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Synthesis, Characterization and Antibacterial Activity of Polypyrrole-Montmorillonite Nanocomposites

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ABSTRACT

Conducting polymers and its composites found to be promising candidate for the medical and electroanalytical application in various fields. Significant functional exercise on Montmorillonite clay proves wide appliction in food additive , for antibacterial activity against tooth and gum decay, as sorbent for nonionic, anionic, and cationic dyes, and the use as catalyst in organic synthesis. Polypyrrole and Montmorillonite clay are used in the synthesis of Polypyrrole/ Montmorillonite nanocomposites by chemical oxidative method. Obtained PPy/montmorillonite composites are characterised by UV, FTIR and morphology and composition analysis are also done by using FESEM and EDX. Biological activities of the Polypyrrole/Montmorillonite conducting polymers composites (CPs) are studied by using the Bacillus, E.Coli, Pseudomonae as a bacterial cultures. PPY/7.5% MMT composite show antibacterial activity for the Bacillus,bacteria but for the E.Coli, Pseudomonaeno no activity.

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Introduction

Polypyrrole (PPy) is an intrinsic conducting polymer. It allows application in variegated fields like batteries, sensors, electronic equipments, solar cells, electrodes, optical devices biosensors etc [1].

Polypyrrole is top-tier candidate among the conducting polymers (CP) because of its easy synthesis route and its stability in chemicals and air. The oxidative polymerization of Pyrrole into polypyrrole can either be through chemical or electrochemical polymerization [2].

PPy in its pure form is insoluble and infusible due to its rigid conjugated structure. Due to its poor processability and poor mechanical properties is incorporated with nano oxides and other materials. Several researches have been trying to reduce these drawbacks, which has led to the innovative experimentations of preparing PPy and blends with other nanomaterials, in turn producing PPy derivatives and composites [3]. Composites of PPy with Zirconium Oxides, Titanium oxides and iron oxide focus the ppy composites with their applications [4-6].

Clay components attracted study due to their smaller size and intercalation character; for the purpose of formation of matrices for polymers [7-10].

Cloisite clay composite films are synthesized using Whey protein isolate by solution casting method and advantageously showed bacteriostatic effect with gram positive bacteria [11]. Waste water purification from the conjugated polyaniline, polypyrrole and polythiophene derivatives are showing the unique redox chemistry through which effective adsorption of the pollutants can be achieved antibacterial and antifungal activity of the MMT clay of the Ag, Zn and Cu ions exchange with some of the fungi which are used as indicator of the pollutant toxicity [12-16].

Montmorillonite Clay with quaternary ammonium salt, MMT loaded with Cu, Zn and Ag shows satisfactory antibacterial activity against two types of bacteria: Staphylococcus aureus and Escherichia coli [17-18].

In this paper, investigating the preparation of polypyrrole-montmorillonite(MMT) clay composites by chemical oxidation technique and testing for its antibacterial activity, while confirming structural and morphological characterizations by UV –visible, FTIR, and FESEM and EDAX. Polymer composites is expected to work for food packaging applications with few modification and analysis.

Materials and Method

Pyrrole monomer used was of Analytical grade. Ferric Chloride (FeCl3) was also of laboratory grade (Fischer Scientific). Montmorillonite fillers were obtained from Sulepet (Korvi Fullersearth company, Gulbarga). Acetic acid and Sodium Lauryl Sulphate (SLS) were obtained from Fischer Scientific.

UV visible analysis of the synthesized polymer composites are studied by using the SHIMADZU UV-2600, UV-VIS SPECTROPHOTOMETER. Solution of the PPY and PPy/MMT composites in methanol media spectra obtained by plotting absorption vs wave length. Base line is set for the methanol media.

The FTIR patterns were recorded using Perkin Elmer 200-3500 nm of wavelength. Since the samples were of Black coloured powder form, ATR (attenuated total reflection) technique was applied while analysis. It is a sampling technique where samples can be examined directly without any prior preparation.

The morphologies of the MMT-PPy composites have been examined using Zeiss Sigma Ultra plus 300 FESEM `analysis equipment. The finely ground powdered form of composites were loaded on the carbon tape and mounted into the instrument, which were then treated for SEM analysis. Composites are also analyzed for the energy dispersive X-ray Spectroscopy for the composition of the composites model BRUKER with an operating power of 20 kV and current 30 mA and Cu Kα radiation (1.5406).

For antibacterial activity of the polymer composites were conducted using disk diffusion method, bacteria cultured used is *Bacillus*, *E.Coli*, *Pseudomonae*.

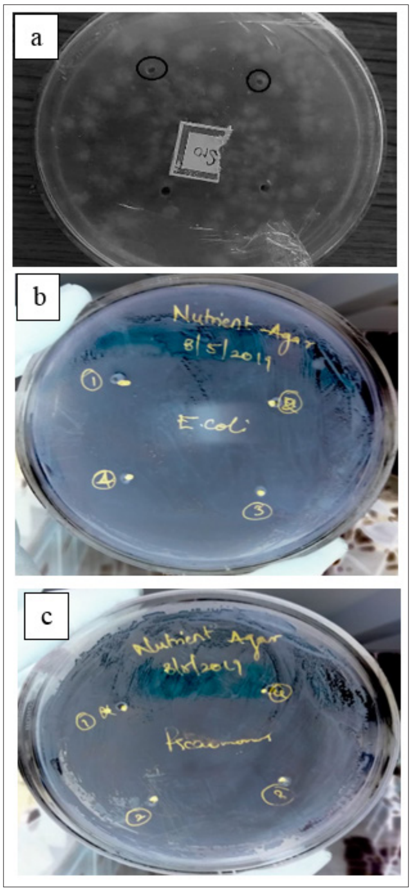

Figure 1: a) Bacillus b) E. Coli c) S. Pseudomonae Cultured Agar Plate for PPy/7.5%MMT Composites for Zone of Inhibition.

Synthesis of Polypyrrole and Polypyrrole /Mmt Composites

Pyrrole (0.011 mol) is added to the mixture of FeCl3 Acetic acid and sodium lauryl sulphate taken in a beaker. Allowed to stir for 4 hours at 0-5 0C in ice bath container on a magnetic stirrer for 4 hours. The total volume of the complete solution was kept at around 50 ml. Polypyrrole obtained was taken in its black greenish powdered form. FeCl3.6H2O was used as the oxidant and acetic acid is used as acidic medium and sodium lauryl sulphate is used as a surfactant. Obtained polypyrrole was filtered using Buchner funnel and washed with methanol, allowed to dry at room temperature for 24 hours.

Above procedure continuous addition of montmorrilonite (MMT) in different weight percentages as a filler in a polypyrrole. Solvent used was surfactant sodium Lauryl sulphate (SLS) dissolved in acetic acid solution. The MMT clay dispersion was prepared, by the addition of 1%, 2.5%, 5% and 7.5% weights in the acidic solution respectively in different batches, under constant stirring for 4 hours. The formation of Polypyrrole/MMT is confirmed by the change of colour of precipitate from light black to greenish black. The reaction mixture was then kept undisturbed for 24 hours at room temperature. After a day, the greenish black ppt was filtered and washed twice and thrice with methanol to remove all traces of unreacted compounds. The product was then kept for drying at room temperature for 24 hours. The powder was kept in airtight container for further use.

The yields varied in all the four composites. Weight of the compounds were 3.0 g, 2.8g, 1.7 g and 1.3 g for PPy/ 1MMT, PPy/2.5MMT, PPy/5MMT and PPy/7.5 MMT respectively.

Antibacterial Activity

The antibacterial activity tests were conducted for the particular CP, Polypyrrole (PPy) and PPy/MMT composites. The preparation of the nutrient broth in Petri plates for bacteria culture are taken. The bacteria cultured were *Bacillus*, *E.Coli, Pseudomonae*. When the nutrient agar plates are rewarmed, few drops of bacteria culture are placed on the agar plate and distributed uniformly. After this agar plate-bacteria culture solidifies, wells are made into it, by drilling the agar volume. Four wells are made for four concentrations of sample in each plate. Filling up of the wells with the samples is then conducted. The petri plates are closed and sealed; and left for 48 hours for the growth of Bacteria.

In case of *Bacillus*, there were observed black circles around the wells. This was an indication that there was no growth of bacteria in that area, due to the presence of PPy sample in the wells. It, in turn, indicated the ability of antibacterial activity of *Bacillus*. The activity was observed upto a length of 10.6 mm and 11 mm for PPy/5MMT and PPy/7.5MMT respectively.

Bacterias E.Coli and *Streptococcus Pseudomonae* from the figure 1 b) and c) do not show any inhibited zone in the presence of Polypyrrole, and hence PPy can display antibacterial activities only in the case of Bacillus from the figure fig.1a). Other composites are also conducted did not showed any significant ihnibition activity so they have not given here.

Most of the literature shows bacterial activity for *E.Coli* with respect to polypyrrole and polypyrrole encapsulated Ag composites are found. But our composites show Bacterial activity for Bacillus bacteria [19-21].

Results and Discussion

Field Emission Scanning Electron Microscope

The figures 2(c) and 2(d) display better ordered and densely knit structure (smaller sizes with high density of granules per unit area) comparing to Figure 2(a) and 2(b). i.e., larger sizes in less density per area. This helps to conclude that the more percentage concentration is the clay in the mixture, increases the compact nature of the dispersion of clay into dense polypyrrole composite. The MMT-PPy-Cl and the MMT-PPy-SLS compositions in the matrix explains that SLS was able to clear out pathways for enhanced characteristic properties.

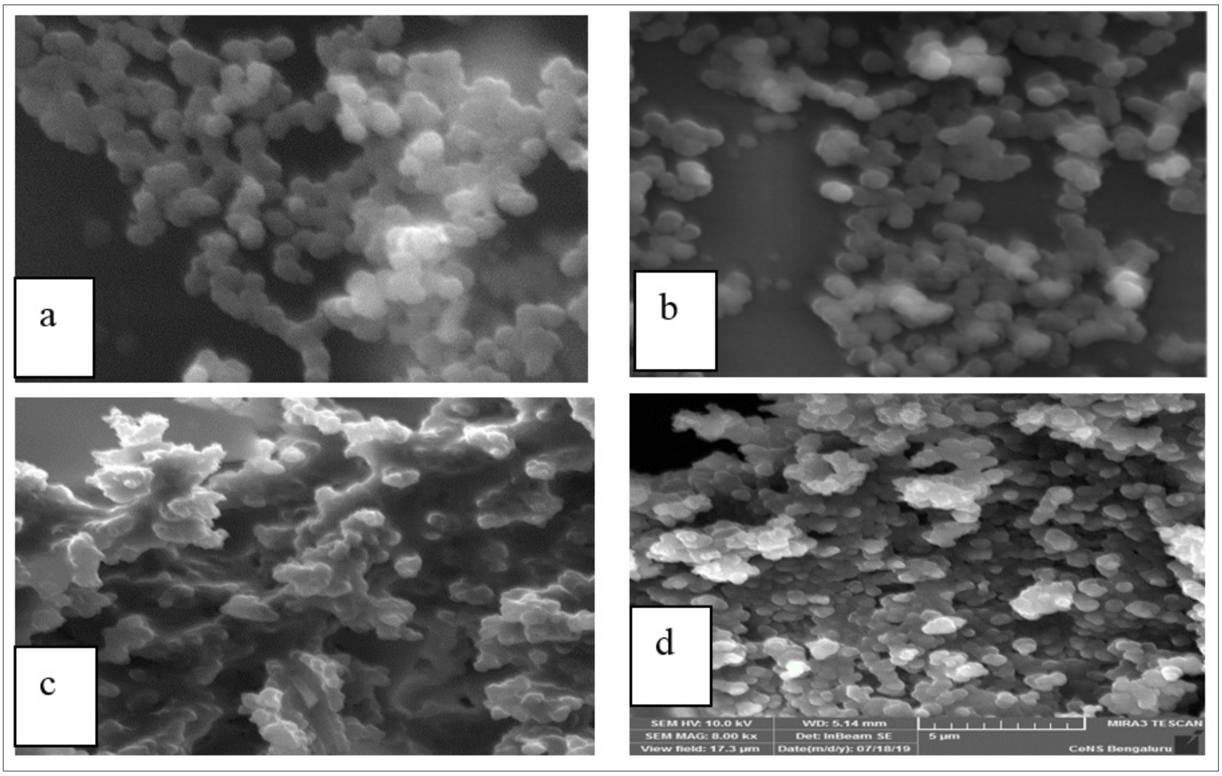

Figure 2: FESEM images of a) PPy/1MMT, b) PPy/2.5MMT, c) PPy/5MMT, d) PPy/7.5MMT

Composites

EDX Analysis of Ppy/MMT Composites

With increase in Montmorillonite concentrations, the concentrations of free nitrogen element, and in turn, free -NH groups have reduced. While on the other hand, the component weight of Silicon had increased due to increase in clay amount. The free carbon content had also reduced due to displacement of polypyrrole components with more of clay components. Hence the PPY/MMT composites compositions are shown in the table 1.

Fourier Transform Infrared Spectroscopy (FTIR)

The peaks in the spectra for polypyrrole, observed at 3436 cm-1, 2900 cm^{-1}, 1524 cm^{-1}, 1310 cm^{-1} from the figure 3. In the spectra of 1% PPy–clay composites, the peak at 3465 cm^{-1} corresponds to -NH stretching vibrations of PPy. The peaks at 2916 cm^{-1} and 2849 cm^{-1} in the spectra of all composites can be attributed to the asymmetric and symmetric stretching vibrations of alkyl C-H bonds in the dopant SLS. The band at 1540 cm^{-1} in the spectrum of PPy corresponds to the backbone stretching vibration of C-C bonds. A C-N ring stretching absorption band was detected at 1250 cm^{-1}. The band at 1470 cm^{-1} can be attributed to C-C ring stretching.

The absorption bands observed 1600 cm-1 1029 cm^{-1}, 880 cm^{-1} and 682 cm^{-1} peaks responsible for MMT clay. The peaks at 1029 cm^{-1} and 1641 cm^{-1} are due to absorbed water. Stretching frequencies are well match with literature [3].

Element	Atomic percentages					Weight percentages				
	C	N	O	Si	Cl	C	N	O	Si	Cl
PPy/2.5MMT	65.9	9.72	12.59	6.15	4.10	45.60	7.84	11.61	9.94	8.38
PPy /5MMT	50.14	7.8	36.28	8.65	2.2	35.44	5.70	35.88	11.69	4.5
PPy /7.5MMT	38.21	5.96	40.84	10.72	1.88	24.22	4.40	34.49	15.90	3.52

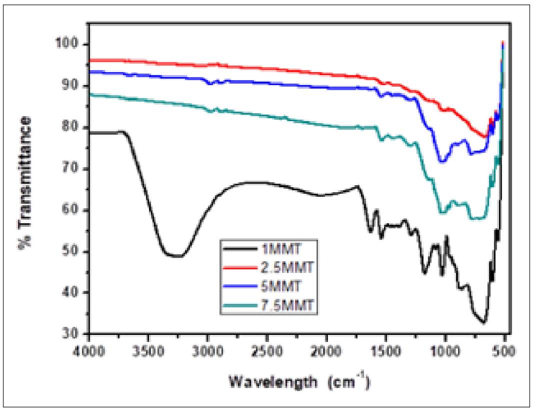

Figure 3: FTIR Analysis of PPy-MMT Nanocomposites

UV- Visible Analysis

PPy exhibits UV-Visible absorption peaks at around 500 nanometers can be seen from the figure 4, but due to the presence of Montmorillonite fillers (literature value 446 nm). The π-π* transition and bipolaron bands are observed at around 450-500 nm range for the different PPY/MMT samples. Different intensity in the absorption indicate the oxidized nature of the PPY. It also resembles the UV-Visible spectra of the pure MMT has absorption band at 250 nm range. The spectrum shows an increased absorption with the increase of wavelength to 480 nm for the PPY/7.5MMT.

PPy/5MMT and PPy/7.5MMT Composites

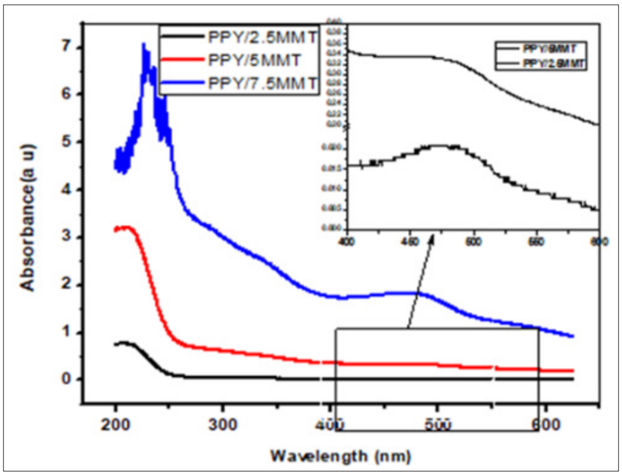

Figure 4: UV-Visible Analysis for PPy/2.5MMT, PPy/5MMT and PPy/7.5MMT Composites

Conclusion

The nanocomposite PPy-MMT-Cl and PPy-MMT-SLS were prepared successfully, with four separate weight percentages of 1%, 2.5%, 5% and 7.5%montmorillonite. The composition and functional group analysis were examined using FTIR analysis and EDAX. The carbon content decreases as the concentration of MMT increases in the composite. Presence of increased concentration of MMT also ensured by increased concentration of Si and O atomic and weight percentages. Microstructures of the products, i.e., their morphologies, were examined using FESEM analysis. As the increased percentage concentration of MMT cluster formation also seen with closer network and association of PPY and MMT composite. The absorption peaks were determined by UV-Visible Spectroscopy. The π-π* transition and bipolaron bands are observed at around 450-500 nm range for the different PPY/MMT samples which are matches with literature values.

Samples were tested for antibacterial activity. Antibacterial activity was calculated using disk diffusion technique. Antibacterial activity was observed very less for the bacterial, namely, E.Coli and Pseudomonae. In case of Bacillus, the length of the activity was 10 mm, near average activity. The activity was displayed due to equal distribution of PPy agglomerates in MMT matrix, with the presence of -NH group and aromatic ring, which had a partially cationic character due to presence of Cl- ion. The other two bacteria under observation, *E.Coli* and *Pseudomonae*, displayed no inhibition in the presence of PPy-MMT. The study has revealed that PPy/7.5MMT composite showed good antibacterial activity for Bacillus rather than for *E.Coli* and *Pseudomonae*.

To prepare polymer -MMT composites suitable for the oil refineries in fact direct MMT have limitations. The composites could serve to be better oil refineries. Biosensors for the detection of components like Glucose, proteins, enzymes or amino acids. Antifungal activities could be explored with PPY-MMT composites. So, it will be more useful in designing the sensors. The route to solubility of PPy composites in inorganic solvents could be experimented upon, since PPy is almost sparingly soluble in organic solvents. PPY-MMT composites also works in food packaging application with suitable modifications.

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