International Journal of Current Advanced Research
ISSN: O: 2319-6475, ISSN: P: 2319-6505, Impact Factor: 6.614
Available Online at www.journalijcar.org
Volume 7; Issue 7(G); July 2018; Page No. 14323-14325
DOI: http://dx.doi.org/10.24327/ijcar.2018.14325.2593

Research Article

A COMPARATIVE STUDY ON THE DC CONDUCTIVITY AND OPTICAL PROPERTIES OF POLYANILINE SYNTHESIZED IN DIFFERENT GREEN SOLVENTS

Smitha T.R[1]., Mamta Binoy[2] and Prema K.H[2]

[1]Department of Chemistry, T.K.M.M.College, Nangiarkulangara, Kerala, India
[2]Department of Chemistry, S.D.College, Alappuzha, Kerala, India

A R T I C L E I N F O

Article History:

Received 7th April, 2018
Received in revised form 16th May, 2018 Accepted 3rd June, 2018
Published online 28th July, 2018

Key words:

Green method, Conducting polymers, Polyaniline

A B S T R A C T

In recent years, the development of efficient green chemistry methods for the synthesis of nano particles has become a major focus of researchers. Green synthesis focuses on minimizing the hazard and maximizing the efficiency of any chemical choice. In this work polyaniline (PANI) was synthesized in various green solvent and conventional solvent HCl. The prepared samples were characterized by Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction (XRD), Thermogravimetry (TG), Scanning Electron Microscopy (SEM), Ultra Violet (UV) analysis and Conductivity studies. The results indicated that the green solvent tamarind juice is more effective for the synthesis of thermally stable emeraldine form of PANI and is competitive in properties with the sample prepared in conventional solvent HCl.

INTRODUCTION

Conducting polymers are polymeric materials with metallic and semiconductor characteristics, a combination of properties not exhibited by any other known material (Elsayed A. H., 2011). These are suitable for the manufacture of electrically conducting yarns, antistatic coatings, electromagnetic shielding and flexible electrodes (Jakeer Husain *et.al*, 2014). They have drawn attention in the development of biosensors (Farghali *et.al*, 2010). Among the conductiong polymers polyaniline is the material of choice for many applications. Ease of synthesis, solubility, high chemical and thermal stability suggests its significant potential technological applicability (Ersel Ozkazanc *et.al*, 2011). It has been found that polyaniline exists in three isolable oxidation states – Leucoemeraldine (fully oxidized), emeraldine (half oxidized) and pernigraniline (fully reduced) (Gordon G. *et.al*, 2009). Among these emeraldine is the only conductive form of polyaniline (Ersel Ozkazanc *et.al*, 2011). Electronic properties of this organic polymer debt to conjugated π-electrons present on its backbone (A.R.Subrahmanyama *et.al*., 2012). The conductivity of these materials can be tuned by chemical manipulation of the polymer backbone, by the nature of the dopant, by the degree of doping, pH of the solvent and by blending with other polymers (Gomes E. C.and Oliveira M. A. S., 2012). Recently, significant scientific and technological interest has been focused on green method of synthesis of nanoparticles.

Corresponding author:* **Smitha T.R
Department of Chemistry, T.K.M.M.College, Nangiarkulangara, Kerala, India

Utilization of natural resources in place of laboratory chemicals has great importance in the present environmental situations. In this study we focused on synthesis of polyaniline by oxidative chemical polymerization method (Parinitha and Venkateshlu, 2013) in green solvent tamarind extract, lemon extract and distilled water and the properties of the samples are compared with the sample synthesized in conventional solvent HCl.

Experimental

All the chemicals used for the synthesis of polyaniline such as aniline, HCl and acetone were purchased from Merck chemical company and ammonium peroxydisulphate (APS) from spectrochem and all are of high purity. Aniline is used after double distillation. Tamarind extract and lemon extract at pH ≈ 2 is prepared in distilled water.

Aniline hydrochloride solution is prepared by dissolving aniline in 100ml 1MHCl solution. To this 100ml APS solution is added drop wise with continuous stirring at 0-5^{o}C (monomer/oxidant ratio=1:1.25). The reaction mixture kept overnight for complete precipitation. The resulting product is filtered and washed with distilled water and acetone to remove any unreacted aniline monomer. The green coloured precipitate of polyaniline is then dried in an air oven at 50^{o}C. The same procedure is repeated for preparing samples using different solvents.

The phase analysis of the samples was carried out using Rigaku D max-B model X-ray diffractometer using Cu Kα radiations, the FTIR spectra was recorded on a Thermo Nicolate Avatar370 (Model) spectrophotometer in KBr medium in the region 4000-400 cm^{-1} having DTGS detector,

SEM analysis of the samples is done with the SEM make JEOL Model JSM-6390LV, TGA studies are carried out on a Perkin Elmer STA 6000 model TG analyzer, conductivity of the sample was measured by a Keithley2001 multimeter and the optical properties by Shimadzu UV-VIS spectrophotometer (UV 2600).

RESULTS AND DISCUSSION

Samples are designated as P1, P2, P3 and P4 for the solvents HCl, lime extract, water and tamarind extract respectively.

X-ray diffraction

Figure 1 depicts the X-ray diffractogram of the samples prepared in different solvents. The broad peak observed at 2θ value around 20^0 and 25^0 (110) in the XRD pattern ensures the formation of PANI in the most conductive emeraldine base form in all the solvents. Broad peaks indicate low crystallinity of the sample which is due to the repetition of benzenoid and qunonoid rings (Senthilkumar *et.al*.,2013).

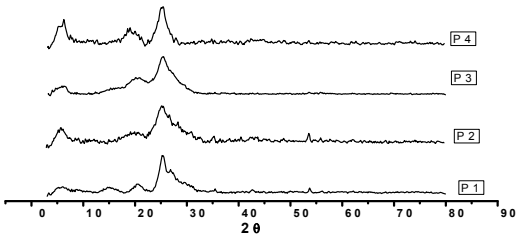

Fig 1 IR spectra of PANI prepared in different solvents. P1) HCl, P2) Lime, P3) Water, P4)Tamarind extract

FTIR

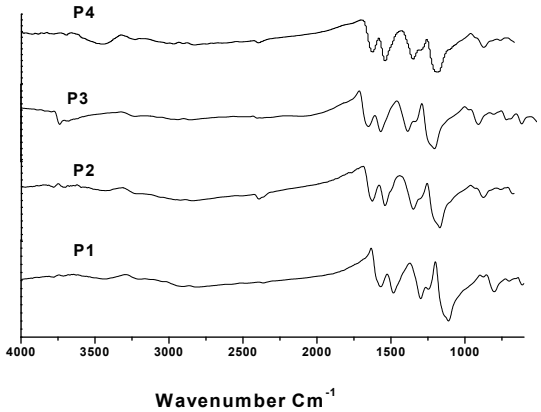

Fig 2 IR spectra of PANI prepared in different solvents. P1) HCl, P2) Lime, P3) Water, P4)Tamarind extract.

IR spectrum of the samples P1, P2, P3 and P4 are shown in Figure 2. FTIR spectroscopy has provided valuable information regarding the formation of polyaniline. All the samples prepared using various green solvents has been given the absorption bands at around 1569, 1485, 1292, 1111 and 798 cm^{-1} as in the case of conventional solvent HCl which confirms the formation of polyaniline in green solvents. The bands appear at 1485 and 1569 cm^{-1} corresponding to C=C stretching vibrations of N-B-N (benzenoid) and N=Q=N (qunanoid) structures respectively. The presence of these absorption bands confirms the formation PANI in the most conductive emeraldine form in all the solvents. Absorption band at 798 cm^{-1} is due to out of plane bending vibration of C-H bond of 1,4- disubstituted benzene ring which confirms the conjugated π system present in PANI. A strong band appears at 1110cm^{-1} has been explained as an electronic or a vibrational band of nitrogen quinone, an inplane bending vibration of imino-1,4-phenylene, and has been reported to be associated with the electrical conductivity of PANI(L.Li *et al*., 2007). This also ensures the protonation of the NH group in the PANI chain. The broad band observed at 3435 cm^{-1} is due to N-H stretching.

Thermal analysis

The results of TGA of all the four samples are depicted in Figure 3. Generally PANI shows three stage degradation processes. The first stage is due to the loss of moisture, which ends at 139^0C. The second one starts at around 153^0C and ends at around 295^0C and is due to the dopant evolution and the final one in the range of 342-689^0 C which is due to the degradation of PANI chain. About 70% of the weight loss occurs during this degradation. From TG curves it is found that all the samples prepared using green solvents are thermally stable and give the same degradation temperatures in the characteristic regions as in the case of conventional solvent.

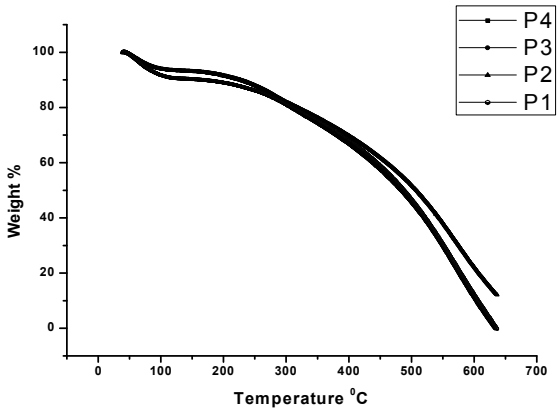

Fig 3 TGA curves of PANI prepared in different solvents. P1) HCl, P2) Lime, P3) Water, P4)Tamarind extract.

Scanning Electron Microscopy

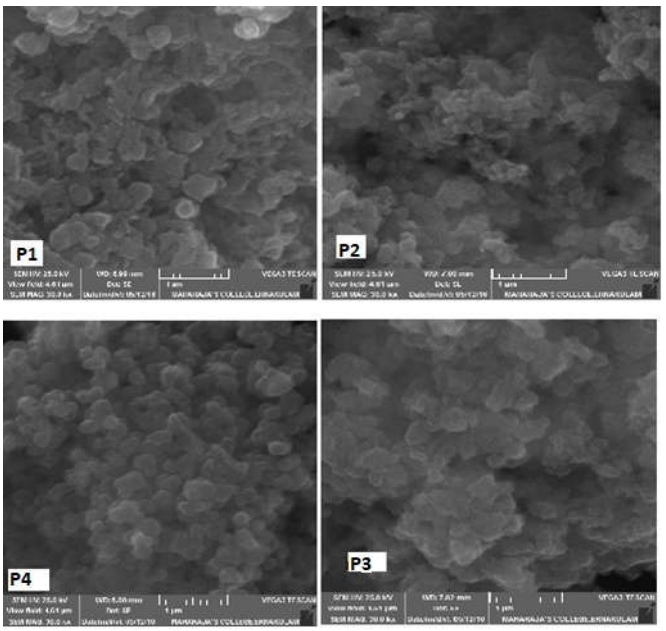

Fig 4 SEM images of PANI prepared in different solvents at K 30000 magnification. P1) HCl, P2) Lime, P3) Water, P4) Tamarind extract.

The surface morphology of the samples was studied using scanning electron microscope and is represented in figure 4. As shown in the images the size and homogeneity of the particles are dependent on the type of the media of preparation because the solvent affects the rate of polymerization. Better

homogeneity is observed in P4 compared to P1. Spherical particles with an average particle size of about 200nm are found to be uniformly distributed. Surface morphology has great role in many of the properties of PANI.

DC Electrical Conductivity

The DC conductivity of the samples are calculated by the equation σ(S/cm) = (I/V)x(*l*/A) where I/V = 1/R the slope of the I-V graphs, *l* is the spacing between the probes in centimeters and A is the area of contact of the probes with the sample in centimeter square. The conductivity values are tabulated in Table 1.

Table 1 Conductivity values of PANI in different solvents. P1) HCl, P2) Lime, P3) Water, P4) Tamarind extract.

Sample	Conductivity S/cm^{-1}
P1	5.019×10^{-4}
P2	9.231×10^{-6}
P3	6.516×10^{-6}
P4	1.184×10^{-4}

All the samples found to have conductivity values in the semi conducting region. Conductivity of the samples prepared in HCl and tamarind medium are of the same order and are hundred times greater than for the samples from other green solvents (p2 and P3). From this tamarind juice can be selected as a better green solvent for the preparation of PANI.

Optical properties

The absorption spectrum of all the samples is given in Figure 5. In all the samples three absorption peaks in the range 310-330, 607-609 and 654-659nm are observed.

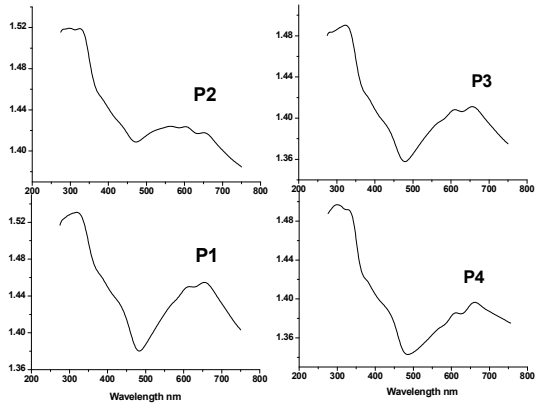

Fig 5 UV-Visible Spectra of PANI in different solvents. P1) HCl, P2) Lime, P3) Water, P4) Tamarind extract

The band observed at 327-365 nm corresponds to n-π* transitions of aniline and the broad bands at 600-620 nm is due to n-π* transitions of quinine-imine groups. These two characteristic peaks are observed in all the four samples. The intensity of the absorption bands is sensitive to the conformation and conjugation length of polymer chain. The spectrum of samples using tamarind extract gives a close agreement to that of conventional solvent HCl.

CONCLUSIONS

In this work, PANI is synthesized using green solvents and conventional solvent HCl and the prepared samples are characterized by FTIR, XRD, TG, SEM and UV analysis. The FTIR and X-ray diffraction analysis proved that all the samples prepared in different media are resulted in the most conductive emeraldine form of PANI. TG analysis infers that thermal stability of the green solvent samples is in par with the conventional solvent HCl. The SEM images show that solvent has considerable effect on the morphology. Well homogeneity of the particles is observed for PANI prepared in tamarind medium. DC conductivity studies show that the sample using tamarind juice has almost the same conductivity value to that prepared using HCl. UV spectrophotmetric studies reveal that UV absorption bands are not affected by the medium of preparation. Thus we can conclude that all the green solvents used are effective for the synthesis of thermally stable emeraldine form of PANI and among those tamarind juice is the most efficient as it is competitive in conductivity with the sample prepared using the conventional solvent HCl. Thus naturally available tamarind juice can be strongly recommended for the synthesisof PANI.

Acknowledgements

We thank KSCSTE, Thiruvananthapuram, for the financial support of the conduct of the project and Department of Physics, S.D.College, Alappuzha and SAIF, CUSAT, Cochin, for the analysis.

References

Elsayed A. H., Mohy Eldin M. S., Elsyed A.M., Abo Elazm A. H. , E.M.Younes and H. A. Motaweh, 2011, Synthesis and Properties of Polyaniline/ferrites Nanocomposites, *Int. J. Electrochem. Sci*., 6, 206 - 221.

Ersel Ozkazanc, Sibel Zor, Hatice Ozkazanc and Ufuk Abaci, 2011, Electrical properties of polyaniline-manganese chloride cimposites, *J.Poly. Eng. And Sci*., 616-623.

Farghali A.A., Moussa M and Khedr M.H., 2010, Synthesis and characterization of novel conductive and magnetic nano composites, *J. Alloy and Comp*, 499, 98-103.

Gomes E. C.and Oliveira M. A. S.,2012, Chemical Polymerization of Aniline in Hydrochloric Acid (HCl) and Formic Acid (HCOOH) Media. Differences Between the Two Synthesized Polyanilines, *American Journal of Polymer Science,* 2, 5-13.

Gordon G.Wallace, Geoffrey M.Spinks, Leon A.P.Kane-Maguire and Peter R.Teasdale, 2009,Coductive Electroactive Polymers: intelligent polymer systems, 3rd ed.,Taylor & Francis.

Jakeer Husain, Chakradhar Sridhar B.and M.V.N.Ambika Prasad, 2014, Synthesis, Sensing and Magnetic properties of Polyaniline/Nickel Oxide Nano Composites, *Int.J.Adv.in Eng.& Tech*., 7, 620-626.

Liangchao Li, Jing Jiang and Feng Xu, 2007, Synthesis and Ferrimagnetic properties of novel Sm-substituted LiNi ferrite- polyaniline nanocomposite*, J.Materials Letters*, 61, 1091-96.

Parinitha M and Venkateshlu A, 2013, Dielectric and Ac conductivity studies of vanadium pentoxide doped polyaniline composites*, Int.J.Eng.and Sci*.2,45-50.

Senthilkumar B., Vijaya Snkar K.,Sanjeeviraja C. and Kalai Selvan R., 2013, Synthesis and physico chemical property evaluation of PANI-NiFe2O4 nano composite as electrodes for super capacitors*, J.Alloys and Compounds,* 553, 350-357.

Subrahmanyama A.R, Geetha V., Atul kumarb, Alakanandanac A. and Siva Kumar J., 2012, Mechanical and Electrical Conductivity Studies of PANI-PVA and PANI-PEO Blends, 2, 27-30.