

Polypyrrole/Multi Wall Carbon Nanotube/Viscose Composites For Smart Fabrics

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Abstract

Owing to the excellent electrical properties of carbon nanotubes and conducting polymers independently, an attempt has been made to combine both these materials for giving a conductive coating for viscose non-woven substrate; which could be used in several applications from anti-static to high performance supercapacitors, actuators. Chemical insitu polymerization has been used to coat carbon nano tubes, Polypyrrole – a conducting polymer over the textile fabric. Polypyrrole was also coated separately over the same viscose fabric with which both the coated fabrics viz. with and without carbon nanotubes, are comparatively studied. The synergism of the materials, carbon nanotubes and polypyrrole has enhanced the electrical properties of the textile substrates when compared with their individual performance.

1.1 Introduction

Natural and synthetic fibers, non-woven fabrics represent an ideal substrate for the applications where high surface-to-mass ratios, good mechanical performance, resistance to chemicals and harsh environmental conditions, flexibility, and ability to be shaped in various forms able to fit end-use requirements. Viscose fiber is exclusively selected for this research as they are 100% biodegradable and it is the only fiber naturally regenerated from pulp i.e. cellulose for more than 100 years rather than all other synthetic fibers are based on crude oil. The fiber properties are similar to

those of natural fibres like silk and cotton but can be modified to meet specific requirements. The result is a soft, smooth, highly absorbent along with broad spectrum of fibre properties which made viscose ideal for a wide range of very different applications, from apparel textiles to nonwoven materials [1]. Therefore, in the present attempt intrinsic conducting polymers and carbon nanotubes are coated on the viscose non woven substrate, which makes it a 'functional intelligent textile'.

Carbon nanotubes (CNTs) have attracted special attention owing to their especially unique structure, high surface area and high thermal and electrical stability. CNTs when inserted into a polymer matrix can improve the electrical conductivity as well as the mechanical properties of the original polymer matrix. CNT play a role as hard templates for conducting polymer (CP) to attain the materials with nano structures, and these materials have promising application as photovoltaic cells, actuators and supercapacitor etc [2].

Conducting polymer (CP) is a kind of polymer with π -bonds and CNTs also have conjugated π -bonds which enable CNT to be also considered as a kind of CP composed solely of carbon. The well known reason for CNT being able to play a role as hard templates for CPs is known as follows: each carbon atoms of CNT has a surplus p-orbital and the electrons in the surplus p-orbitals form highly delocalized big π bonds. These delocalized π electrons can bond with the π electrons with CPs to form π - π non-covalent bonds, so that the energy of the system can be reduced to form a new stable system. Thus the CPs bond with the side walls of CNT in the form of π - π non-covalent bonds and the CP-CNT composites with core shell structures can be obtained [3]. Therefore, multiwall carbon nanotubes (MWCNT) was employed along with polypyrrole and coated over viscose nonwoven substrate for preparing smart textiles in our research.

1.2 Materials

Multiwall carbon nanotube was purchased from SRL chemicals, Mumbai. Pyrrole monomer (extra pure) was used as received from SRL chemicals, Mumbai and stored at -10°C . Ferric chloride hexahydrate 98% ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) is used as an oxidant as received from Alpha Aesar, Great Britain. Non-Woven Viscose fabric was purchased from Ginny filaments and was used as base fabric.

1.3 Methods

1.3.1 Functionalization of MWCNT

As functionalized MWCNT gives higher performance than pure MWCNT due to presence of functional groups in their walls of MWCNT, MWCNT was functionalized and used. For the oxidative functionalization of MWCNT, 0.15 g of the MWCNTs was mixed with 35 ml of nitric acid solutions by mechanically stirring in a hot plate for 15 min at 60°C . In order to minimize tube damage, a low power sonicating bath and a relatively low acid exposure time were used. Therefore, the mixture was sonicated in an ultrasonic bath for only 2 h, promoting MWCNT disentanglement within the acid solution. Then, the slurry was filtered and thoroughly washed with distilled water.

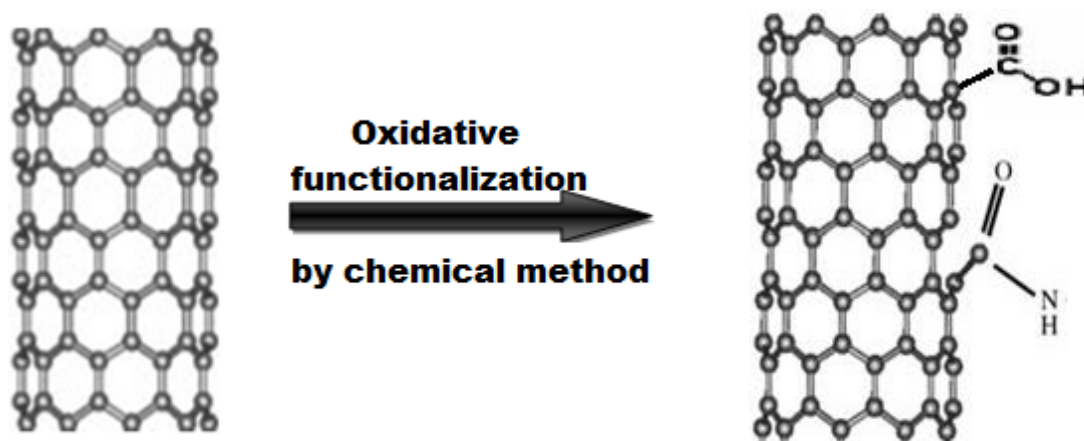


Fig 1.1 Depiction of functionalization of CNT

The solvent was exchanged with hydrogen peroxide (30% v/v) and the procedure was identically repeated. The subsequent treatment with H_2O_2 was given in order to complete the oxidative process started by HNO_3 , but in a gentle manner. Finally, the slurry was dried in a hot air oven at $150^\circ C$ for 4 h. This treatment promotes the formation of O-H, C=O groups over the walls of MWCNT by which they can disperse properly in water for further in-situ polymerization with PPy and also these groups helps in linkage both with fabrics and PPy which enhances the overall property of the composite [4] as shown in Fig 1.1.

1.3.2 Synthesis of PPy/MWCNT/Viscose composite:

Several methods for preparing polymer-CNT composites have been developed. The most promising method to obtain more dispersive CP-CNT-fabric composites is to polymerize monomer insitu in the presence of CNT, as it satisfies the particular two important factors viz. the even polymerization of monomer and the well dispersion of CNT. The synthetic route followed is summarized below, MWCNT were dispersed into the solution containing ferric chloride through sonication for 2hr. The viscose non woven fabric (5x5cm) was immersed in this solution and stirred for half an hour. Pyrrole was separately sonicated in aqueous media for half an hour. This reaction initiator pyrrole monomer was added slowly to the above said ferric chloride-CNT-fabric solution with constant stirring, to initiate the polymerization process. Then the reaction was allowed to proceed in room temperature for another 6 hrs. During the polymerization, the reaction system was quite stable without any evident precipitation. Finally, the polymerized fabrics were rinsed with acetone, methanol and water repeatedly, and then obtained black fabric was dried in vacuum at $60^\circ C$ for 24 hrs. Two percentage of MWCNT was employed and they are 0.05%, 0.1% with monomer: dopant ratio as 1:1 under 0.05, 0.1, 0.2 M concentration of Pyrrole [5].

Pyrrole was also polymerized with fabrics for better understanding of the properties of the conductive fabrics by comparing them with PPy/CNT/Viscose fabrics. PPy/Viscose fabrics were prepared with the same procedure of insitu polymerization discussed above, just without the addition of MWCNT.

1.4 Characterization

The deposition of electroactive materials on viscose fabric was characterized by using Perkin Elmer FT-IR spectrometer (Model Paragon 500) in the transmittance mode and it was compared with the bare viscose. X-ray powder diffraction (XRD) pattern of samples were recorded on PANalytical X'PERT PRO system with Bragg-Brentano geometry using Cu $K\alpha_1$ radiation, operating at 40 kV and 30 mA, where $\lambda = 1.54 \text{ \AA}$ for the Cu $K\alpha_1$ line. Conductivity of PPy coated viscose fabric was measured using four probe conductivity meter, Model: DFP-02 BESTO at room temperature.

1.5 Results and discussion

1.5.1 FTIR studies

The prepared PPy-MWCNT-Fabric was spectrally analyzed through FTIR and the FTIR spectra of bare viscose, 0.2 M PPy/Viscose, 0.2 M PPy/MWCNT/viscose fabric composites are compared and shown in Fig 1.2. The IR Spectra of the bare viscose shows a peak at 2896, 3318.9 cm^{-1} corresponds to C-H and O-H stretching respectively. There are various functional groups present in the viscose (C-C)str, (C-O)str, and (C-O-C)str which shows peak at 1128, 1056, 881 cm^{-1} respectively as shown in figure 4.6. Natural ageing of cellulose causes partial oxidation of alcoholic to carbonyl functional group due to which a peak appears at 1695 cm^{-1} [6].

The FTIR spectra of 0.2M PPy/Viscose shows the presence of characteristic absorption bands at 1510, 1456 cm^{-1} (N-H, C = C stretching of pyrrole ring), 1299 cm^{-1} (C-N stretching vibration in the ring), 1141 cm^{-1} (C-H inplane deformation), 1006 cm^{-1} (N-H in-plane deformation), 900 cm^{-1} (C-H out-of-plane deformation), 885 cm^{-1} (C-H

out-of-plane ring deformation) and 669 cm^{-1} (C-C out-of-plane ring deformation or C-H rocking) [7].

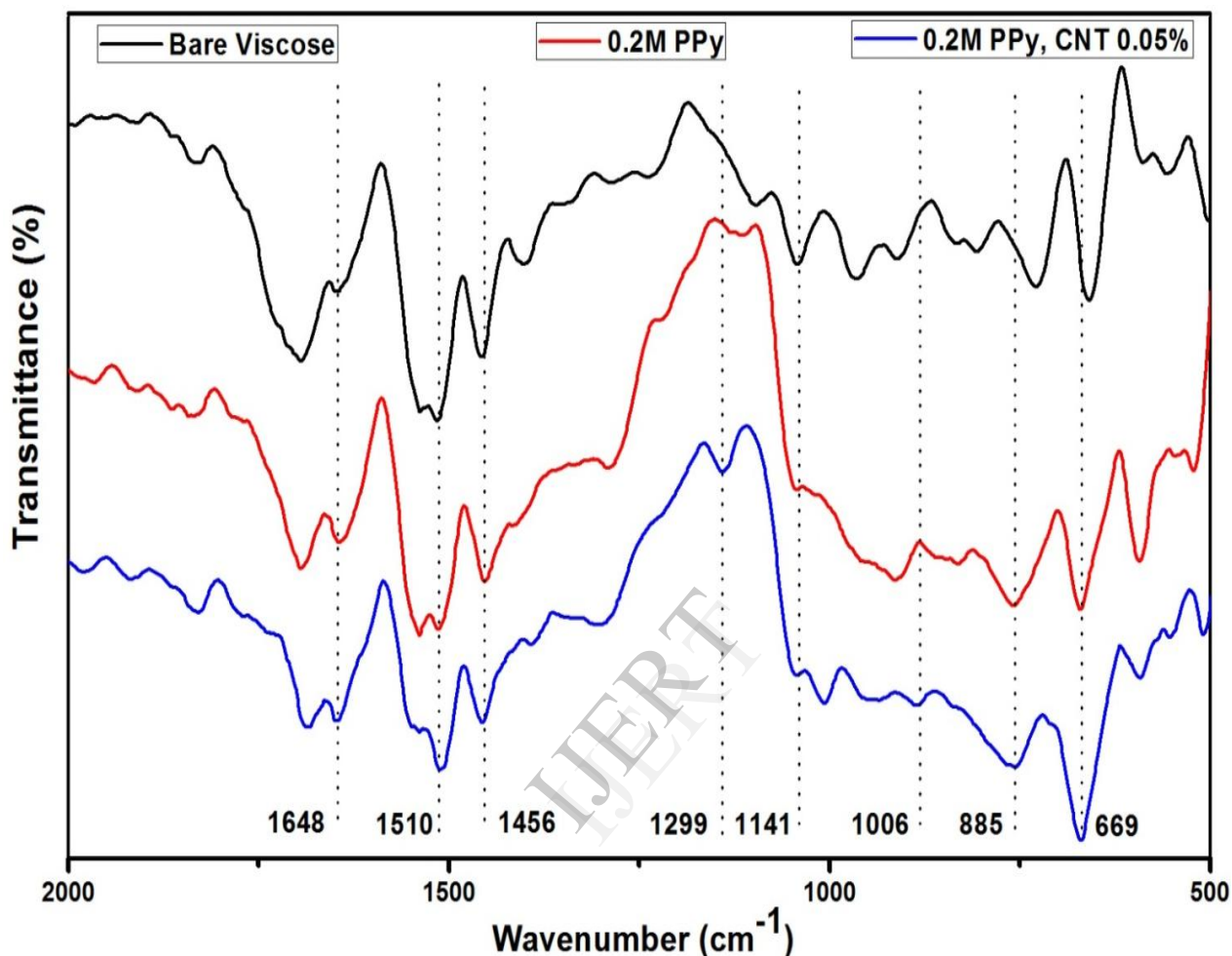


Fig 1.2 FTIR spectra of bare viscose, 0.2M PPy treated viscose, 0.2M PPy CNT-0.05% treated viscose

The IR spectrum of 0.2M PPy/MWCNT (0.05%)/Viscose fabric composite shows important absorption bands of MWCNT at 3411 cm^{-1} (attributed to OH stretching), 2869 cm^{-1} (assigned to asymmetric CH_2 stretching), 1648 cm^{-1} (assigned to conjugated C=C stretching), and 1097 cm^{-1} (corresponding to C-O stretch in alcohols), the aliphatic hydroxyl bending (1456 cm^{-1}) bands. The presence of these functional groups on the PPy/MWCNT composite implies that they were introduced during the oxidative functionalization of MWCNT. PPy/MWCNT coated viscose composites shows the

spectral features of both PPy as well as MWCNT with some shifts which means that there is an interaction among MWCNT and PPy without any damage to the backbone structure of the PPy [3, 8].

1.5.2 XRD studies

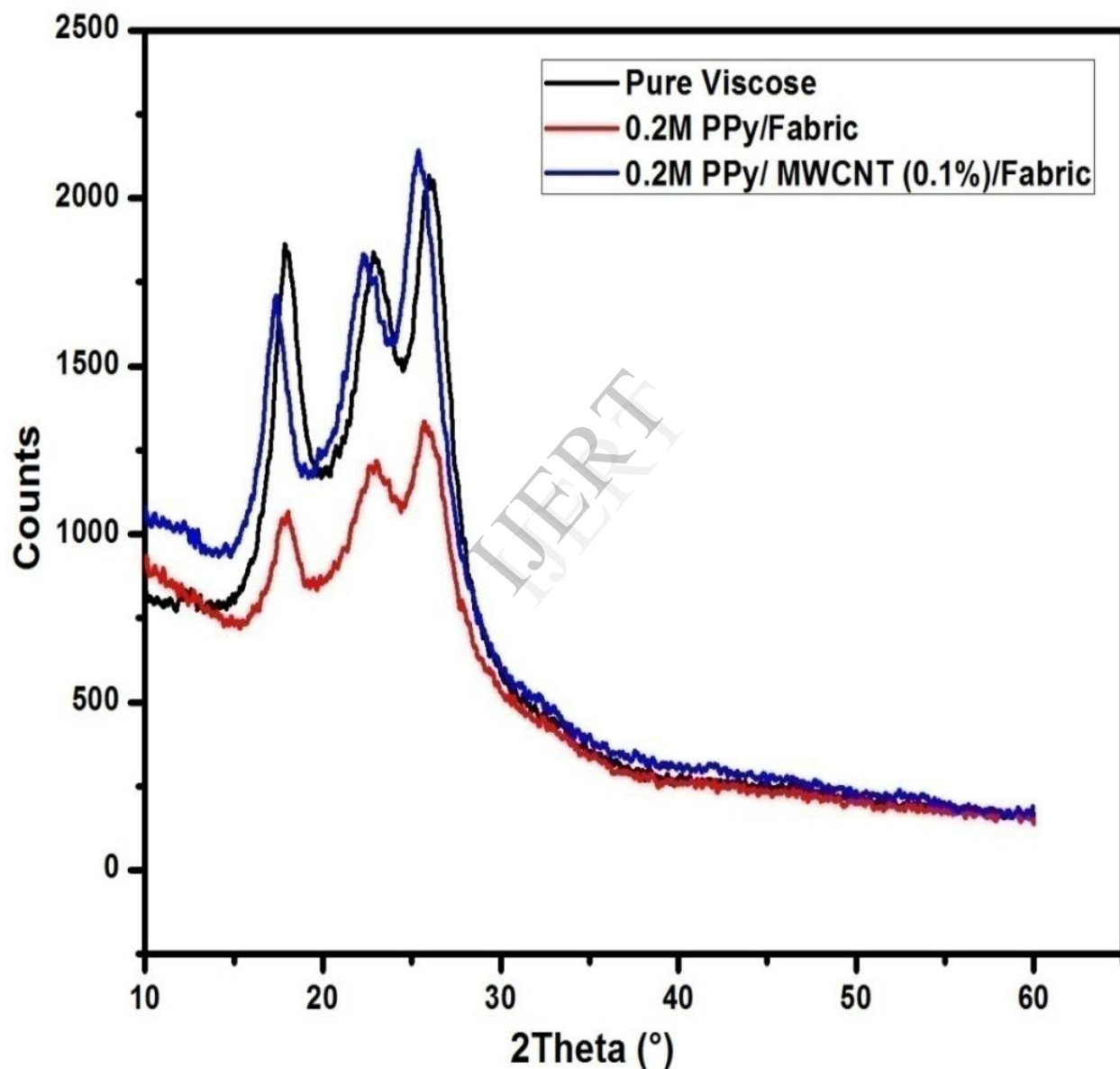


Fig 1.3 XRD of pure viscose, 0.2M PPy/Fabric, 0.2MPPy/CNT(0.1%)/Fabric

The XRD spectra of pure viscose, 0.2M PPy, 0.2M PPy/MWCNT(0.1%)/Viscose fabric composites are shown in Fig 1.3. The pure viscose and PPy-MWCNT composite shows peaks at 17.86, 22.861, 25.97° and 17.30, 22.34, 25.34° respectively. There is a small shift and narrowing of peak is observed between them. The 0.2M PPy coated composites shows peak at 18.05, 22.99, 25.7° which shifts largely from pure viscose. This large shift and blunt peak shows the uneven coating of PPy over the fabric surface. But the XRD patterns of PPy/MWCNT/Viscose composites are very similar to those of pure viscose showing the uniform coating of PPy-MWCNT over the entire fabric surface. The amorphous structures of PPy/MWCNT composites may have an improved spatial order which was confirmed by the narrowed shape of the XRD pattern. The broad characteristic peak at about $2\theta = 22^\circ$ of PPy as well as PPy/MWCNT coated fabrics exhibits that PPy coated fabric is amorphous [3, 8, 9].

1.5.3 Electrical properties

The electrical conductivities of the PPy, PPy/MWCNT viscose fabric composites are as shown in the Figure 1.4. It can be very well found that the electrical conductivities of PPy-MWCNT-Fabric composites are higher than that of PPy coated fabrics with monomer: dopant ratio as 1:1. The increase of electrical conductivity may be owed to the charge transfer from PPy to MWCNT and the improvement of the compactness of PPy by MWCNT. Increased compactness means more amount of PPy is present in the fabric (more π - π interaction) which will lead to more, faster charge transfer leading to enhanced conductivity.

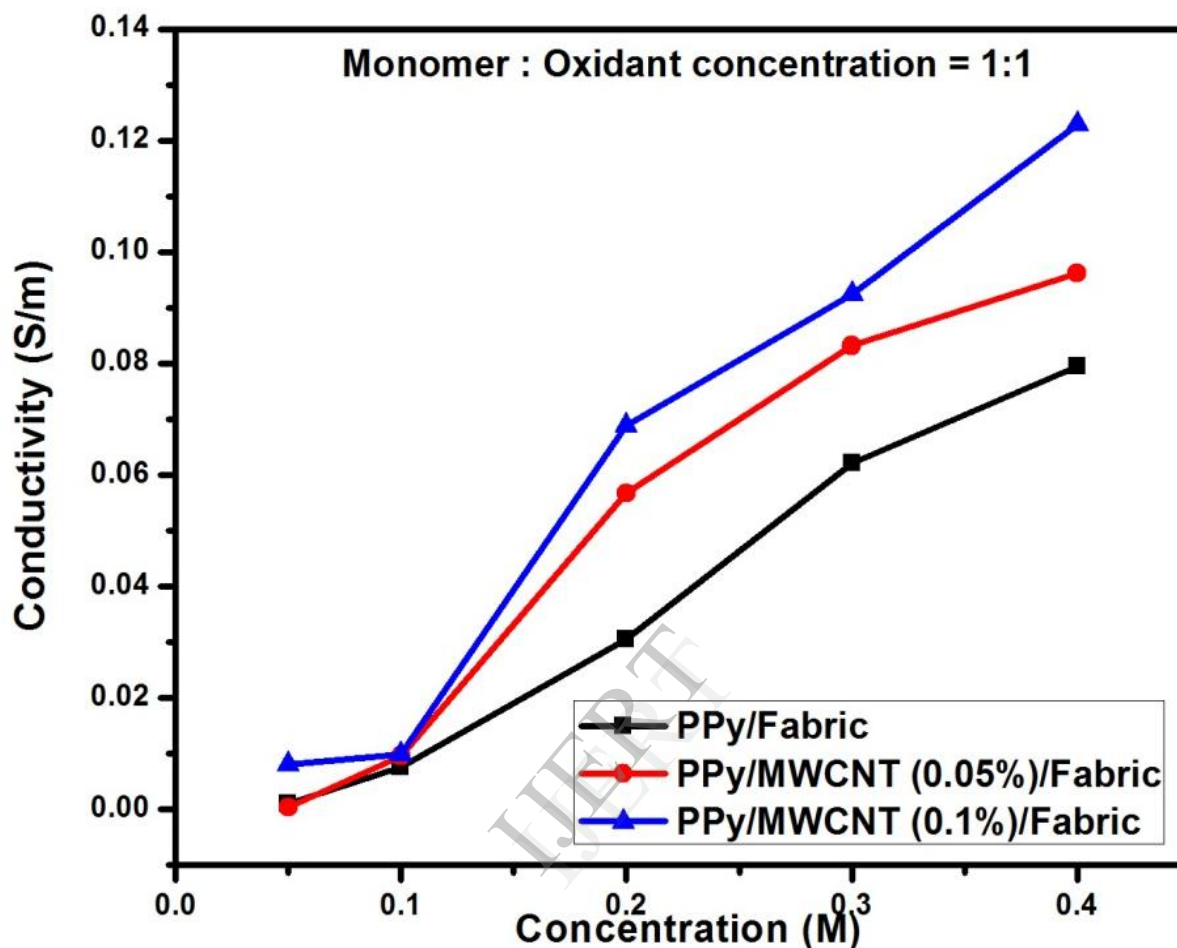


Fig 1.4 Conductivity of the composite fabrics

The electrical conductivity enhanced with the increase in the weight percentage (0.05, 0.1%) of MWCNT in the composite as expected. This is also shown in the Fig 1.4. Obviously the reason for enhanced conductivity is due to the fact that higher amount of MWCNT will definitely provide larger area for deposition of PPy which will lead to increased charge availability as well as charge transfer. The compactness of PPy also will definitely increase which in turn increases the overall conductivity of the fabric [9].

1.6 Conclusion

In summary, a uniform polypyrrole with well dispersed functionalized MWCNT film has been successfully coated over viscose non-woven fabric through an in-situ chemical oxidative polymerization. FT-IR and XRD studies clearly indicated the interaction of PPy with functionalized MWCNT. The deposition of PPy, MWCNT over viscose non-woven fabric exhibit higher conductivity than PPy coated fabric indicating the π - π interaction between MWCNT and PPy. This nano-composite coated fabric will encompass application in especially fabricating the desirable performance of various electronic devices, actuators, mechanical sensors.

1.7 Acknowledgement

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1.7 References

1. Walter Roggenstein, "Viscose fibres with new functional qualities", *Lenzinger Berichte* 89 (2011) 72-77
2. David W. Hatchett and Mira Josowicz, "Composites of Intrinsically Conducting Polymers as Sensing Nanomaterials", *Chem. Rev.* 2008, 108, 746-769
3. Hongfan Guo & Hong Zhu & Haiyan Lin & Jiqiao Zhang, "Polypyrrole–multi-walled carbon nanotube nanocomposites synthesized in oil–water microemulsion", *Colloid Polym Sci* (2008) 286:587–591
4. Dimitrios Tasis, Nikos Tagmatarchis, Alberto Bianco, and Maurizio Prato, "Chemistry of Carbon Nanotubes", *Chem. Rev.* 2006, 106, 1105-1136
5. A. Malinauskas, "Chemical deposition of conducting polymers", *Polymer* 42 (2001) 3957-3972.
6. X. Colom, F. Carrillo, "Crystallinity changes in lyocell and viscose-type fibres by caustic treatment", *European Polymer Journal* 38 (2002) 2225–2230
7. T K Vishnuvardhan, V R Kulkarni, C Basavaraja And S C Raghavendra, "Synthesis, characterization and a.c. conductivity of polypyrrole/Y2O3 composites", *Bull. Mater. Sci.*, Vol. 29, No. 1, February 2006, pp. 77–83.
8. K. Firoz Babu, R. Senthilkumar, M. Noel, M. Anbu Kulandainathan, "Polypyrrole microstructure deposited by chemical and electrochemical methods on cotton fabrics", *Synthetic Metals* 159 (2009) 1353–1358
9. A. Varesano and C. Tonin, "Improving Electrical Performances of Wool Textiles: Synthesis of Conducting Polypyrrole on the Fiber Surface", *Textile Research Journal* 2008 78: 1110-1115