

Conducting Polymer/CNT Coated Flexible Electrode for Supercapacitors

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Abstract

Conducting polymers (CP), Multi-Wall Carbon nanotubes (MWCNT) when synthesized chemically or electrochemically as free standing films, they exhibit poor mechanical properties, which hinder their practical applications. This limitation is overcome by allowing the polymerization to take place on flexible surfaces such as textiles to produce conductive materials with excellent mechanical properties which could be used as electrode material (high energy density due to low weight of electrode) in supercapacitor (SC). The composite materials of PPy/CNT/Fabric have improved conductivity, mechanical stability, specific capacitance and processability which make them suitable for supercapacitance applications.

1. Introduction

Supercapacitor (SC) is a tool that meets the growing energy demands by giving high energy density in a small package. The capacitance properties of Polypyrrole (PPy) conducting polymers can be greatly enhanced by forming composites with other materials such as carbon (carbon nanotubes), inorganic oxides and hydroxides, and other metal compounds.

Nanotubes have high conductivity, large surface area (1 to >2000 m²/g), good corrosion resistance, high temperature stability, percolated pore structure, and can be functionalized to optimize their properties, have chemical and mechanical stability. MWCNTs are electron acceptors and PPy is an electron donor so the two form a charge-transfer complex and gives extraordinary properties [1]. Surface conditions are extremely important for achieving high capacitance, with porosity playing a vital role. Textiles are versatile materials with a fiber network structure, are typically flexible and porous. This morphology, together with their rich surface chemistry and reliable stability, allow the wide use of textiles in non-aesthetic applications. Textiles meet all the requirements perfectly to utilize it as the substrate to coat conductive materials for using it as electrode in supercapacitance applications. Polypyrrole (PPy) conducting polymer is combined with Multi Wall Carbon Nano Tubes (MWCNTs), coated over

fabrics and studied for its capability to use it as the electrode for supercapacitor.

2. Materials

Pyrrole (SRM chemicals, Mumbai) was stored in refrigerator and used without any distillation. Ferric Chloride hexahydrate (FeCl₃) is used as oxidizing agent for the preparation of PPy was used as received from Alpha Aesar. Commercially available 100% Polyester (PET) and 100% Linen fabric were used as coating substrate.

3. Methods

The procedure for coating the MWCNT with PPy over fabrics is presented here: MWCNT was dispersed in ferric chloride solution with 50ml of millipore water under sonication. Due to the lower dispersibility of MWCNTs in water, ultrasound was applied to achieve a better dispersion of MWCNTs in aqueous solution before and during chemical Polymerization. Fabric was immersed in this oxidant/MWCNT solution for 45minutes. Pyrrole was sonicated in 50ml of millipore water and added drop wise to the solution of oxidant/MWCNT/fabric. This makes polymerization to start and PPy/MWCNT starts to deposit over the fabric making the fabrics conductive. The irradiation of ultrasound without changing the molecular bonding patterns of PPy, the ultrasound caused emulsification by the rapid motion of the molecules which resulted in efficient mixing, thereby enhancing the properties of the fabrics [2].

4. Characterization

Scanning electron microscope (SEM), HITACHI Model S-3000H was employed to characterize the morphology of the composite with various magnifications. X-ray diffraction data sets were collected at room temperature on a PANalytical X'PERT PRO system in Bragg-Brentano geometry using Cu-K α_1 (1.540Å) radiation. The powder diffraction covered the 9° < 2 θ > 60° range with 0.0170° steps. FT-IR spectra were recorded using PerkinElmer FTIR spectrophotometer, Model Paragon 500. The cyclic voltammetry of the PPy coated fabrics was

measured by IM6 electrochemical analyzer, Germany using Thales software.

5. Results and discussion

5.1. Morphological studies

The substrate morphology of controlled PET and the PPy/MWCNT/PET were observed by Scanning Electron Microscope (SEM) and is shown in Fig.1. PET fibres are covered completely with the hybrid material and the surface has a rough appearance with presence of polypyrrole aggregates over the fabric's surface. Elements of high atomic weight backscatter more electrons, so in the micrograph are observed as white color zones due to the presence of PPy/MWCNT. All the aggregates of PPy/MWCNT over fibres appear white colored, indicative that MWCNT is distributed homogeneously in the entire textile surface.

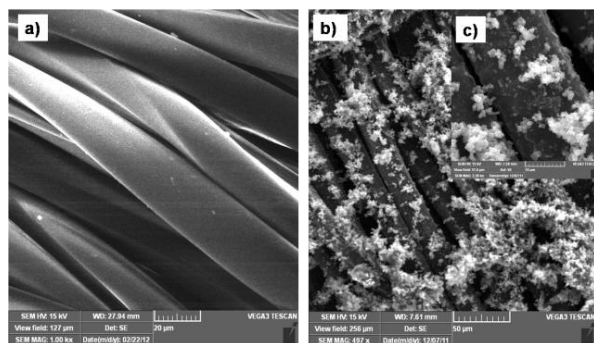


Fig 1 SEM image of bare PET, 0.2M PPy/ 0.05% CNT/ PET fabric

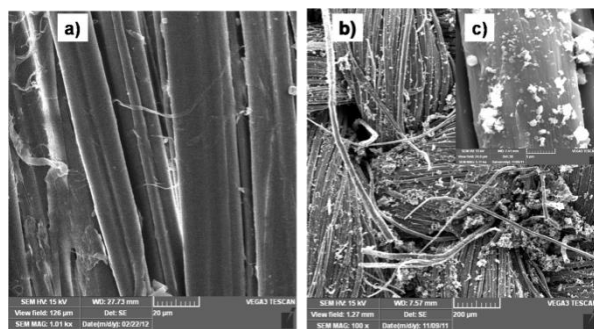


Fig 2 SEM image of bare Linen, 0.2M PPy/ 0.05% CNT/ Linen fabric

SEM micrographs of Linen and the PPy/MWCNT/Linen are shown in Fig. 2. In the figure PPy/MWCNT exhibit a nice 'cauliflower like' appearance with the uniform PPy/MWCNT over layer on the surface of the Linen. The surface of the fabric is covered with a more tightly packed layer of PPy, producing a more continuous morphology. Since no isolated PPy particles are evidenced from the micrographs, the speculation is that the PPy are well attached with MWCNT on the fabric surface, and herein a good compatibility between fabric and PPy/MWCNT components is achieved.

5.2. FTIR studies

The FTIR spectra of MWNT/PPy/ linen in Fig 3 showed the characteristics peaks for both MWNTs and PPy. The characteristic band for the PPy ring fundamental vibration appeared at 1552 cm^{-1} , and the C-H in-plane vibration and C-N stretching vibration appeared at 1456 and 1058 cm^{-1} , and at 1139 cm^{-1} , respectively. The peak for C=O groups was seen at 1645 cm^{-1} and the presence of the carboxylic groups on the nanotube surface is likely to give the interfacial interaction between the polymer and the nanotubes [3].

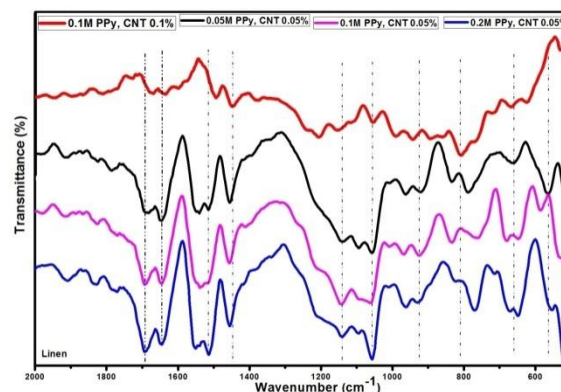


Fig 3 FTIR spectra of PPy/MWCNT/Linen composites

Fig. 4 shows the spectra of PPy/MWCNT/PET composites with two percentage of MWCNT viz. 0.05, 0.1%. The band centered at 1550 cm^{-1} associated to the pyrrole ring stretching vibration (C=C). The characteristic bands of the bending vibration of pyrrole can be observed at 727 , 1072 and 1155 cm^{-1} . Other bands overlapped with PET bands partially can be observed; like C-C stretching (1446 cm^{-1}) and C-N stretching (1596 cm^{-1}). The effect of MWCNT concentration in the FTIR spectrum can be observed in Fig. 4. It can be seen a general increase of all the bands mentioned previously when the concentration of pyrrole is increased from 0.05% to 0.1% which shows the uniform deposition of PPy/MWCNT [4, 5].

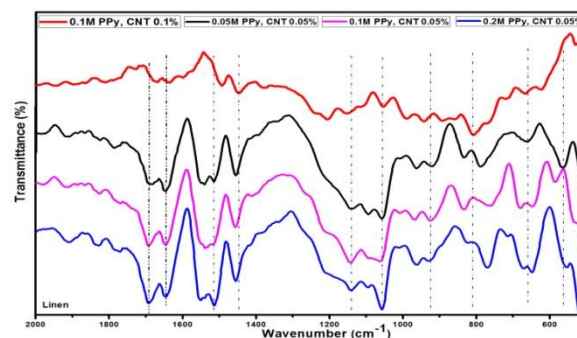


Fig 4 FTIR spectra of PPy/MWCNT/PET Composites

5.3. XRD studies

For the MWNT/PPy/Linen composites, the X-ray diffractograms as shown in Fig. 5, both the characteristic PPy broad peaks and the strong MWCNTs peaks. The pure PPy showed broad diffraction peaks at $2\theta = 25.4^\circ$ due to the pyrrole intermolecular spacing. Two broad peaks at $14.46, 17^\circ$ in the XRD pattern bare linen. The characteristic peaks of linen get shifted and sharpened from 23.19° to 22.96° after the fabrics were treated with PPy/MWCNT indicating the amorphism of the PPy as well thin and even deposition of PPy/MWCNT.

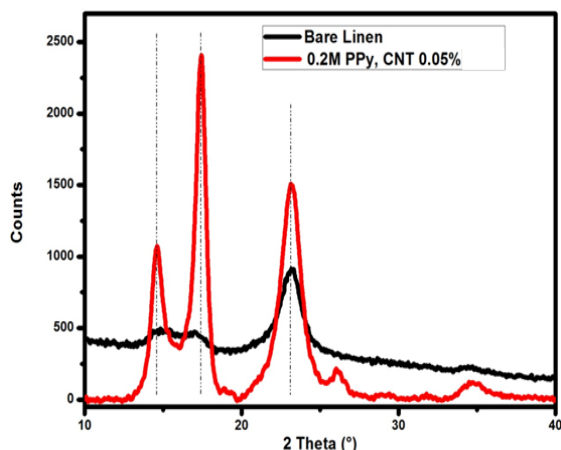


Fig 5 XRD spectra of PPy/MWCNT/Linen composites

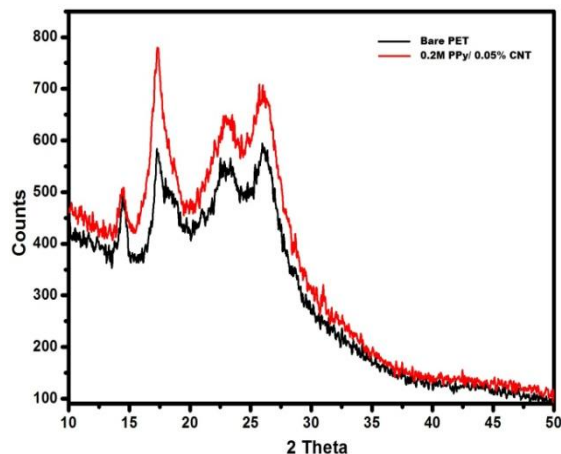


Fig 6 XRD spectra of PPy/MWCNT/PET composites

Fig 6 shows the characteristic XRD pattern of pure polyester and PPy treated polyester fabrics. The bare PET shows peak at $14.45, 17.28, 22.60, 26.06^\circ$ whereas the PPy treated fabric shows peak at $14.41, 17.28, 22.60, 26.06^\circ$. there was no big shift are sharper peaks observed like linen fabric which shows that PPy is highly dispersed and the surface of PPy/PET fabrics are not fully covered with PPy [4, 6].

5.4. Cyclic Voltammetry (CV)

The electrochemical performance of the PPy/MWCNT/Linen and PPy/MWCNT/PET composite electrode was evaluated by the CVs of the two-electrode cells assembled with the same electrode. The voltammograms obtained for the MWCNT/PPy/Linen and MWCNT/PPY/PET composite electrode at different scan rates are presented in Figure 7, 8 respectively. The CVs of both fabric composite electrode look almost like rectangular shape with good symmetry at all scan rates, showing highly efficient capacitive behavior with good charge propagation. From the cyclic voltammograms, the presence of CNTs in the composite changes the electrochemical properties of the polymers. It was suggested that there is chemical reaction between the CNTs and polypyrrole, and the CNTs enhances the property of the overall capacitance properties [7].

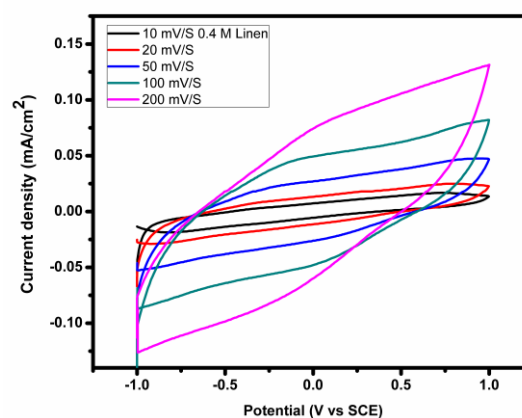


Figure 7 PPy/MWCNT/Linen fabrics composite at different scanning rates.

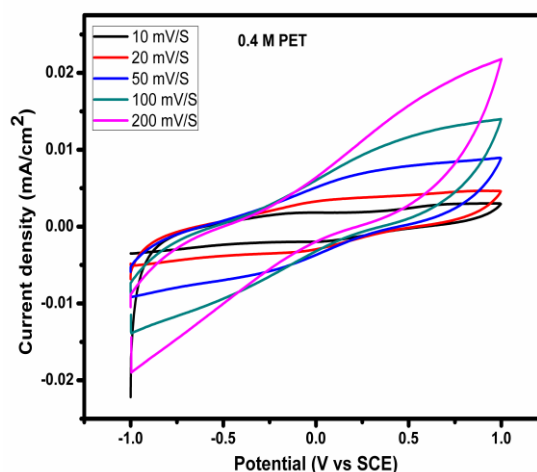


Figure 8 PPy/MWCNT/PET fabrics composite at different scanning rates.

The interactions were the strongest on linen than PET which has active end groups that interacted as secondary bonding sites with MWCNT. PET did not rely on the same type of secondary bonding force interactions and it has a reduced level of adhesion, although this interaction

was still reasonably strong due most likely to Vander Waals interaction.

6. Conclusion

Polyester and Linen fabrics were chemically polymerized with PPy, MWCNT successfully. SEM shows the presence of PPy/MWCNT aggregates over the fabric surface. FTIR, XRD, studies indicated that there was an interaction between substrates and electro-conductive polymers dictating strong adhesion between them. CV studies revealed a rectangular shape curve which shows the high capacitance of the prepared composite materials which can definitely used as electrode materials in supercapacitor.

7. Acknowledgement.

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8. References

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