

# Abstract

Polypyrrole (PPy), one of the most important members of the class of conducting polymer (CP), has been extensively researched and utilized in cell material studies. Synthesis of PPy is mostly carried out by chemical or electrochemical methods though other methods involving photochemistry, metathesis, concentrated emulsion, inclusion, pyrolysis, and soluble precursor preparation routes involving solid-state and plasma polymerization techniques are also used in polymerization of pyrrole. Chemically synthesized PPy like other CP's, are initially in neutral state and hence insulators. It can be made conductive only by supplying mobile charge carriers required for its conductivity through oxidation (p-doping) or reduction (n-doping). In case of PPy, the polymer backbone is neutral in the reduced state and positively charged in the oxidized state. Therefore, in order to maintain electro neutrality some counterions are required to diffuse into the polymer chain during charging and emerge out of it during neutralization. The process of oxidation may be accompanied by significant change in polymer volume on engrossing of the anions and this property can be utilized in its actuator applications. Incorporation of biological moieties on CP can be an effective tool for tailoring specific material properties which can provide novel solutions in emerging fields like actuator applications, bio-sensing, tissue engineering, drug release, microelectronics etc. PPy is potentially feasible and highly chosen CP's for such works because of its very high bio-compatibility and associated bio-functionality. Among the different methods of polymerization, chemical synthesis gives a low cost easy to handle method of preparation of PPy which can be used for bulk production also. In the present work, we have adopted this method. This involves mixing of the monomer solution with a strong oxidizing agent (e.g.  $\text{FeCl}_3$ ). Incorporation of bio-molecule is carried out during the process of oxidative polymerization. The process is based on surface chemistry of the polymer solution and interaction of the surface forces between the polymer and the bio-molecule. Thus the successful incorporation of bio-molecule in chemical polymerization of pyrrole (Py) is a time consuming exercise depending on different parameters like polymer concentration, temperature, polymerization time, pH of the media and the type of bio-molecule added.

In this dissertation, we describe the synthesis of PPy incorporated with bile acid and bile salt extracted from animal species and cellulose extract from plant bodies and study the effect of

incorporation on the structural, morphological and electrical properties of the polymer. This thesis is divided into seven chapters with the detail lay-out as follows.

**Chapter 1: Introduction** embodies the general principles on which the present work is based on. It gives a brief overview of CP system in general and PPy in particular. The process of chemical oxidative polymerization of Py with  $\text{FeCl}_3$  as oxidant is described along with the general methods of bio-molecule incorporation in the polymer. The recent trend and process of bio-molecular incorporation and the underlying surface interaction for attachment of bio-molecule with the polymer chain is highlighted. Towards the end, a brief note on each of the chapters is included.

**Chapter 2: Materials and methods** deals with the experimental section where we discuss about the materials used and the methods of synthesis of PPy incorporated with different bio-molecular species. Also the experimental techniques are described for ethanol sensing. The experimental technique for cellulose incorporation is described along with the reaction schemes. This chapter also illustrates different characterization techniques, viz. FTIR, UV-Visible and photoluminescence spectroscopy, SEM, TEM, XRD, GPC system and NMR which have been used in this work. Methods of measurement of electrical properties viz. conductivity measurement by I-V characteristics and impedance measurement are also described.

**Chapter 3: PPy/Cholic acid composite for sensing ethanol vapour** describes in-vitro incorporation of cholic acid, a kind of bile acid, in polymerization of PPy by chemical oxidative polymerization resulting in the formation of a polymer blend different from PPy. The change is visualized from the formation of nanosheath as observed in TEM image of the composite while the AFM picture shows structural modification of PPy from 1D to 3D in the composite. The composite blend is used for sensing ethanol vapour which is visualized in changing electrical conductivity with applied dc bias 0-1 V and low frequency ac bias of 0-5 V. The change in resistivity of the composite from  $3.03$  to  $0.71 \text{ Ohm cm}^{-1}$  is observed after ethanol exposure, while low frequency dispersion of PPy is more prominent in the ethanol exposed composite which shows a linear trend in I-V characteristics at 50 Hz. The linearity in I-V curve is not observed for higher frequencies though.

**Chapter 4: Bile salt incorporated polypyrrole for ethanol sensing** describes synthesis of PPy incorporated with bile salt and its use for sensing ethanol vapour. The sensing is visualized through changes in morphological, structural and optical properties. The ethanol

exposed film shows larger agglomeration as revealed from SEM pictures and greater crystallinity as seen from XRD spectra. FTIR and NMR spectroscopy also give signature of the presence of bile salt and alcohol. Alcohol incorporation results in increased electrical conductance which changes from  $7.08539 \times 10^{-5}$  mA/V to  $8.0356 \times 10^{-5}$  mA/V, as determined from I-V characteristics. Average molecular weight ( $M_n$ ) changes from 16160 to 20300 on ethanol intake. PL intensity is quenched and the PL peaks shifts from 430 to 409 nm on ethanol exposure.

**Chapter 5: Incorporation of cellulose in oxidative polymerization of PPy** describes synthesis of PPy incorporated cellulose in which continuous matrix of cellulose is observed around PPy particles, initially in irregular phase, but becomes distinguishable with spherical shape particles, in higher polymerization time. Increased polymerization time shows increased crystallinity. Dielectric constant is found to vary with frequency. Electrical conductivity shows power law behaviour in the lower polymerization time and becomes steady at higher polymerization time. This behavior probably arises due to predominance of ionic conduction in the composite.

**Chapter 6: Polypyrrole nanocoating on bamboo cellulose fibre** describes how a PPy nanocoating on bamboo fibres affects their surface morphology and ac conductivity. The changes in surface morphology and particle distribution studied by SEM and TEM indicates formation of a nano-coating of PPy over the fibre surface, as the average diameter of the particles forming the surface layer is found to be  $\sim 50$  nm. FTIR spectroscopy reveals that the chemical structure of the natural fibres remains unchanged even after the nano coating, though certain individual characteristics of PPy appears therein. Resistance of the coated fibre decreases with increasing pyrrole concentration. The value ranges from 1075 to 0.159 k $\Omega$  for Py content range of 0.1% to 5% pyrrole. Further, it shows ohmic nature for both the coated and uncoated fibres. Dielectric behavior of the current-voltage (I-V) plots of the coated fibres exhibits highly dispersive dielectric loss and similar behavior in its ac conductance, at low frequency range up to 7 kHz; beyond which its conductance is stabilized.

**Chapter 7: Overall summary** gives the summary of the experimental findings described in all the chapters. The results are displayed in a tabular form at the end of this chapter for better visualization and ready comparison of all the results.

Finally in **Appendix** the list of publications in the referred journals which emerges out of the works carried out in this thesis is displayed, along with the seminar/conference/workshop attended by the author

