



SYNTHESIS AND FTIR CHARACTERIZATION OF POLYPYRROLE/ METAL OXIDE COMPOSITE PREPARED IN NON-AQUEOUS SOLVENT

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(Total No. of Table: 04 / Total No. of Figures: 04)

Abstract:

A group of conducting polymers is the subject of many research and they are also important and promising for many applications due to their vital properties. Conducting polymers like Polypyrrole (PPy) polymerized chemically by a wide variety of oxidizing agents to give a black conducting powder. Chemical polymerization has an advantage over other methods because it is suitable for both conducting and non-conducting substrates and is not restricted by area and surface shape of substrates. Furthermore, chemical method is convenient and rapid and gives good product of different physical parameters for further characterization.

Keywords: Polypyrrole (PPy) ; Conducting Polymer ; FTIR ; polymerization; etc.

1. Introduction:

Conductive polymer, such as Polypyrrole, Polyaniline, Polythiophene, and their derivatives, has been extensively studied recently because of the wide prospects for their application. Among all these conducting polymers, Polypyrrole (PPy) is the most thoroughly investigated polymers because of its high electrical conductivity in wide range of pH values, flexible method of preparation, ease of surface modification, excellent environmental stability, ion exchange capacity, biocompatibility and wide range of various applications such as in electronic device¹, semiconductor apparatus², biosensor³, polymeric battery⁴ and electromagnetic interference shielding⁵.



Thus, the synthesis of conducting polymer has recently been an increasingly important subject of intensive research. In general, PPy can be synthesized by anodic electro-polymerization, oxidative chemical polymerization and Plasma enhanced polymerization. Out of all these, Chemical polymerization has an advantage over other methods because it is suitable for both conducting and non-conducting substrates and is not restricted by area and surface shape of substrates. Furthermore, chemical method is convenient and rapid.

It was first noted in 1968⁶ that pyrrole could be polymerized electrochemically, and in 1973⁷ that it could be readily polymerized chemically by a wide variety of oxidizing agents to give a black conducting powder. Since this time, research activity in the field has continued to proceed at a constantly increasing pace. However, this polymer has greater cost, a low mechanical strength and is very brittle, which substantially restricts its potential applications. One of the best ways to solve this problem is to prepare composite systems in which an elastic support would provide the required mechanical properties and the conducting polymer would be the active component.

We have synthesized PPy/Metal Oxide composite by chemical oxidative polymerization in non-aqueous⁸ medium of diethyl ether. Anhydrous FeCl₃ was used as oxidant. All results depended on the FeCl₃ / pyrrole feed composition. The product was analyzed by FTIR Spectroscopic techniques.

2 : Experimental

2.1 : Reagents and Raw Materials

Pyrrole (AR Grade –Aldrich, India) monomer was distilled under reduced pressure, put in desiccators and stored in the refrigerator to use. Ethyl Ether (AR grade, S.D. Fine Chemicals, India) was used as solvent, and anhydrous FeCl₃ (Laboratory grade) as oxidant. Ethanol, acetone, ZnO, PbO, MnO₂, (AR grade, S. D. Fine Chemicals, India) were other

analytical reagents and added in proportionate quantity. Double distilled water was used for the preparation of all the solutions.

2.2 : Sample Preparation :- PPy containing metal oxidant were prepared according to following method⁸ _

Ethyl Ether 50 ml was added to a specific amount of anhydrous FeCl_3 in 100 ml round bottom flask with continuous stirring with a magnetic stir bar, and then 1 g of distilled pyrrole and 1 g PbO / ZnO / MnO_2 were added to the stirred solution at 0°C . After a reaction time of 1.5 hrs, the black precipitate was obtained as a composite material. The product was washed by water, followed by ethanol, and dried in hot air vacuum which was named as PPy- FeCl_3 / PPy - PbO / PPy - ZnO / PPy - MnO_2 respectively.

3 : Result and Discussion:

3.1: Solubility :

Solubility of PPy- FeCl_3 , PPy- ZnO , PPy- PbO , and PPy- MnO_2 composite was tested in many organic solvents at room temperature. It is summarized in table 1 and 2. It has been seen that almost all the polymers are partially soluble only in strong hydrogen bonding solvents like DMF, DMSO, THF and are insoluble in common organic solvents like ethyl alcohol, benzene etc.

S. No.	Polymers	Solvents	Solubility
1	PPy - FeCl_3	DMF, DMSO, THF	Partially Soluble
2	PPy - ZnO	DMF, DMSO, THF	Partially Soluble
3	PPy - PbO	DMF, DMSO, THF	Partially Soluble
4	PPy - MnO_2	DMF, DMSO, THF	Partially Soluble

Table 1: Solubility in Strong hydrogen bonding solvents



S. No.	Polymers	Solvents	Solubility
1	PPy - FeCl ₃	Ethyl alcohol / Benzene	Insoluble
2	PPy - ZnO	Ethyl alcohol / Benzene	Insoluble
3	PPy - PbO	Ethyl alcohol / Benzene	Insoluble
4	PPy -MnO ₂	Ethyl alcohol / Benzene	Insoluble

Table 2: Solubility in common organic solvents

3.2: Melting temperatures of Polymers:

Generally when polymer melts, the low molecular weight part of it melts first while the high molecular weight part of it melts later. Due to this there is no sharp melting point as such but a range of temperature. The melting range (i.e. the temperature at which the samples starts phase separation and the temperature at which melting completes with no solid phase) of polymer has to be noted instead of melting point. Table 3 gives the melting point of the polymers. All the polymer samples shows the melting point above 350^oC that means all these polymers are highly thermally stable due to the crystalline nature of the macromolecules.

S.No.	Polymers	Melting Point
1	PPy – FeCl ₃	Above 350 ^o C
2	PPy – ZnO	Above 350 ^o C
3	PPy – PbO	Above 350 ^o C
4	PPy – MnO ₂	Above 350 ^o C

Table 3 : Melting point data

3.3: FTIR Spectra:

FT-IR Spectra have been constantly applied in the determination of structure of molecule due to the polymer possess specific absorption bands in the infra red region of the spectrum. The extensive application of FTIR Spectroscopy is mainly due to the concept of structural group of atomic vibration. Any structural changes like substitution or addition of groups or atoms in a molecule affect the relative mode of vibration of the group special interest resulting into,

- i) Change in band position
- ii) Change in relative intensities and appearance of new bands
- iii) Splitting of single peak into two or more peaks

In the present investigation, FTIR Spectra of a number of a different sample prepared from pyrrole. The different transitions metals oxides were interred calculated into the polymer chain. The results are presented in the table 4.

Polymer Probable assignment	PPy - FeCl ₃	PPy - ZnO	PPy - PbO	PPy - MnO ₂
Stretching vibration of C = C bond (1540 cm ⁻¹)	1560.7	1657.0	1652.1	1619.4
Stretching vibration of C-C bond (1298 cm ⁻¹)	1303.1	1405.5	1403.3	1401.1
Stretching vibration of N - H (3400 cm ⁻¹)	3125.3	3217.7	3206.5	3142.9
Stretching vibration Of bond of pyrrole ring	1460	1180	1036	780

Table 4 : FTIR spectral data

Figure 1 to 4 displays FTIR transmission spectra of PPy with different oxidants using KBr pellet was recorded in the range of 4000 – 500 cm⁻¹. The specific bands appears at 1560.7, 1657.0, 1654.1, 1619.4 cm⁻¹. They are closed to reported data.⁹⁻¹⁰ Stretching vibration (1540 cm⁻¹) of C=C bond, Stretching vibration (1298 cm⁻¹) of C-C bond,

Stretching vibration (3400 cm^{-1}) of N-H bond and bonds (1460 , 1180 , 1036 , 900 , 780 cm^{-1}) of pyrrole ring.

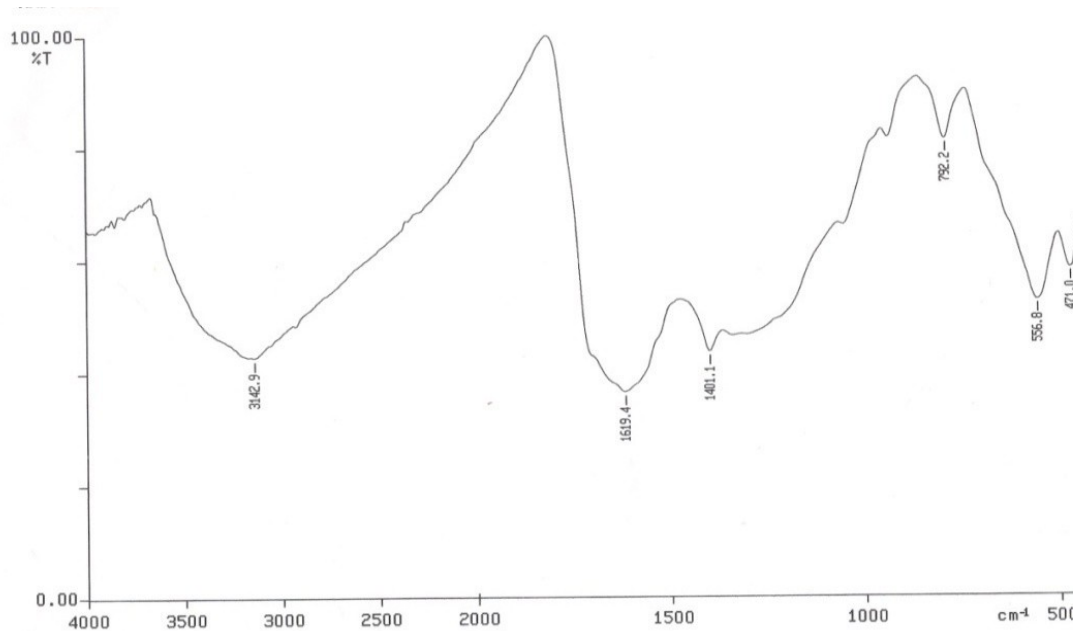


Fig. 1: FTIR Spectra of PPy - FeCl₃

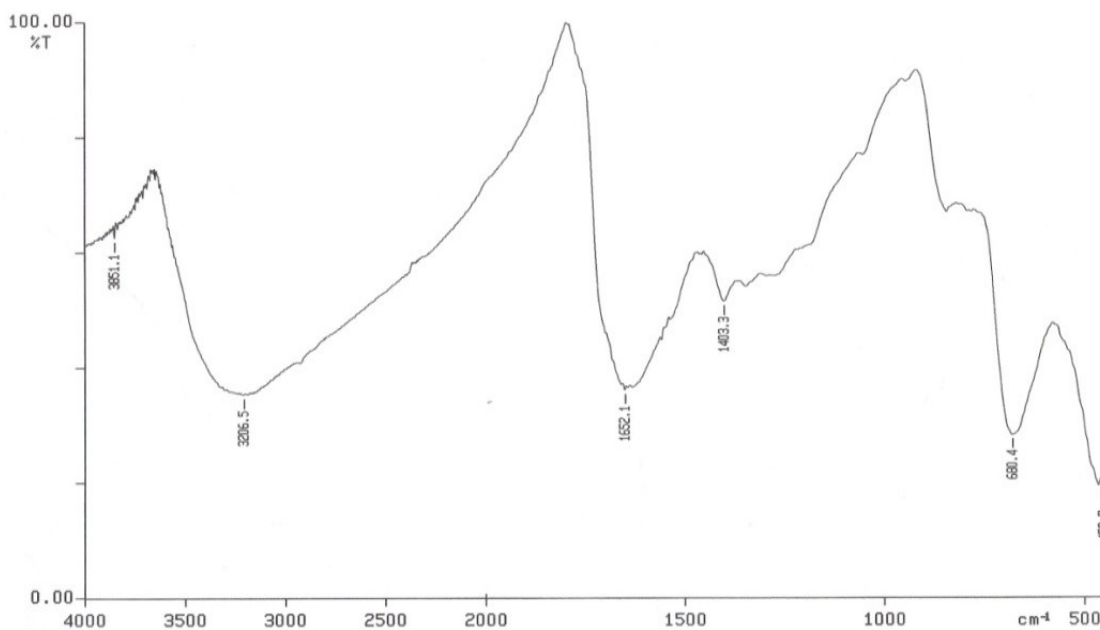


Fig. 2: FTIR Spectra of PPy - ZnO

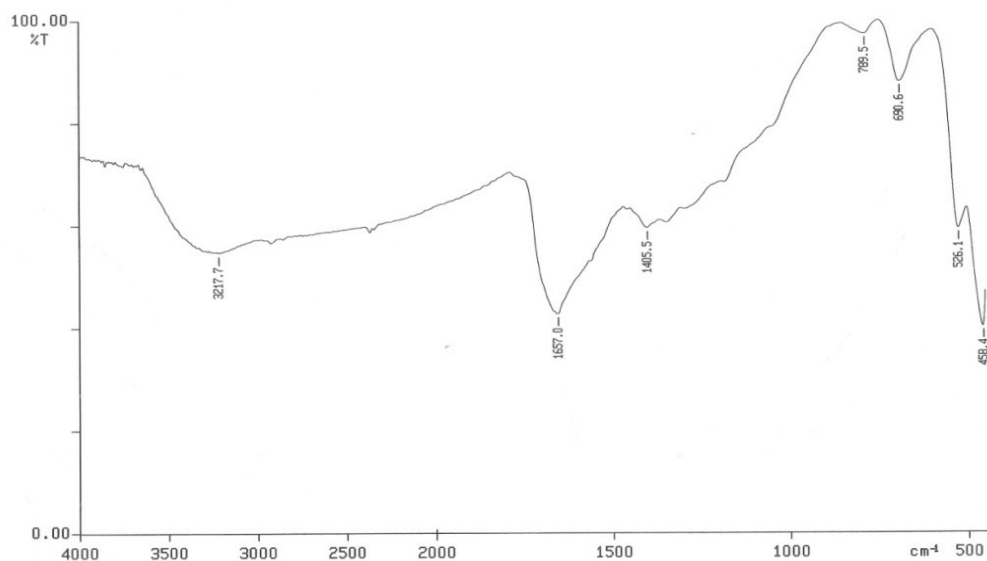


Fig. 3: FTIR Spectra of PPy – PbO

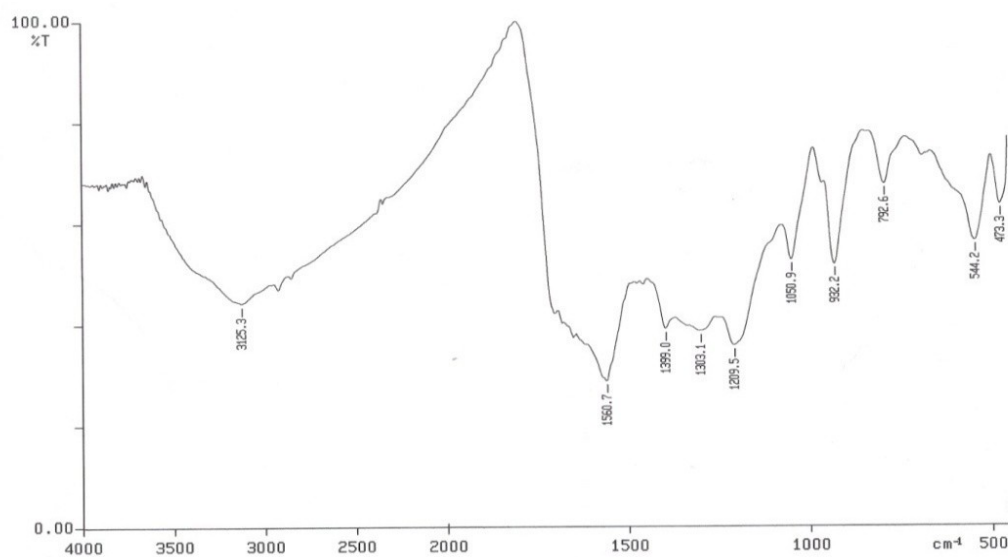


Fig. 4 : FTIR Spectra of PPy – MnO₂

Conclusion

Polypyrrole with transition metal salt composite polymer has been prepared by using oxidation polymerization. The samples have been characterized by Fourier transform infrared spectroscopy (FT-IR) (Avatar 380 FT-IR spectrophotometer). The dried PPy powder was mixed with



powder KBr, ground, and compressed into a pellet. Its spectrum was recorded as a reference to be compared with that of the PPy/metal oxide.

FTIR confirmed the polymeric linkage, the attachment of the salts and indicate strong interaction between oxide and the PPy polymer. The effect of oxide particles on the chemical polymerization of pyrrole in solution was investigated and found to significantly influence the morphology (size and shape) and other physicochemical properties of the PPy.

Melting temperature of polypyrrole with transition metal salt composite polymer is recorded above 350^o C. It is concluded that these composite polymers are thermally stable. Pure discrete PPy with a much higher resistivity are formed over a long reaction time in the presence of oxide particles and are observed to have an improved thermal stability with a higher decomposition temperature

The interaction between the metal salts mainly negatively charged at neutral P_H, and the delocalized positive charge along the PPY chain induces changes in capacitance of their nanostructure material. The use of a wide range of counter ions will provide significant change in affinity at the PPY ion-exchange sites. As the surface microstructure become more complicated, for the construction of more complex nanostructure. Some degree of molecular self-assembly will be needed and conducting polymer become more complex, versatile and will find the new applications. New nanotechnological approaches to overcome, in such cases polypyrrole will find proper place in future molecular technology.

Acknowledgement :

Authors are thankful to The Director, Sophisticated Analytical Instrumentation

Facility, Panjab University, Chandigarh – 160014 for providing facilities.



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