Chapter 7

Overall Summary

Bio-molecule incorporated PPy shows remarkable change in electrical conductivity of the polymer due to change in its surface morphology and structural changes. The modified composite can be used for chemical sensing or other applications in the field of micro-electronics, bio-engineering etc depending upon the nature of conductivity change in the composite compared with pure PPy. We have used the composite formed by PPy with bile acid and bile salt for sensing of ethanol vapor in terms of changes in conductivity and other intrinsic properties, viz. surface morphology, particle size, crystalline nature, chemical bonding pattern and spectroscopic parameters like UV-Visible and PL absorption. The ethanol exposed film of PPy bile shows definite change pattern confirming our assumption of potential application of the composite as a chemical sensor for ethanol vapor. When cellulose is incorporated in the polymerization process the resulting polymer blend shows change in conductivity of the cellulose fibres which is imprinted from incorporation of PPy in cellulose and vice versa. This observation is visualized in modification of AC and DC conductivity of bamboo cellulose when a PPy nanocoating is incorporated as a surface layer in virgin bamboo fibres. Changes in conductivity are attributed to the changing dielectric properties of the composite compared with pure PPy.

Introduction of Cholic Acid (CA) results in considerable change in surface morphology as well as its molecular weight. Particles in the PPy/CA composite are dispersed in different forms and sometimes nucleated to make it a multi phase pattern on exposure to ethanol. Resistance of PPy in unexposed state is 3.03 kΩ which changes to 0.71 kΩ, while the resistance of the polymer composite changes from 2.3 kΩ to 0.39 kΩ when exposed to ethanol. Low frequency impedance spectra for 50, 100, 200 and 500 Hz shows maximum current in the lowest frequency i.e. 50 Hz which has gradually decreased with increasing frequency (i.e. for 100 Hz, 200 Hz and 500 Hz) on exposure to ethanol. I-V shows a linear trend up to applied voltage of 1V in all the frequencies, while this trend gradually disappears in higher frequencies. The composite shows a linear pattern in I-V in the entire range of applied bias at 50 Hz, which is the threshold frequency for changeover to non linear nature in both the exposed and unexposed samples.

Ethanol sensitivity is more prominent in PPy when bile salt is incorporated in it. The PPy-bile salt composite shows agglomeration of particles and greater crystallinity when exposed to ethanol vapor. FTIR and NMR spectroscopy reveals the presence of bile salt in the composite which gives signature of ethanol in the ethanol exposed one. Alcohol exposure results in increase in electrical conductance from 7.08539 x 10^{-5} mA/V to 8.0356 x 10^{-5} mA/V. The number average molecular weight (M_n) of PPy composite in unexposed and exposed state are 26790 and 28780, while its weight average molecular weight (M_w) increases from 26990 to 28780 on exposure to ethanol. PL intensity is quenched and the PL peak shifts from 430 to 409 on ethanol intake. The changes are indicative of greater feasibility of PPy incorporated with bile salt for prospective use in ethanol sensing.

Changes observed in PPy with incorporation of cellulose and study of its morphological, structural and electrical properties are also undertaken**.** Chemical polymerization of Pyrrole incorporated with cellulose shows that the shape of the PPy particles depends on polymerization time. Increased polymerization time also results in increased crystallinity. Dielectric constant varies with frequency - increases exponentially in the low frequency range in the initial hours of polymerization and reaches a steady state with gradual increase in polymerization time. Conductivity is also found to increase exponentially in the low frequency and gradually increases with frequency, becoming steady in polymerization time of

48 hours. Cellulose incorporation in PPy results in a composite which shows predominance of ionic conduction.

From this finding, we carried out an experiment for introducing a PPy coating on bamboo cellulose fiber. Scanning and transmission electron microscopy reveals the formation of a nano-coating of polypyrrole, with the average diameter of particles in the range of 50 nm over the fibre surface. FTIR spectroscopy reveals that the chemical structure of the natural fibres remains unchanged even after the nano coating, though the individual characteristics of Py appeared therein. Electrical resistance of the coated fibre shows a decreasing trend with increasing Py concentration. The value ranges from 1075 kΩ cm^{-1} to 0.159 kΩ cm^{-1} with monomer concentration from 0.1% to 5%. Further, it shows Ohmic nature for both the coated and uncoated fibres. Dielectric behavior of the current-voltage (I-V) plots of the coated fibre exhibits highly dispersive dielectric loss and similar behavior in its AC conductance also, at low frequency range up to 7 kHz; beyond which its conductance is found to be stabilized.

To conclude, we say that we have successfully incorporated bile salt and bile acid in PPy and studied its ethanol sensing property. The sensing property is found to be more prominent in bile salt/ PPy composite and in each case surface modification of the PPy particles act as the driving force for sensing experiment observed through changes in electrical conductivity. A drastic change in electrical properties of PPy is also observed when cellulose is incorporated in it. The electrical conductance shows Ohmic nature in PPy on introduction of cellulose in it. Dielectric behavior of PPy is introduced in cellulose fibre when a PPy nanocoating is introduced in the latter. Both the dielectric and electrical properties of PPy are found to be effected by the surface morphology and particle size, on incorporation of the bio-molecule. Based on these results we anticipate fabrication of ethanol sensor by means of the synthesized PPy composite in future and also try to find out the changes in their mechanical properties with the introduction of bile acid, bile salt and cellulose.

Table 7.1 Overall Summaries

Studies	PPy/CA	PPy/Bile salt	PPy/Cellulose	Cellulose with PPy nanolayer
SEM	Composite layer with cavities	Agglomeration and aggregation of particles	Spherical shape on 48 hours polymerization time (PT)	Agglomeration of PPy particles on cellulose surface. PPy monolayer of particle size 80 to 50 nm
TEM	Nanosheet with layered structure		Increased Compactness with higher PT and formation of CNF	Pattern like quantum entanglement with homogeneous layer at 5% Py
AFM	Layered structure with “pull off” adhesion			
XRD		Peaks at 22 ° and 27° merges to form a sharper peak at 26° on ethanol expose	Crystalline nature arises higher Polymerization time.	
FTIR		Bands at 1400, 726,474 in addition to PPy peaks	Peaks for cellulose : 3400,2374,1642,1658 Peaks for PPy are blue shifted with cellulose incorporation	Both Cellulose and PPy peaks are found. Main Cellulose peaks are present after the layer is introduced
Mol. weight		M_w: 26990 to 28780		

		M_n : 26790 and 28780		
PL		430nm to 409 nm		
Electrical conductivity	Resistance of PPy changes from 3.03kΩ cm^{-1} to 0.71kΩ cm^{-1} and composite from 2.3kΩ cm^{-1} to 0.39 kΩ cm^{-1}	7.08539 x 10^{-5} mA/V to 8.0356 x 10^{-5} mA/V		
Dielectric Properties	Z inversely proportional with time and frequency, with different trend at 500 Hz		$\varepsilon^{/}$ and $\varepsilon^{//}$exhibit stronger dispersion at low frequency range. Conductivity shows non-linearity above 3kHz	PPy coated fibres exhibit remarkable AC conductivity in the low frequency range 10 Hz to 7 KHz showing an increasing conductivity with increased Py concentration