Characterisation of PPY/$CECl_3$ Composite Synthesized By Simple Chemical Polymerization Method

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Abstract

Organic conducting polymers and their composites have become increasingly important for technical applications and the use of organic or inorganic fillers (dopants or composites) can prepare a new polymeric material with interesting combinations of physical mechanical and electrical properties. Among all organic conducting polymers polypyrrole is one of the most promising material for multifunctionalised applications.This contribution deals with structural modification of polypyrrole by doping it with rare earth metal salt $CeCl_3$ to study its dynamic physical, mechanical and electrical conducting properties. The conducting PPy/ $CeCl_3$ composite was synthesized by chemical oxidative polymerization method in aqueous media with ammonium peroxydisulphate as an oxidant at low temperature.The monomer to oxidant ratio was 1:1M. The concentration of $CeCl_3$ was varied from 0.01-0.2. All the composite samples were characterized through FTIR/NMR/Mass analysis. IR result show that interaction exist between PPy and $CeCl_3$.

Key words: pyrrole, ammonium peroxydisulphate, Polypyrrole, triply distilled water etc.

Introduction

The discovery of electronically conducting polymers offers a promise to open many new applications for polymeric material. An advantage of the conducting polymers is that they can be synthesized and processed on a large scale at relatively low cost. These polymers have become the subject of increased research interest due to a great variety of applications in many fields such as electrochromism, electroluminescence, sensors, energy storage devices and solar cells etc.[1-2]

Among these polymers special interest has been focussed on Polypyrrole (PPy) due to its excellent thermal and environmental stability. It has excellent mechanical, electrical and optical properties. It is generally regarded as one of the conducting polymer with the high potential in commercial applications.[8] For the commertial use of this conducting polymer, a complete understanding of its properties is necessary. The conducting properties of PPy are not only depend upon nature ,concentration and oxidation state of dopant but also on doping level with type and concentration of different types of oxidant used. The properties of the polymers can be modified by adding various concentrations of different types of dopant to their structure.[3-5]

In this present research work conducting polymer PPy/ $CeCl_3$ composite was synthesized through chemical oxidative polymerization route by using ammonium peroxydisulphate as an oxidant at low temperature.The monomer to oxidant ratio was 1:1M. The concentration of $CeCl_3$ was varied from 0.01-0.2 M. All the composite samples were charactrised through FTIR analysis.

Experimental Methods

All the chemicals required in the present work like monomer pyrrole, oxidizing agent, ammonium peroxydisulphate and dopant $CeCl_3$ heptahydrate are of A.R.Grade. PPy/ $CeCl_3$ composite was synthesized by simple chemical oxidative polymerization method. The aqueous solution of 0.1 M Ammonium peroxydisulphate was prepared. To this solution 0.2 M aqueous solution of dopant $CeCl_3$ was added with constant stirring. After a vigourous stirring at 5^0 C drop by drop 0.1 M solution of monomer pyrrole was added. It was observed that as soon as monomer solution was added the colour of reaction mixture changes instantaneously and the solution becomes dark green/black in colour. The reaction was carried out at 5^0C. There was an increase in temperature of solution during the reaction was carried out, This was an indication of exothermic reaction. The reaction was stirred for few hours on magnetic stirrer which gives rise to formation of precipitate of polymer composite. This reaction mixture was allowed to stand for 24 hours in order to complete polymerization process. The resulting product was vacumm filtered. The precipitate was washed with copius amount of triply distilled water. Until the washing was clear. The polymer composite was dried in dessicator and again dried in an oven at 40-50^0 C. The synthesized product was further characterized by FTIR Aanalysis.

Result and Discussion

The FTIR Spectrum of PPy ,PPy/0.01 M $CeCl_3$ and 0.2 M $CeCl_3$ are shown in following fig. The FTIR analysis was used to confirm PPY/$CeCl_3$ composite formation. In FTIR spectrum characteristic six principle bands are observed at 3400, 3120.42, 1563.23, 1206.27, 1050.32, 929.31cm^{-1} for pure polypyrrole, 3392.51, 2918.48, 1555.44, 1194.42, 1047.45, 925.44 cm^{-1} for PPy/0.01 M $CeCl_3$ composite, and 3100, 2352.28, 1548.23, 1180.80, 1045.22, 918.22 for PPy/0.2 M $CeCl_3$ composite. Thse six principle bands are characteristic to represent N-H, Ar-C=C-H, C=C, C-N, C-C stretching vibrations and C=C-H bending vibrations respectively. The peaks below 800 cm^{-1} in PPy/0.01and 0.2 M $CeCl_3$ composites may be assigned to C-Cl, Ce-C, Ce-Cl bondings.

It is observed that the bands obtained show vibrating frequencies vibrating frequencies are shifted to lower frequency region as concentration of $CeCl_3$ increases from 0.01-0.2 M compared with bands obtained in Pure PPy. This indicates that there is increase in conjugation due to doping which is responsible for Variation in conducting properties of the materials.

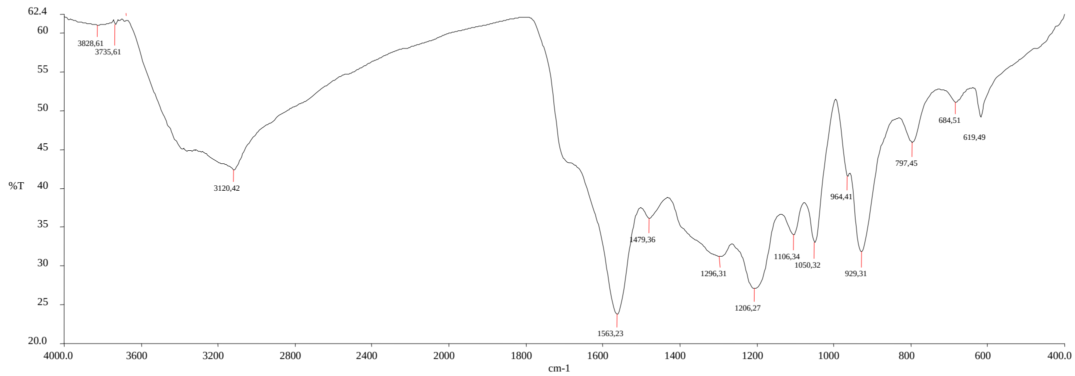

Fig. 1. FTIR Spectrum of Polypyrrole

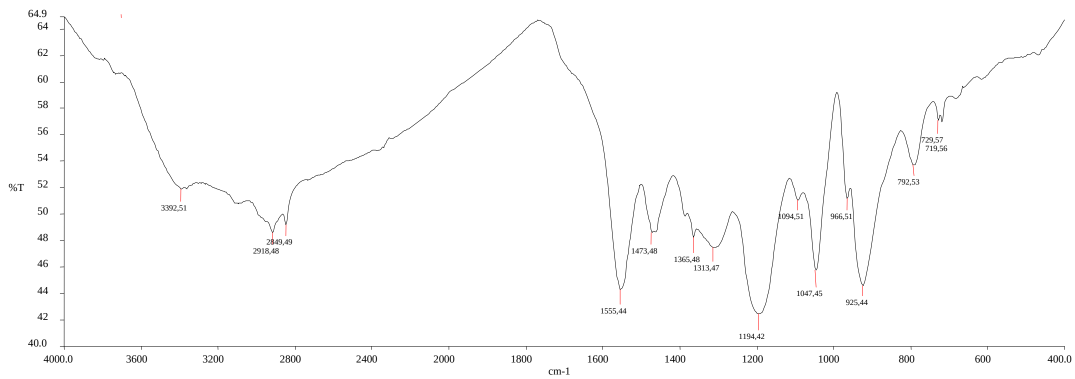

Fig. 2. FTIR Spectrum of Polypyrrole / 0.01 M $CeCl_3$ composite

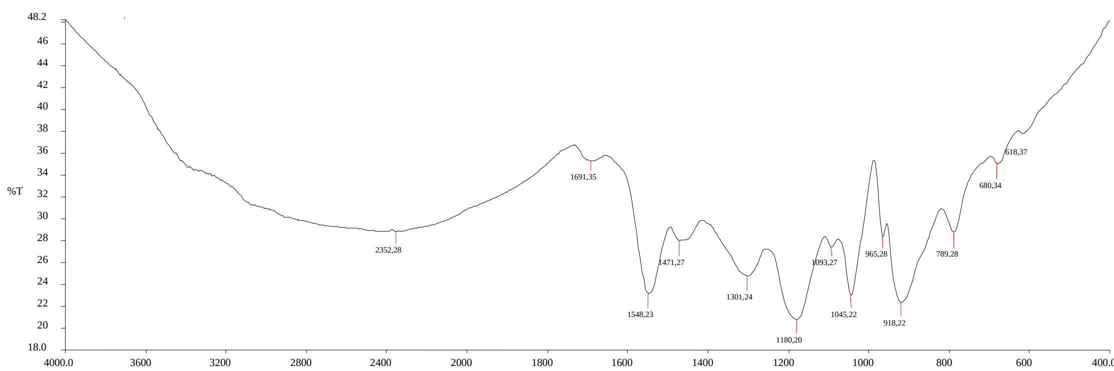

Fig. 3. FTIR Spectrum of Polypyrrole / 0.2 M $CeCl_3$ composite

The conductivity of conductive polymer composite can be tuned from insulating regime to conducting regime by chemical modifications or by degree and nature of doping. Large number of research work have shown that extensive delocalisatin of electrons along the polymer backbone is responsible for a polymer to behave as an electrical conductor. In organic solids intramolecular interactions are mainly covalent but intermolecular interactions are due to much weaker vanderwalls and London forces. The double bond consist of 6-bond and Pi-bonds. The electrons in 6-bond form the backbone of the chain dominating characteristic mechanical properties of the Polymers. Due to conjugation pi-obital overlap is possible which fascile the Pi-electrons to delocalize along the entire chain which gives rise to semiconducting and conducting properties to the polymers.

Conclusion

The PPy/$CeCl_3$ composite were synthesized by chemical polymerization method. It is a simple and low cost method for synthesis. The composite formation was confirmed by FTIR analysis. The IR study that the interaction exist between PPy and $Cecl_3$. The six principle bands obtained IR spectrum of each composite confirms aromatic and highly conjugated polymeric structure. The bands below 800 cm^{-1} in PPy/0.01and 0.2 M $CeCl_3$ composites may be assigned to C-Cl, Ce-C, Ce-Clintractions. As the concentration of dopant increases from 0.01 M to 0.2 M there is shift in bands at lower frequency region indicates increase in conjugation due to doping which affect the conducting properties of the polymers.

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