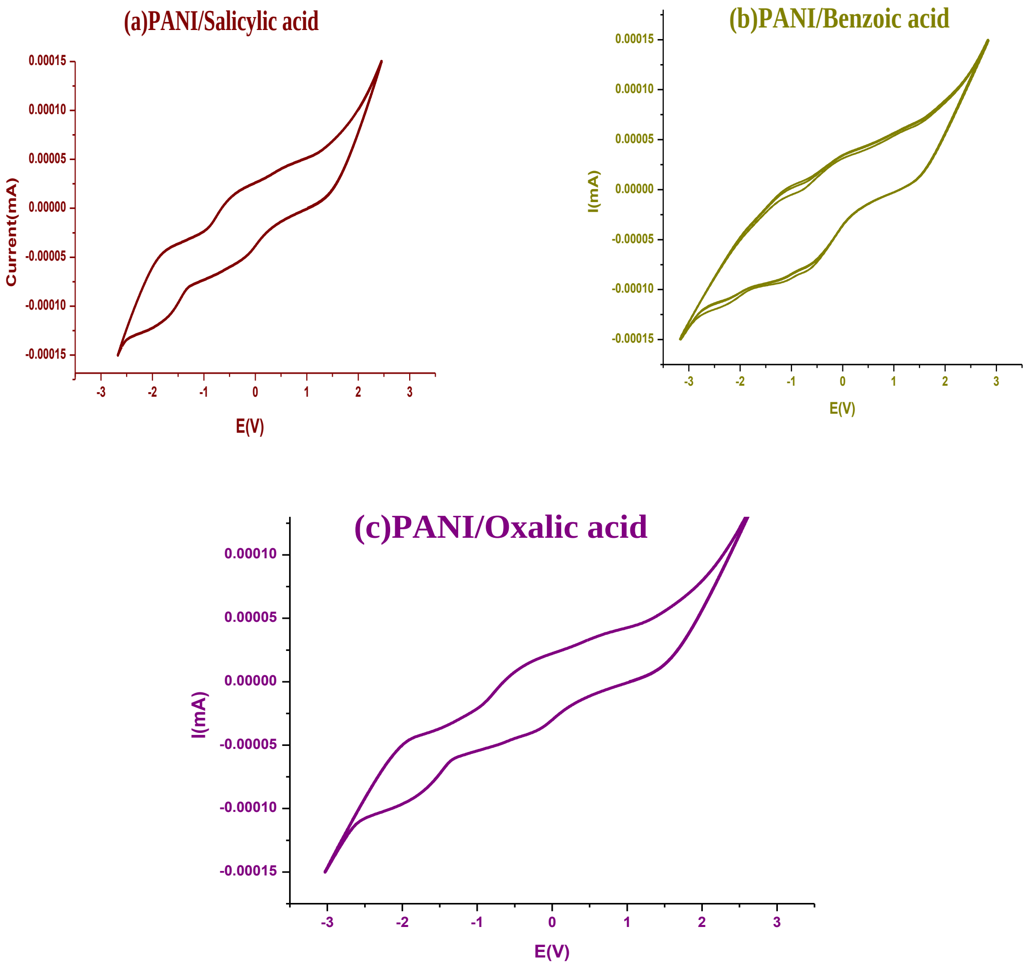

Figure 1: Electrochemical curves of PANI doped with (a) Salicylic, (b) Benzoic and (c) Oxalic acids respectively.

3.2. Electronic Absorption Spectra

The optical properties of the synthesized organic acids doped PANI compounds were determined from electronic absorption measurement in the range 200–1100 nm at 310 K in DMF solvent medium and their spectrum was depicted in Figure 2. The optical absorption spectra of PANI doped with salicylic, benzoic and oxalic acids show the absorption peak at 370, 375, 372 nm respectively, which indicates that the π–π* transition and this transitions was attributed to the electron transfer from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) [20–24] i.e., the blue region shift was observed in all the compounds. Moreover, the additional one more absorption peak was observed in all the compounds around in the region between 550-558 nm which indicate that the π–π* transitions of quinone–imine groups present in the conducting emeraldine salt in the polymeric compounds [25, 26].From the optical absorption coefficients (α) and incident photon energy (hν) can be correlated to the following equation as

$$\alpha = A(h\nu - E_g)^n / h\nu$$

Direct band gap (E_g) of the sample is evaluated by plotting $(\alpha h\nu)^2$ against $h\nu$ and then extrapolating the straight portion of the curve on $h\nu$ axis. The calculated band gap values are listed in Table 1. From Table 1, PANI doped with oxalic acid compound show low energy band gap value than other compounds. The energy band gap decreases with increasing doping agent because doping increases the conductivity of PANI. The similar band gap observations were made by H. S. Abdulla *et al* [27].

Table 1: Energy band gap values of organic acids doped PANI compounds

Compounds	Energy band gap value (eV)
Salicylic acid	2.54
Benzoic cid	2.01
Oxalic acid	1.62

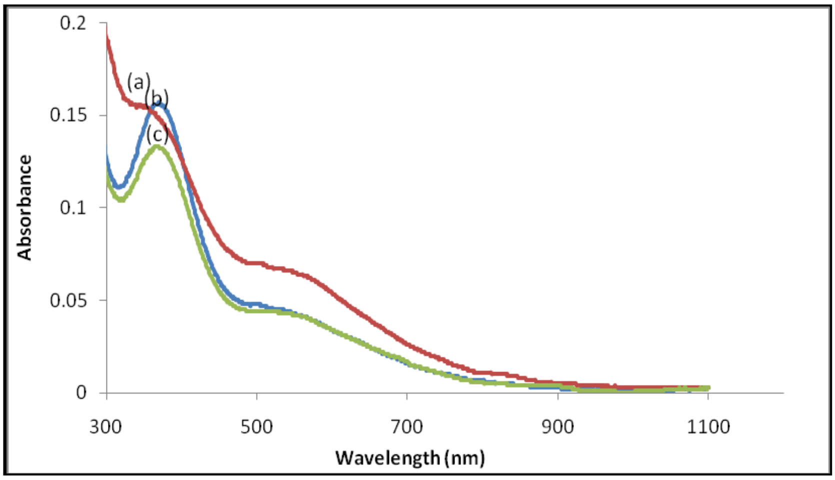

Figure 2: Electronic absorption spectra for PANI doped with (a) Oxalic, (b) Benzoic and (c) Salicylic acids respectively.

4. CONCLUSIONS

In this work, the Emeraldine salt form of PANI were synthesized from aniline (monomer) with three organic acids like salicylic, benzoic and oxalic acids (dopent) by chemical oxidative polymerization method in the presence of ammonium peroxydisulphate (oxidant). The synthesized polymeric compounds were structurally characterized by cyclic voltammetric and UV–visible spectral techniques. From the CV analysis, all the compounds show well resolved oxidation and reduction peaks which indicates low resistive and high electro conducting nature. Furthermore, the PANI doped with oxalic acid shows low energy band gap values which indicate high electrical conductivity than other compounds. From these spectral studies, It is conclude that the synthesized PANI doped with oxalic acid emeraldine salt can act as a significant role in electronic device fabrication.

ACKNOWLEDGEMENT

The authors communicate their sincere thanks to the Managing Board, Principal and Head of the Department of Physics, VHNSN College (Autonomous), Virudhunagar and Sree Sowdambika College of Engineering, Aruppukottai for providing research facilities, moral support and constant encouragement throughout this investigation.

REFERENCES

[1] R.H. Baughman, L.W. Shacklette, in: Science and Applications of Conducting Polymers, Eds. W.R. Salaneck, D.T. Clark, E.J. Samuelsen, Adam Hilger, Bristol 1991, p. 47; T.F. Otero, J. Rodriguez, in: Intrinsically. Conducting Polymers: An Emerging Technology, Ed. M. Aldissi, Kluwer Academic Publishers, Dordrecht 1993.

[2] T.A. Skotheim, R.L. Elsenbaumer and J.R. Raynolds Eds., *Handbook of Conducting Polymers,* Marcel Dekker, New York, 1998.

[3] M.R. Anderson, B.R. Mattes, H. Reiss, R.B. Kaner, Synth. Met. **41**, 1151 (1991).

[4] W.Li . and M.Wan : Synth. Met., 1998, **92**,121.

[5] X. Jing , X. Wang, Y. Geng. *et al*.: Synth. Met., 1995, **69**, 265.

[6] E.Genies , A.Boyle , M. Lapkowski and C.Tsintavis : Synth.Met., 1990, **36**, 139.

[7] H.L. Wang, A.G. MacDiarmid, Y.Z. Wang, D.D. Gebler, A.J.Epstein, Synth. Met. (1996), **78**, 33.

[8] L. Ding, M. Jonforsen, L.S. Roman, M.R. Andersson, O. Inganas,Synth. Met. (2000), **110**, 133.

[9] S.A. Jenekhe, K.J. Wynne (Eds.), Photonic and Optoelectronic Polymers, ACS Symposium Series, American Chemical Society, Washington, DC, (1997), **672**, 395.

[10] A.G. MacDiarmid, Photonic and optoelectronic polymers, Naval Research Reviews, Office of Naval research, Two/1997, vol. **XLIX**, 6–11.

[11] S.S. Pandey, M.K. Ram,V.K. Srivastava, B.D. Malhotra, J. Appl. Polym. Sci. (1997), **65**, 2745.

[12] S.S. Pandey, C.K. Misra, S. Chandra, B.D. Malhotra, J. Appl. Polym. Sci. (1992) ,**44,** 911.

[13] H.K. Chandhari, D.S. Kelkar, J. Appl. Polym. Sci. (1996), **61**, 561

[14] K. Lakshmi, H. John, K.T. Mathew, R. Joseph, K.E. George, Acta Mater., (2009), **57(2),** 371.

[15] D.A. Kaplin, S. Qutubuddin, *Polymer*, (1995),**36**, 1275.

[16] J.G.Masters, Y.Sun, A.G.Macdiarmid and A.J,Epstein,Synth.met (1991),**41**,715.

[17] A. Mirmohseni, G. G. Wallace, Polymer 2003, **44**, 3523.

[18] R. Montazamia, V. Jain, J. R. Heflinc, Electrochimica Acta (2010)**56**, 990–994

[19] *A. Arslan, E. Hür Int. J. Electrochem. Sci.,* (2012)**,7,** 12558– 12572

[20] S. L. mu. Y. kong and J. wu. Chinese journal of polymer science,(2004), **22**,405–415.

[21] R.Khan, and M. Dhayal, Chitosan/Polyaniline Hybrid Conducting Biopolymer Base Impedimetric Immunosensor to Detect Ochratoxin–A. *Biosensors and Bioelectronics*, (2009),**24**, 1700–1705.

[22] A.A.Ansari, R.Khan, K.N.Sood, and B.D.Malhotra. Polyaniline–Cerium Oxide Nanocomposite for Hydrogen Peroxide Sensor. *Journal of Nanoscience and Nanotechnology*, (2009),**9**, 4679–4685.

[23] A. Kaushik, R. Khan, V. Gupta, B.D. Malhotra, and S.P. Singh, Hybrid Cross Linked Polyaniline–WO3 Nanocomposite ,Thin Films for NOx Gas Sensing. *Journal of Nanoscience & Nanotechnology*, (2009),**9**, 1792–1796.

[24] A. Kaushik, J. Kumar, M.K.Tiwari, R. Khan, B.D. Malhotra, V.Gupta, and S.P.Singh, Fabrication and Characterization of Polyaniline–ZnO Hybrid Nanocomposite Thin Films *Journal of Nanoscience & Nanotechnology*, (2008),**8**,1757–1761.

[25] V.Chabukswar, S.Bhavsar , CHEMISTRY & CHEMICAL TECHNOLOGY, (2010),**4**,4 .

[26] A.B.P. Lever, *Electronic spectra of* d^n *ions in Inorganic Electronic Spectroscopy*, 2nd Edn, Elsevier, Amsterdam, The Netherlands (1984).

[27] H. S. Abdulla and A. I. Abbo, *Int. J. Electrochem. Sci.,* (2012), **7**, 10666 - 10678.