STRUCTURAL CHARACTERIZATION OF POLYANILINE

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Abstract

Conducting Polyaniline has been prepared with chemical oxidative polymerization method. In this work K₂Cr₂O₇ has been used as an oxidant which helps in the polymerization of the conducting polyaniline. The various characterization techniques like X-ray diffractometry (XRD), Fourier Transform Infrared (FTIR) Spectroscopy have been used to analyze the structure of polyaniline. These characterizations have been done for the conformation of emeraldine salt formation of polyaniline. Emeradine salt form of polyaniline also physically distinguished with the appearance of green colour when it was protonated with the acidic dopant. Therefore, 1M HCl was used during the synthesis of polyaniline.

Keywords: Polyaniline, Pot.dichromate (K₂Cr₂O₇), chemical oxidative polymerization, Hydrochloric acid.

Introduction

Polymers are well known for their class of sensitivity of heat, flexibility, and insulating nature of folded polymeric chains (Mostafaei et al., 2012). It was the great surprise for the scientific community when conducting polymers replace the metal in various materials application. The exploitation of properties of conducting polymers changed the world. The conducting polymers perform as unique candidates for number of applications like sensors, electromagnetic interference shielding, corrosion and super-capacitors etc. The versatility of material in these applications is due to the matrix incompatibility, weight and integrality of the environment (Kumar et al., 2016). Along with light weight material, resistant in corrosion other properties were also made-to-order for development. There are number of conducting polymers which exist like polypyrrole, PEDOT: PSS, polyfluorenes, polythophene (Song et al., 2013; Sharma et al., 2015, 2016, 2017, 2018; Kumar et al., 2010, 2013, 2014, 2015, 2019). The electrically conducting polymers were initially exposed in 1976. In 1970s, polyacetylene was the chief conducting polymer which was accidentally prepared by the scientist Shirakawa. In 1976, three scientists Hideki Shirakawa, Alan MacDiarmid and Alan Heeger, collectively worked on polycetylene (PA) for their electrical property. They have improved the electrical conductivity up to the six orders of magnitude when it was treated with reluctant iodine. It was found that the conductivity were improved from 10⁻⁴ S/cm to 10² S/cm. It was the great change in the electrical conductivity. This phenomenon of improvement in conductivity with reductant is known as doping. Among all these conducting polymers polyaniline has the greater kind of attraction due to ease of processibility, environmental stability, less expensive and processibility. In consort with these qualities of polyaniline its morphology is also very attractive. It exists in granular, fibrillar, both granular and fibrillar, tube and rod form. These types of morphology tuned the property in better ways which are helpful in the application part.

The different structures of polyaniline have unlike stabilities, shades and electrical conductivity. It is well known that Leucoemeraldine has no colour as described through absorption spectroscopy (absorption band at 343 nm) in N-methylpyrrolidone (NMP) solvent (Mudila et al., 2018, 2019, 2016, 2018; Boeva et al., 2014; Kumar et al., 2018). Meanwhile this material comprises merely amino groups and benzene; it gradually oxidizes in air and existing as insulating polymer. It is expected that Leucoemeraldine might be oxidized in medium (merely acidic) to the electrically conducting emeraldine salt (ES). The second existing structure i.e Pernigraniline is made up of irregular amino-benzene along with quinone-dimine trashes. For the reason that the quinone-dimine is not stable in the company of pernigraniline nucleophiles and specifically water its salts forms freely go moldy in presence of air. The ES form of polyaniline is shaped during the protonation of the EB (emeraldine base) with acids like organic and inorganic. When polyaniline in the state of EB is cured by means of acids, protons mainly cooperate by the imine atoms of N; therefore, gives an impression of pol-cation. Since charges (positive) confined on adjacent N atoms rise the energy of polymeric structure, the density of electron inclines to undergo reorganization (Kumar et al. 2017).

Materials and Methods

Reagents and chemicals

Chemicals Used: Aniline, HCl and Potassium dichromate (K₂Cr₂O₇), Polymethylmethacrylate, ethanol, petridish containing Mercury, dichloromethane (DCM).

Synthesis of polyaniline (PANI)

Chemicals Used: Aniline, HCl and Potassium dichromate (K₂Cr₂O₇) Add 5.0 millilitre of aniline monomer into 100 millilitre of aqueous hydrochloric acid (1M). Then, stir the solution so that solution gets dissolve completely. Now, place the solution in ice bath at 0 degree temperature. Then, add the solution of K₂Cr₂O₇ dropwise for half an hour. On addition, dark suspension of aniline changes its colour into green. Now place the solution at 20 degree for 24 hour. Then, filter the reaction solution using wattman paper and washes with 1M HCl solution. Now dry the materials at 50°C in the oven. PANI is formed in a green powder form.

Results and Discussion

X-ray diffractometry

Figure 1 shows X-ray pattern of polyaniline prepared by Rxⁿ. The figure indicates that the chains are strongly
disordered. Two broad peaks were observed at around 2θ of 20° and 25°. These can be assigned as the (020) and (200) reflections of PANI in its emeraldine salt form. Polyaniline displays merely a peak at 2θ = 25° which indicate the semicrystalline nature of the polymer (Figure 1) (Shaban et al. 2018; Kumar et al. 2017).

**Fig. 1**: X-Ray Diffraction pattern of PANI

### FT-IR spectra

It has been observed from figure 2 that there are six principal absorptions band at 1504, 1482, 1306, 1245.9, 1148 and 803 cm⁻¹ which correspond to the formation of polyaniline. The intense peaks observed at 1482 and 1504 cm⁻¹ are corresponding to the stretching vibration of C-C ring. It has also been found that the peaks 1245.9 cm⁻¹ and 1306 cm⁻¹ relate to symmetric component of the C-C and N-H bending (or C-N) stretching modes. The bands which have been observed at 803 cm⁻¹ and 1148 cm⁻¹ accredited to the out-of-plane and in-plane C-H bending modes, respectively (Figure 2).

**Fig. 2**: FTIR Spectra pattern of PANI

The peak of polyaniline emeraldine salt also displays about 3460 cm⁻¹, 1653 cm⁻¹, 684 cm⁻¹. The observed band at 3460 cm⁻¹ may possibly be credited because of the stretching mode of NH₂ however the peak at 1653 cm⁻¹ correspond to the NH₂ vibration (bending). The wagging for NH₂ is explained by the 684 cm⁻¹ band. The conducting structure of PANI is also explained by the band detected nearly 1246 cm⁻¹. It understood that bi-polaron structure for conducting PANI assigned for stretching vibration of C-N. The observed band at 1580 cm⁻¹, authorizes the occurrence of imine in protonated form. The peak observed at 590 – 700 cm⁻¹ expose the stretching peak for C-Cl. (Puthirath et al. 2015; Palaniappan et al. 2008).

### Conclusions

PANI has been successfully prepared by oxidative polymerization method in aqua medium. The synthesized conducting polyaniline was characterized by using XRD and FTIR spectroscopy. X-ray reveals that prepared material has the semi-crystalline nature. The oxidant K₂Cr₂O₇ was used for the oxidation purposes which assist in the polymerization of the polyaniline.

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