SYNTHESIS AND CHARACTERIZATION OF CHITOSAN/POLYPYRROLE NANO HYBRIDS

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ABSTRACT

Present work focuses on the synthesis of Chitosan/Polypyrrole nano hybrids by in situ chemical oxidative polymerization of Pyrrole monomer in presence of Chitosan. Chitosan is a biopolymer, a polysaccharide having –OH and –NH_2 groups present along the polymer chain. Polypyrrole is a special class of organic polymer with extended conjugation along the polymer chain. The synthesized hybrids were characterized by Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction, Field Emission Scanning Electron Microscope (FESEM), Transmission Electron Microscope (TEM) and Thermogravimetric Analysis (TGA). The FTIR spectrum of the nano hybrids exhibits a synergistic interaction between Chitosan and Polypyrrole. The X-ray Diffraction study reveals its amorphous nature. The FESEM and TEM micrographs of the nano hybrids reveal the formation of distinct spherical particles of Chitosan and Polypyrrole clustered together. The TGA analysis of the nano hybrids exhibits good thermal stability. of the nano hybrids.

Keywords: Polypyrrole , Chitosan, Nano Hybrids, FTIR

1. INTRODUCTION

Nano materials are of considerable interest now a days because of their unique combination of properties and excellent applications in various fields. Conjugated polymers like Polypyrrole, Polyaniline, Polythiophene etc. have received a great deal of attention because of their interesting physical and electroconductive properties [1, 2]. Among them, Polypyrrole (PPy) is the most suitable electroactive polymer for drug-delivery applications. It is biocompatibile and has antioxidant activity [3, 4]. However, PPy suffers processability problems because of its poor mechanical properties and high chemical sensitivity [5, 6]. Chitosan is a polysaccharide present in the exoskeleton of sea crustaceans. It is a biopolymer that is biodegradable, biocompatible, nontoxic in nature [7]. It is a sea food waste which is produced in abundance at coastal areas. However, this humble looking material possesses outstanding combination of properties required for water purification, food industries, cosmetics, biomedical applications. It shows antibacterial properties and has excellent membrane forming ability [8, 9].

Present investigation focuses on the synthesis and characterization of Chitosan/Polypyrrole (Cs/PPy) nano hybrids to design a product with good biocompatibility and improved mechanical and antibacterial properties. A facile method of synthesis of the nano hybrids is reported here.

II. SYNTHESIS OF CHITOSAN/POLYPYRROLE (CS/PPY) NANO HYBRIDS

In the first step, Chitosan was dissolved in mildly acidic solution of acetic acid (1 wt%). During this process, the polymer chains open up and the $-NH_2$ groups present in the Chitosan chain become protonated ($-NH_3^+$), converting it to a polycationic electrolyte. The chemical oxidative polymerization of pyrrole monomer was carried out in chitosan solution at room temperature. An oxidant, $FeCl_3$ was added to carry out polymerization process, whereas, sodium salt of *p*-toluene sulphonate (*p*-TS) was added as surfactant. The molar ratio of $FeCl_3$:Pyrrole:*p*-TS was taken to be 2:1:0.5.. The suspension was stirred till the appearance of black coloured nano particles. The resultant nano hybrids were filtered, washed and dried in a vacuum oven at 60 °C. The schematic of the synthesis is shown in Fig. 1.

III. CHARACTERIZATION

FESEM (FESEM, NOVA NANO SEM 430, FEI, USA) and TEM (TEM, Tecnai TMG F30, FEI) are used to study the microstructural features of the nano hybrids. FTIR (Nicolet 5700) were recorded in the spectral range of 4000-600 cm^{-1} to analyse the chemical structure of the nano hybrids. X-ray Diffractograms (XRD) was obtained using Bruker, D-8 advanced diffractometer. Thermogravimetric Analysis (TGA) was performed between the temperature range of 25 to 600 °C using a Mettler Toledo TGA/SDTA 851 with a heating rate of 15 °C/min in nitrogen atmosphere.

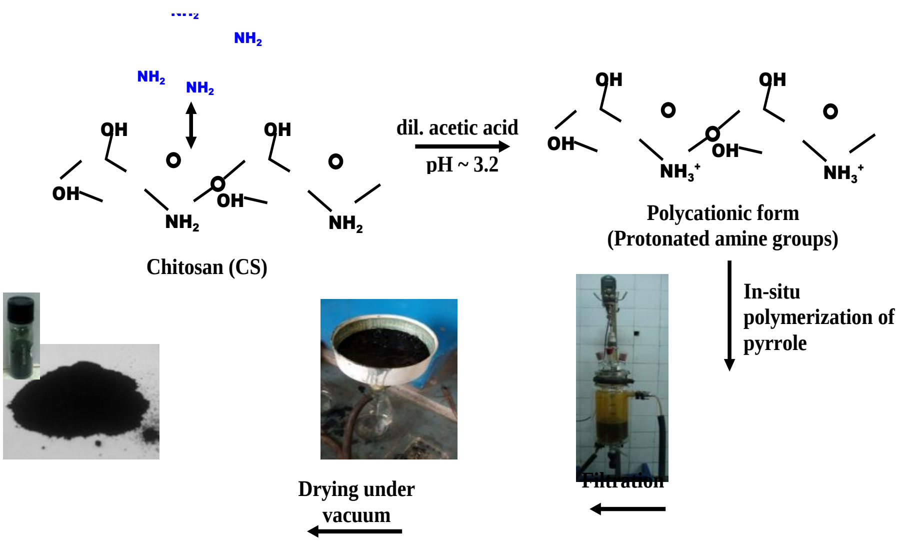


Fig. 1 Schematic of the Synthesis of Chitosan/Polypyrrole (CS/PPy) Nano Hybrids

IV. RESULTS AND DISCUSSION

4.1. Microscopy

Fig. 2a and b show the FESEM and TEM micrographs, of the CS/PPy nano hybrids respectively. The micrographs revealed a clustered polymeric structure composed of well defined spherical nano particles. The size of the nano particles were between 40 to 50 nm. The particles are observed to be arranged in a regular pattern.

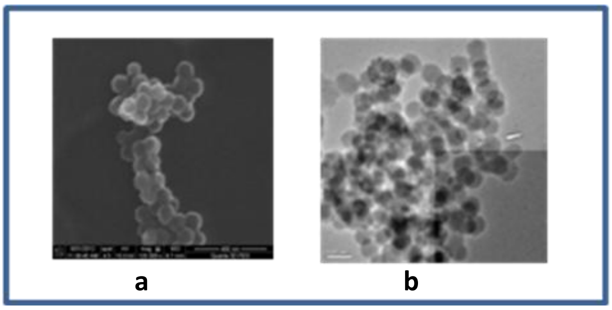
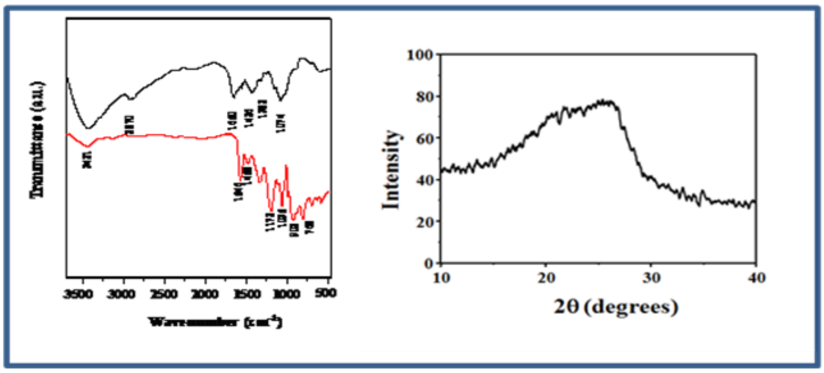


Fig. 2 (a) FESEM and (b) TEM micrograph of Chitosan/Polypyrrole (Cs/PPy) nano hybrids

4.2 FTIR and XRD of the Chitosan/Polypyrrole (Cs/PPy) nano hybrids

Fig. 3a exhibits the FTIR spectra of Chitosan and Chitosan/Polypyrrole (Cs/PPy) nano hybrids. The FTIR spectrum of Chitosan shows a broad band at 3200-3650 cm^{-1} due to axial stretching of O-H and N-H bonds. A peak at 1650 cm^{-1} is assigned to amide I vibration and peaks at 1426 and 1382 cm^{-1} is the result of coupling of C-N axial stretching and N-H angular deformation. The stretching vibration of C-O-C linkage in the glucosamine rings peaks appear at 1155, 1074 and 1024 cm^{-1}. The FTIR spectrum of Cs/PPy hybrid exhibits a broad band at 3421 cm^{-1} due to the N-H stretching of pyrrole and O-H stretching of Chitosan. The characteristic peaks of Polypyrrole at 1546 cm^{-1} (C=C benzoic form), 1458 cm^{-1} (C-N stretching) was observed [10, 11]. A characteristic strong amino peak is noticed at 1317 cm^{-1}. The peak at 1172 cm^{-1} (S-O stretching) and 1035 cm^{-1} (S-C stretching) confirm the formation of Chitosan/Polypyrrole hybrid doped with *p-TS*. The other peaks at 902, 768 and 670 cm^{-1} are due to the C-H out of plane deformation vibration of the ring. The XRD plot (Fig. 3b) of the Cs/PPy hybrid shows a broad diffraction pattern between 2θ 20°-30°, indicating the amorphous nature of the hybrid.

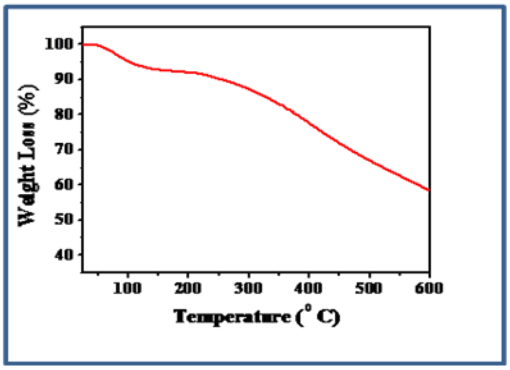


(a) Chitosan **(b) Cs/PPy**

Fig. 3(a) FTIR of Chitosan and Chitosan/Polypyrrole (Cs/PPy) Hybrid, (b) XRD of Chitosan/Polypyrrole Hybrid.

4.3. TGA Analysis of the Chitosan/Polypyrrole (Cs/PPy) Nano Hybrids

Fig. 4 presents the TGA thermogram of Chitosan/Polypyrrole (Cs/PPy) nano hybrids. The thermogravimetric analysis is carried to evaluate the thermal behaviour of the material. The nano hybrids show three stage weight loss behaviour over the entire range of temperature. In the first stage, 8-9 % weight loss of Cs/PPy was noticed at 100 °C. It is attributed to the loss of residual water molecules from the polymer matrix [12]. The second stage weight loss (from 100 to 220 °C) for Chitosan/Polypyrrole (Cs/PPy) nano hybrids is found to be 9-10 %. This could be due to the removal of residual surfactant from the polymer matrix. The third stage of weight loss which started at 250 ° C is basically due to the thermal degradation of polymer backbone. The results show that the synthesized nano hybrids have a good thermal stability. The Cs/PPy hybrids show a char residue of 58 % at 600 °C.



Cs/PPy

Fig. 4 TGA Thermogram of Chitosan/Polypyrrole (Cs/PPy) Hybrid

V. CONCLUSIONS

Chitosan/Polypyrrole nano hybrids were successfully synthesized by in situ chemical oxidative polymerization of pyrrole in chitosan solution. The synthesized nano hybrids were found to have spherical morphology (diameter ~ 40-50 nm). The FTIR analysis exhibits synergistic interaction between Chitosan and Polypyrrole. The X-ray diffraction studies revealed the amorphous nature of the nano hybrids. The TGA profile clearly demonstrated good thermal stability of the nano hybrids. The nano hybrids could find useful applications for water purification, food packaging, drug delivery, cosmetics, biomedical applications etc.

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