Abstract

Conductive polymers (CP) are gaining interest day by day due to their growing fields of sophisticated uses. Conventional polymers are generally known to be insulators with their limited use as electrical insulators in any device making purpose. But these have high degree of mechanical strength and mold procesability to facilitate them constructing desirable materials. CPs on the other hand can attain near metallic electrical conductivity at their highest doped state. So they can be thought as good replacement for metals in many aspects. But the problem is not so simple, as the CPs at highest doped state are not at all processable, have very low mechanical strength and mostly not stable also. CPs have characteristic feature of tunable electrical and optical properties, which make them suitable for various device applications. In fact, retaining the electrical and optical properties, if some strength and processability property can be incorporated, CPs can play havoc. That is no wonder why CPs demand in US is rising by 5.8 percent annually.

Polyaniline (PANI) and polypyrrole (PPY) are particularly attractive materials amongst CPs due to their excellent environmental stability along with other features such as, low cost, high conductivity upon doping, and ease of synthesis. In spite of all these advantages, their device applications are limited due to their unprocessable nature. These can neither be solution processable (as they are not soluble in any solvent) nor melt processable (as they decompose before reaching a softening or melting temperature). There are various methods to overcome these problems, one of them, which has been adopted by us is to blend the CPs with some conventional polymers, like polyvinyl alcohol (PVA), polyvinyl chloride (PVC), poly- methylmethacrylate (PMMA) etc. The resulting blend will obviously have improved mechanical property of the latter and electrical conductivity of the former. However it is seen that in this process one has to sacrifice some electrical conductivity. Basically, one has to tactfully compromise between the two factors to attain some meaningful applications. Lately, the rapidly expanding field of nano CP composites is generating many exciting new materials with novel properties. It is therefore of immense significance to explore nanostructures of these CP composites’ performance in these already established areas.
Furthermore, whether reliable and scalable synthetic methods can be developed for the synthesis of PANI-PVA and PPY-PVA microstructures and nanostructures in order to provide the necessary materials base for both research and industry. The main objective of the present work is the quest for processibility of these CP, blends/composites at micro as well as nanoscale. This thesis has been organized into 5 chapters. Chapter 1 embodies the general introduction to CPs, their structure and mechanism of conduction, method of synthesis, doping, processibility, drawbacks and methods to overcome their processibility problems, CP composites, blends and their preparation methods, applications, advent of nanotechnology, composites, microscale as well as nanoscale synthesis and current applicative studies of conducting polymers. Finally, aims and scope of the thesis are briefed.

Chapter 2 deals with the materials used and methods of synthesis formation of composites of PANI and PPY with PVA and film preparation. Further, this chapter illustrates different characterization techniques for optical (FTIR), morphological (FESEM), structural (XRD) and electrical (conductivity, I-V characteristics and temperature dependent electrical conductivity properties of spin-cast films). At last, their application for fabricating FET is discussed.

Chapter 3 includes the synthesis and characterization of PANI with PVA by dispersion polymerization method. The said polymerization process is repeated for various molar ratios of aniline to vinyl alcohol repeat units in PVA (1 M/M-13 M/M) in order to obtain various types of PANI-PVA blends. FTIR spectroscopy results indicate very strong cross link between the PVA and PANI molecules in the dispersion of all ratios. The absence of band at 3400 cm$^{-1}$ (N-H stretching) and stronger band at 1131 cm$^{-1}$ indicate some type of tubular alignment in 1:11 ratio film. The FESEM results show an increase in homogeneity and decrease in particle size with rise of PVA content. According to their grain sizes, the composite films are classified into three categories depending upon the PANI-PVA ratios:

- In the range 1:1 to 1:3, nanocomposites show micron range particles with particle size 0.3 to 1.2 μm.

- In the range 1:5 to 1:9, nanocomposites show nanometer range spherical particles with particle size 100 to 20 nm. With increase of PVA there is a decrease in particle size and an increase in alignment.
• For the ratio 1:11, the composite shows tubular or rod structure with diameter and length of 100 to 500 nm, and 3 to 16 μm respectively.

• Beyond 1:11 ratio, the composite does not give any meaningful structure.

XRD pictures depict an increase in crystallinity induced in the films with increase in PVA contents. There is a decrease in conductivity value with increase in PVA content, but a slight rise with respect to 1:11 ratio film. The I-V characteristics follow a nonohmic behaviour showing current value to have power law dependence i.e, $I \alpha V^n$ with $n$-values ranging from 1.80 to 0.15 and for 1:11, it is 1.26 i.e., it decreases with the increase of PVA content but except in 1:11 ratio film. The temperature dependence of electrical conductivity follows the two-dimensional variable range hopping model. But for 1:11 ratio film, there is a sort of phase transition.

Chapter 4 includes the synthesis and characterization of PPY- PVA composite. PPY is prepared by interfacial polymerization method at the toluene water interface. The polymerization is done at two different temperatures, one at 310 K and the other at 273 K. The blend is formed by mixing PPY and PVA, and the films obtained from this are characterized by usual techniques. FTIR spectroscopy results indicate very strong cross linking between PVA and PPY molecules in the composite. The FESEM results show the change in morphology with polymerization temperature. Nanorods of dimension 30-50 nm in diameter and 0.5-3.0 μm in length are found for PPY prepared at 310 K and spherical particles of average grain size 200 nm are observed for PPY prepared at 273 K. XRD pictures demonstrate an increase in crystallinity induced in the films with increased polymerization temperature. Conductivity value (0.35 and 0.60 S/cm) is also found to be increased with increase in polymerization temperature. The I-V characteristics follow a nonohmic behaviour showing current value to have power law dependence i.e $I \alpha V^n$, $n$ value (0.08 and 0.20) is found to increase with increase of polymerization temperature. The temperature dependence of electrical conductivity follows the two-dimensional variable range hopping model.

Chapter 5 focuses on one potential application of the synthesized PANI and PPY blend films to field effect transistor (FET). The PANI- PVA and PPY- PVA blend films spin cast on different substrates are used to fabricate FETs. The I- V characteristics resemble the behaviour of a FET. The source-drain current decreases with increasing gate voltage ($V_G$) which demonstrate that
the device operates like a FET. The majority carriers are hole as expected for doped PPY and PANI. The threshold voltage $V_{TH}$ of the blend films are found positive which implies that the active layer accumulates sufficient holes in the conduction channel, before negative gate bias is applied which is expected from PPY and PANI. Furthermore, the films shows good mobility and transconductance.