

Development of Carbon-Epoxy Composites with Enhanced Electrical Conductivity

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Declaration

I hereby declare that the matter embodied in this report is the result of investigation carried out by me in the Department of Chemistry, Indian Institute of Technology Hyderabad under the supervision of **Dr. M. Deepa**.

In keeping with general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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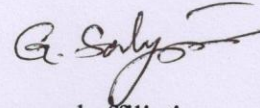
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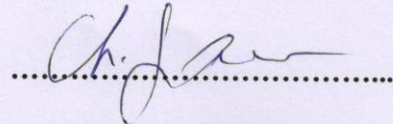
Approval Sheet

This thesis entitled “**Development of carbon-epoxy composites with enhanced electrical conductivity**” by Rini Majumder is approved for the degree of Master of Science from IIT Hyderabad.



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Dedicated to
My parents and family

Abstract

Highly conducting carbon-epoxy composites were developed in this project. The surfaces of carbon epoxy-composites were modified to increase the electrical conductivity of the composites. Conductive polymers namely poly (pyrrole) or (PPY) and poly(3,4-ethylenedioxythiophene) or PEDOT, PPY and PEDOT coated multiwall carbon nanotubes (MWCNTs) and metal nano-moieties (Cu nanoparticles, Cu nanowires) were used as reinforcement matrix for C-epoxy nanocomposites (CFRPs). For this purpose, *in-situ* polymerization of the monomers pyrrole and EDOT in the presence of carbon nanotubes was carried out by using sodium bis (2-ethylhexyl) sulfosuccinate (AOT) template and ferric chloride oxidant. The composites were characterized by Raman spectroscopy, Thermo gravimetric analysis and scanning electron microscopy. 2D laminated C-epoxy composites were prepared and the effect of different conductive reinforcement concentration (0wt%, 0.25wt%, 0.5wt% and 1.0wt%) on the electrical properties of the resulting composites were studied. Electrical conductivities were determined by using I-V and impedance methods. The inclusion of MWCNT/conducting polymers improved the electrical conductivity of C-epoxy composites considerably. These findings may have a significant bearing on realizing cost effective conducting C-epoxy composites with the ability to avoid static charge accumulation, especially for aerospace applications.

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1. INTRODUCTION:

Carbon-epoxy composites are extensively used in aerospace applications like missiles and aircrafts as they offer significant weight savings and withstand corrosion, fatigue [1-4]. However since the exterior surface of the carbon-epoxy composite is electrically insulating, as a consequence, there is accumulation of static charge on the surface, which leads to EMI/EMC problems during operation [5-7]. To circumvent this issue of static charge accumulation, it is imperative to increase the electrical conductivity of the carbon-epoxy composite, which can effectively prevent static charge build-up and thus allow smooth unhindered operation of the aerospace system [8-9]. Since it is the surface of the epoxy composite which tends to accumulate static charge, the conductivity of the surface or top layers of the composite needs to be improved either by introduction of electrically conductive moieties into the resin slurry for the top layers or by applying an external electrically conductive paint on the epoxy composite surface [10-12]. The focus is only on either increasing the conductivity of the topmost layers of the composite or by application of conductive paint coatings on the exterior surface, so that the mechanical properties (toughness and strength) of the epoxy composite remain unchanged. Conventional methods to improve electrical conductivity of epoxy based materials involve the incorporation of noble metal nanoparticles [13-15]. However, to achieve an excellent trade-off between good mechanical properties and a highly conducting surface for the composite, the most appropriate approach would involve inclusion of conducting moieties to the resin slurry that will be used for preparing the top layers of the epoxy composite, to ensure a uniform distribution of conducting moieties on the surface of the composite. The conducting nano-moieties that can be used for making the composite surface conductive can include any one and a combination of any two of the following: metal nano-moieties (Cu, Ag, Au- nanoparticles, nanowires or nanoribbons - these can be introduced into the resin slurry in the form of colloids) [14,15] and conducting polymer nanoparticles or fibers (these can be synthesized by electro-assisted methods or chemical polymerization, examples are poly(3,4-ethylenedioxythiophene), poly(pyrrole) etc and can be dispersed in the resin slurry) [16-18], carbon nanofibers decorated with metal nanoparticles (CNTs decorated with Ag nanoparticles) [19-20]. Elongated fibrillar conducting moieties were preferred as

they are expected to exhibit superior interconnectivity (and therefore higher conductivity) in comparison to regular nanoparticles.

2. Experimental details:

2.1 Raw materials:

Diglycidyl ether of bisphenol - A (DGEBA) epoxy resin and diethyl toluene diamine (DETDA) hardener were used as a matrix system. T-300 carbon fabric with satin weave was used as reinforcement. Conductive polymers like poly pyrrole (PPY), poly (3,4-ethylenedioxythiophene) or PEDOT, PPY and PEDOT coated multiwalled carbon nanotubes (MWCNT) are used as conductive reinforcements in the present study. Iron (III) chloride hexahydrate, functioned as the oxidant and dopant, was obtained from Sigma Aldrich. Sodium dodecylsulfo succinate (AOT), used as surfactant and dispersant, was purchased from Sigma Aldrich. Methanol, used in washing process, was purchased from Qualigens.

Epoxy resin:

1. Chemical Formula : diglycidyl ether of bisphenol A
2. Viscosity : 10,000Cp at 30⁰C
3. Density : 1.2 g/cc
4. Acid Value : 85-120
5. Commercial name : LY-556

Hardener:

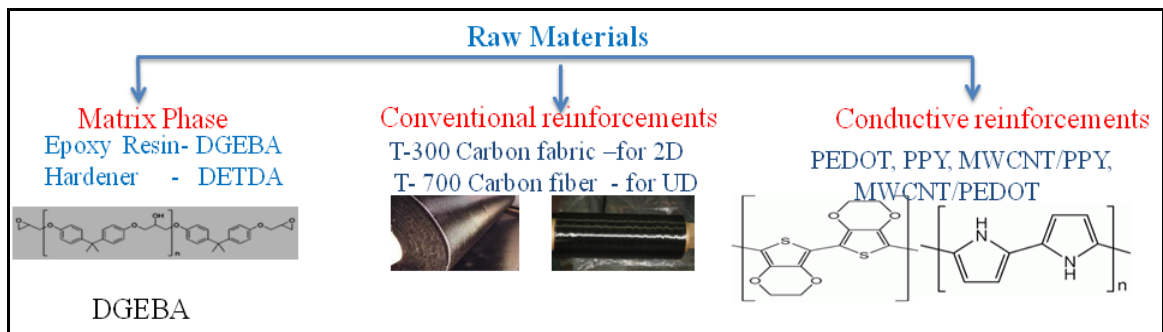
1. Chemical Formula : Diethyl toluene diamine
2. Viscosity : 200 at 25⁰ C
3. Density : 1.0 g/cc

Carbon fiber specification:

1. Tow size : 3K (3000 filament in tow)
2. Weaving pattern : 8 H satin
3. Density of fiber : 1.75 – 0.05 (g/cc)
4. Areal density of fabric : 380 g/m²
5. Thickness of fabric : 0.45 – 0.05 mm
6. Tensile strength(tow) : 3.5 GPa Avg
7. Tensile modulus(tow) : 180 GPa
8. Commercial name : T-300 grade fabric

Multiwalled Carbon Nanotubes (MWCNTs):

1. Purity : 99%
2. Metallic impurity : not more 1 wt%
3. Diameter : 100-200 nm
4. Length : 10-20 microns



2.2 Composite fabrication:

For fabricating the composites, initially conductive reinforcement (0,0.25,0.5 and 1.0wt% by weight of epoxy resin) were dispersed in the epoxy resin by using high speed mechanical stirrer at 1000 rpm(Remi motors, model-124 A) for 60 minutes followed by sonication at 50MHz frequency with a bath type sonicator (TRANS-O-SONIC, M/s Shanti Industrial Estate, India) for 90 minutes. CNFs-epoxy mixture was added with the hardener (24 parts of hardener to 100 parts of epoxy resin by weight) and this mixture was further sonicated for 15 minutes. C-fabric was cut into specific dimensions and impregnated with conductive reinforcement dispersed resin hardener mixture. Impregnated fabric layers were stacked and compressed. Curing was carried out for 2hours at 120°C followed by three hours curing at 180°C. Volume fractions (V_f) of the composites were controlled at 60% ($\pm 1\%$). V_f of the fabricated composite laminates was studied with acid digestion test, using concentrated nitric acid following ASTM D3171. Thus different 2D C-epoxy composites with different conductive reinforcements (conductive polymers, conductive polymer deposited MWCNTs and metal nanoentities) were fabricated. Electrical conductive properties for the prepared samples were measured by using I-V characteristics curves and

impedance spectrum .A minimum of three numbers of specimens were tested for each of the measured property and the averages were calculated. Microstructure of the fractured samples were analyzed with environmental scanning electron microscopy (ESEM-FEI Quanta 400, The Netherlands).

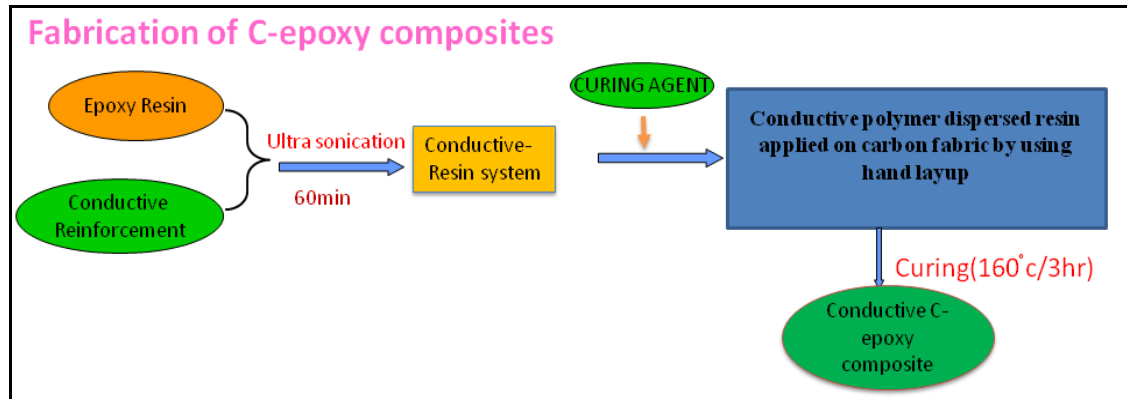
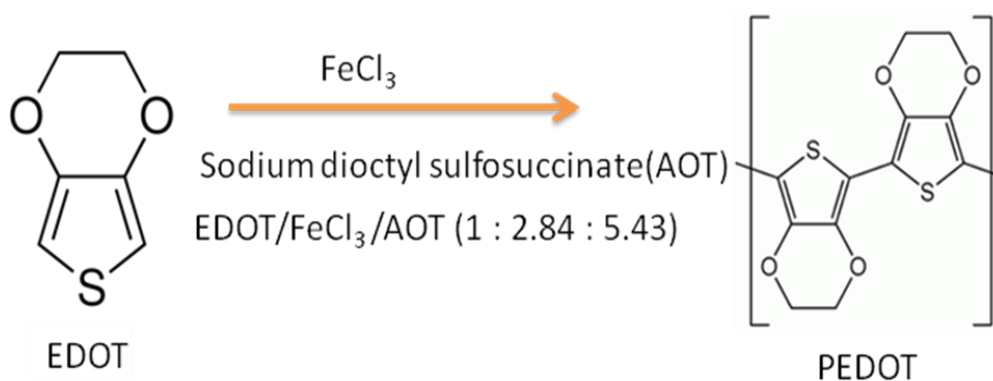


Figure 1: Schematic Diagram of fabrication of C-epoxy composites

2.3 Preparation of PEDOT:

PEDOT was prepared by *in-situ* polymerization of the monomer EDOT, by using sodium bis(2-ethylhexyl) sulfosuccinate (AOT) as template and ferric chloride oxidant [21]. A rapid, room temperature, reverse emulsion polymerization method to chemically synthesize bulk quantities of micrometers nano spheres of electrically conducting poly (3, 4-ethylenedioxythiophene) (PEDOT) is synthesized. A reverse micro emulsion was first prepared by dissolving AOT (sodium bis(2-ethylhexyl) sulfosuccinate) (19.12 mmol) in 70 mL of *n*-hexane and adding a solution of FeCl₃ (10.0 mmol) in 1.0 mL of water to it. The resulting orange-colored mixture was gently stirred for 5 min followed by addition of EDOT monomer (3.52 mmol). After 3 h under gentle magnetic stirring, the blue/black precipitate of PEDOT nanotubes was suction filtered and washed with copious amounts of methanol and acetonitrile. Drying under dynamic vacuum for 12 h at 80 °C yielded a blackish blue powder.



2.4. Preparation of (polypyrrole) PPY:

PPY was prepared by in-situ polymerization of the monomer pyrrole by using sodium bis (2-ethylhexyl) sulfosuccinate (AOT) as template and ferric chloride oxidant. Initially AOT (19.12 mmol) was dispersed in 70ml of n-hexane, then add a solution of FeCl₃ (10.0 mmol) in 1.0 ml of water to it. The resulting orange colored mixture was gently stirred for 5 min followed by the addition of pyrrole (2.0 mmol). After 3 h under gentle magnetic stirring, the black precipitate of PPY Was suction filtered and washed with copious amount of methanol and acetonitrile ,the resulting filtrate was then dried under vacuum.

2.5 Preparation of functionalized MWCNTs (MWCNT-COOH):

Pure MWCNTs (2 gm) were first ultrasonicated in tetrahydrofuran (THF) for 1 h at room temperature and then refluxed at 120°C for 4h using a round bottom conical flask with a magnetic stirrer (mild stirring). After cooling, the mixture was washed with distilled water. Then unmodified MWCNTs were dispersed in an acid solution consisting of 3:1 concentrated H₂SO₄/ HNO₃ mixture (200 ml) and were refluxed for 24h at 80°C [22]. After refluxing, the solution was filtered with distilled water and acetone until the P^H reached 6-7. The purpose of acid modification is to exfoliate graphite layers [23].

2.6 Synthesis of Conductive polymer deposited MWCNTs composites:

The synthesis procedure of conductive polymer deposited MWCNTs was as follows: COOH-MWCNTs were dispersed in 70 mL of n-Hexane and stirred under ultrasonication conditions for 15 min. Next AOT (sodium bis(2-ethylhexyl) sulfosuccinate) (19.12 mmol) was added to the above mixture, adding a solution of FeCl₃ (10.0 mmol) in 1.0 mL of water to it. The resulting orange-colored mixture

was gently stirred for 5 min followed by addition of EDOT monomer (3.52 mmol) and pyrrole (2.0mmol). After 3 h under gentle magnetic stirring, the blue/black precipitate of PEDOT and PPY coated MWCNTs were suction filtered and washed with copious amounts of methanol and acetonitrile, the resulting filtrate was then dried under vacuum.



3. Characterization:

Raman spectra of MWCNTs, conductive polymers (PEDOT and PPY) and conductive polymer coated MWCNTs were recorded on a Bruker senterra dispersive Raman microscope with a laser excitation of wavelength of 532 nm. The thermo gravimetric analysis of the combustion synthesized catalysts were recorded on TG/DTA, TA Instruments SDT Q600 in air flow from room temperature to 900°C with a heating rate of 10°C min⁻¹. Powder X-ray diffraction data of chemical synthesized Cu nanoparticles were collected on PANalytical X'pert Pro powder X-ray diffractometer with Cu Ka (1.5418 Å) radiation. The acceleration voltage and the applied current were 40 kV and 30 mA, respectively. The average crystallite sizes were calculated with the Scherrer equation with the full width at half maxima (FWHM) data. During electrochemical impedance spectroscopy (EIS) measurements an ac voltage of 10 mV superimposed over a dc potential of 0 V was applied to the sample with respect to reference electrode and (counter electrode). Z' versus Z'' plots were obtained over a frequency range of 10⁶–10⁻² Hz. The electrochemical characteristics were obtained using linear sweep voltammetry (Autolab PGSTAT 302N Potentiostat/Galvanostat coupled with a Nova 1.7 software) between -1.0 and +1.0 V at potential sweep rates of 10 mVs⁻¹. The surface morphologies of prepared conductive polymers, conductive polymer deposited MWCNTs and conductive reinforced C-epoxy composites were observed by scanning electron microscope (SEM) (ESEM-FEI Quanta 400, The Netherlands) at an accelerating voltage of 10 kV and magnification of 1000-50000.

4. Results and Discussion:

4.1 Thermogravimetric Analysis:

Changes in intrinsic polymer properties brought about by the addition of MWCNTs are indicative of nanotube-matrix interactions [24]. Improved thermal stability in polymer/CNTs composites systems relative to the individual polymers have been observed [25]. Therefore, thermogravimetric analyzer measurements of the PPY/MWCNT, PEDOT/MWCNT composites were carried out, and the results are shown in Fig. (2) MWCNTs are comparatively stable and showing no dramatic decomposition. However, for pure PPY, two steps rapid mass loss occurred at around 210°C and 320°C, for pure PEDOT at around 230°C which is attributed to the thermal oxidative decomposition of PPY and PEDOT chains. Both PPY/MWCNT and PEDOT/MWCNT composites show more delay decomposition compared to pure PPY and PEDOT. The improved thermal stability of Polymer/MWCNT composites indicates that there should exist interfacial interaction between CNTs with polymer shell [24].

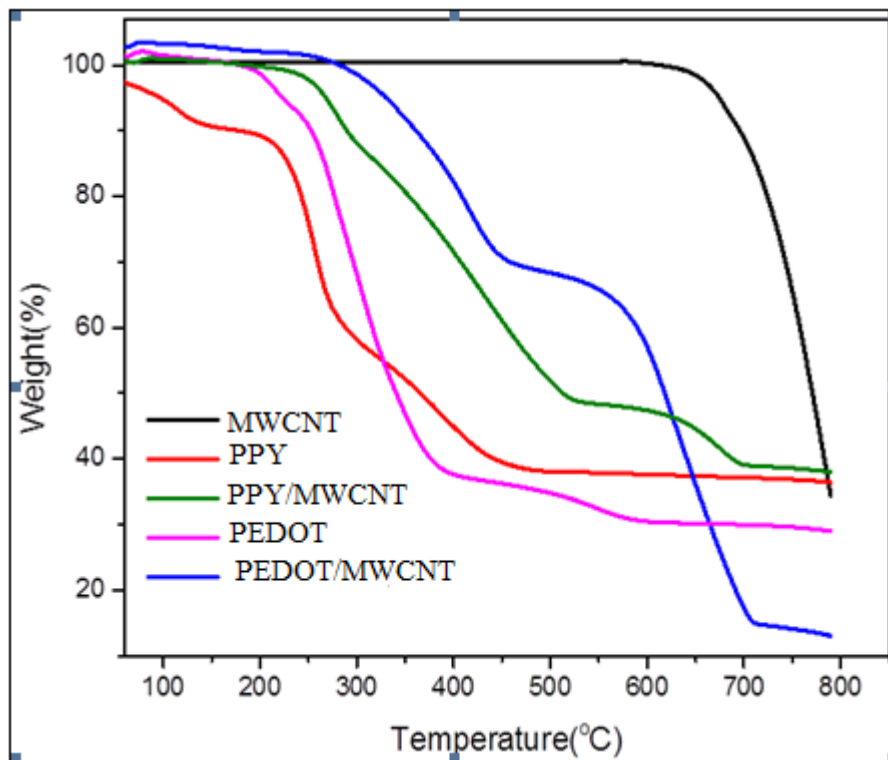


Figure 2: TGA analysis of MWCNT, PPY, PEDOT, PPY/MWCNT and PEDOT/MWCNT

4.2 Raman Analysis:

Raman spectroscopy has also been used to investigate the surface and interfacial properties of MWCNTs, PPY/MWCNT and PEDOT/MWCNT composites. From the room temperature Raman spectra of MWCNTs, PPY/MWCNT and PEDOT/MWCNT composites, we can see in fig(3) that the typical peak of pristine MWCNT at $1,591\text{ cm}^{-1}$ (G-band) is attributed to E_{2g} mode of graphite wall. The band at $1,334\text{ cm}^{-1}$ (D-band) is assigned to slightly disordered graphite [26]. Clearly, after the deposition of conductive polymers on MWCNTs surface, some additional Raman peaks are found for both PPY/MWCNT, PEDOT/MWCNT composites. The G-band and D-band of MWCNT clearly change with PPY and PEDOT coatings, demonstrating the interfacial interactions between the MWCNT and conductive polymer [27].

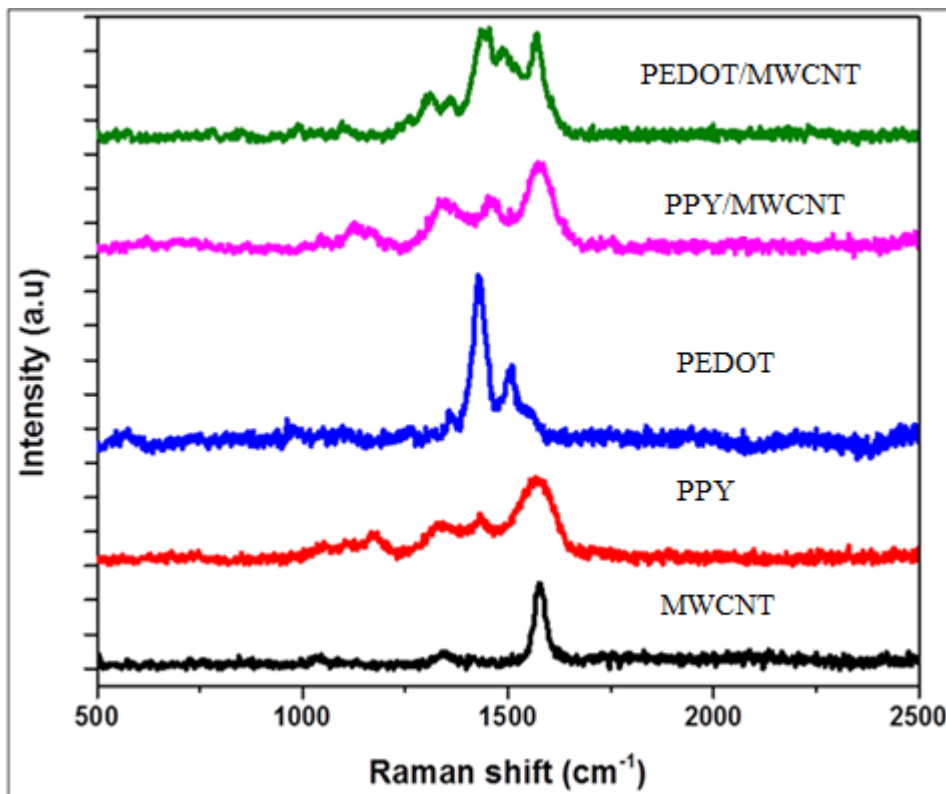


Figure 3: Raman spectra of MWCNT, PPY, PEDOT, PPY/MWCNT, PEDOT/MWCNT

4.3 SEM Analysis:

The SEM image of PEDOT fig.4 (a) shows a porous granular morphology with aggregated particles of non-uniform sizes, typical of conducting polymer. The SEM image of PPY fig.4 (b) shows the presence of interconnected elongated globules with smooth surfaces. The micrographs of both PEDOT/MWCNT fig.4 (c) and PPY/MWCNT fig.4 (d) show a network of polymer particles (PEDOT or PPY) overlapping with the tubular shapes of MWCNTs. The micrographs indicate that the PPY and PEDOT coat the MWCNTs fairly well.

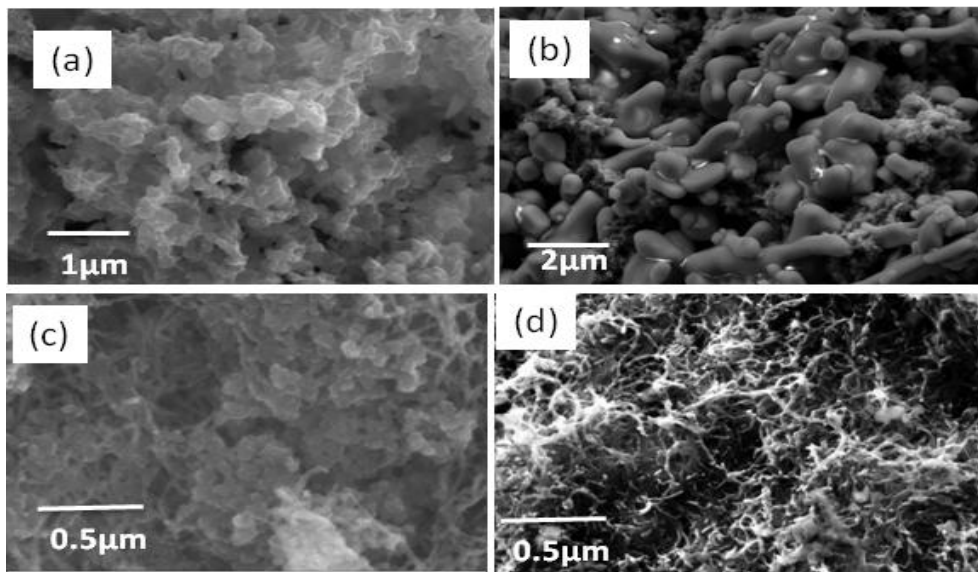


Figure 4: SEM images of (a) PEDOT (b) PPY (c) PEDOT/MWCNT and (d) PPY/MWCNT

4.4 Electrical conductivity of C-epoxy composites by I-V measurement:

Fig.(5) shows the I-V Characteristic curves of C-epoxy composites at different conductive reinforcement contents. Electrical resistance was measured by ohms law ($1/R=I/V$) and from this resistance value measure the conductivity ($1/\rho=1/R.l/a$). The electrical conductivity of blank sample was 4.2×10^{-4} S/cm and it gradually increased with different conductive reinforcements like conductive polymers and conductive polymer deposited MWCNTs. Electrical conductivity of C-epoxy composites also depends on wt% of the conductive reinforcements, in our present study 0.5wt% conductive reinforcement C-epoxy gives best conductivity values when compared to 0.25wt% and 1.0wt%. The 1.0wt% conductive reinforced epoxy composites exhibited lower conductivities than 0.5wt% reinforced C-epoxy

composites resulting from the micro cracks between the matrix and carbon fabric, as evidenced by SEM images (Fig.7). These micro cracks were the causes of discontinuous electron transmission pathway. On the other hand, 0.5wt% reinforced C-epoxy composites demonstrated good interfacial interaction between the matrix and fiber, increasing electrical conductivity of the composites.

The electrical conductivities of Blank-C-epoxy, 0.5wt% PPY-C-epoxy, 0.5wt% PEDOT-C-epoxy, 0.5wt% PPY/MWCNT-C-epoxy and 0.5wt% PEDOT/MWCNT-C-epoxy composites were 4.2×10^{-4} , 1.67×10^{-3} , 1.26×10^{-3} , 6.7×10^{-3} and 6.4×10^{-3} S/cm respectively in (table.1). PPY/MWCNT, PEDOT/MWCNT have higher conductivities than PPY and PEDOT due to increase the π - π stacking between polymer chain and COOH-MWCNTs, which facilitates an efficient charge transport between the conductive polymer and CNTs. It is clear that the significant conductivity improvement is due to conductive polymer coated MWCNTs, as the strong chemical bonding between conductive polymer and MWCNTs enhanced delocalization of charges and charge carrier mobility. The above results clearly demonstrate that functionalization is an effective method to enhance interfacial adhesion and achieve sufficient charge transfer from MWCNTs to a polymer.

Table.1 of conductivity value C-epoxy composite-

Composition	Ele. Conductivity (S/cm)
Blank	4.2×10^{-4}
0.5wt% PPY	1.67×10^{-3}
0.5wt% PPY/MWCNT	6.7×10^{-3}
0.5wt% PEDOT	1.26×10^{-3}
0.5wt% PEDOT/MWCNT	6.4×10^{-3}
0.5wt% Cu NP	1.1×10^{-3}
0.5wt% Cu NW	7.3×10^{-3}

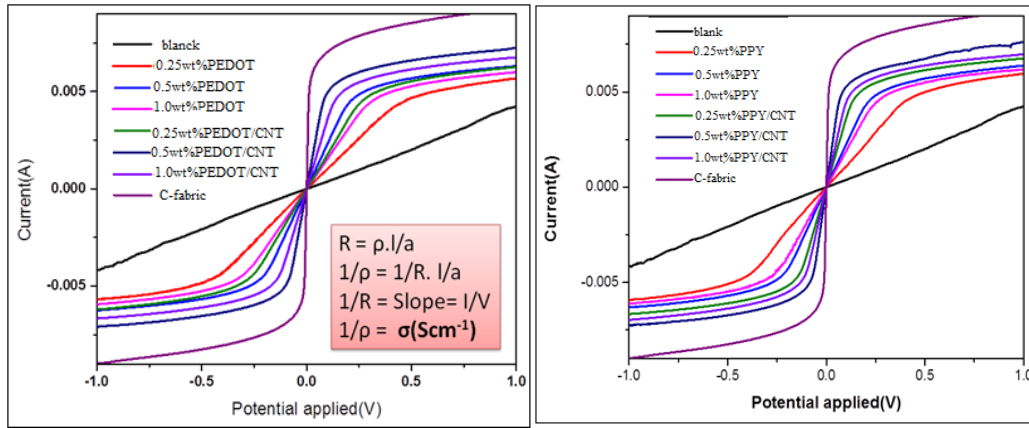


Figure 5: I-V characteristics curves of C-epoxy composites

4.5 Impedance spectroscopy measurements:

The resistance of the composites was measured by using Impedance spectroscopy. Fig.6 shows the Nyquist plots of different conductive reinforcement reinforced C-epoxy composites. Variations of the electrical resistivity of the composites are shown in X-axis of the Nyquist plots. The electrical resistance of blank sample was around 220 ohms and it gradually decreased with change in conductive reinforcement from individual conductive polymers to conductive polymer deposited MWCNTs.

PPY and PEDOT show resistance 42 ohm and 91 ohm. When MWCNTs are added to the both PPY and PEDOT the resistance value of C-epoxy composite sharply decreased to 27 and 36 ohm. The decreased resistance can be attributed to the better coating of both PPY and PEDOT on MWCNTs achieved in the presence of acid modified MWCNTs and also due the π - π stacking interaction between COOH-MWCNTS and polymer chains.

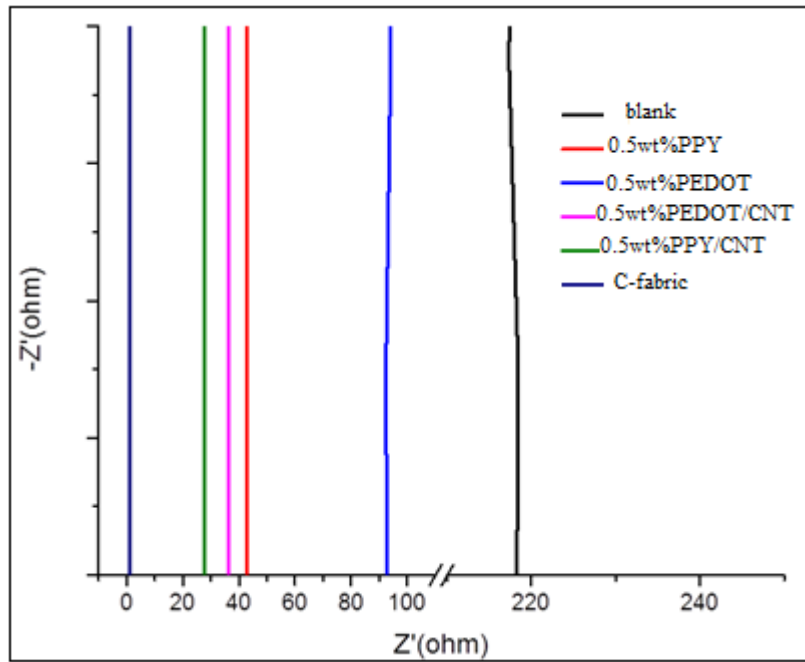


Figure 6: Nyquist plots of different conductive Polymer reinforced C-epoxy composites

4.6. Mechanism for electrical conductivity of C-epoxy composites at different wt%:

Electrical conductivity improvements due to conductive reinforcements in C-epoxy composites are primarily due to enhanced C-fiber –matrix interface interactions (Fig.7 a and b) imparted by these reinforcements. These properties will start to show a downward trend beyond optimum loading (0.5wt%). This is due to declining interface quality beyond optimum loading and micro cracks developed between the fiber and matrix (Fig.7 c and d).

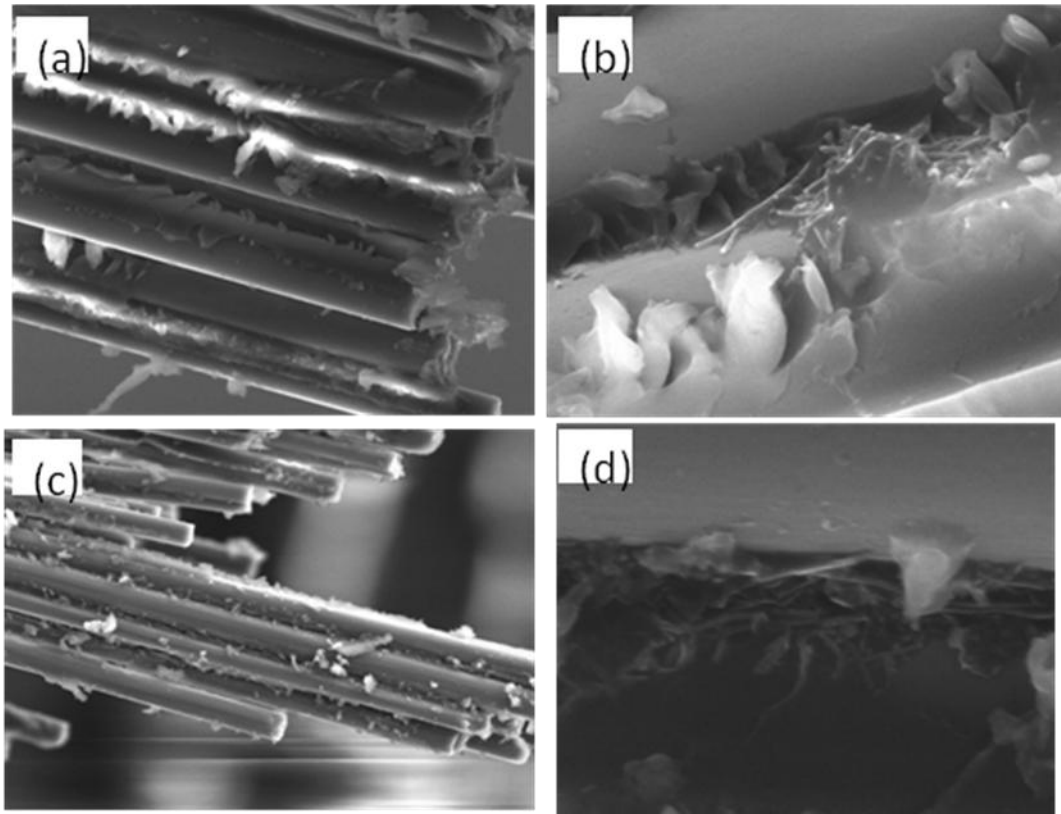


Figure 7: SEM images of (a and b) 0.5wt% PPY/MWCNT-C-epoxy showing good interfacial bonding between fiber and matrix, (c and d) 1.0wt% PPY/MWCNT-C-epoxy showing some interfacial cracks between the fiber and matrix.

5. Conclusion:

To increase the electrical conductivity of carbon-epoxy composite, we used conductive polymers, functionalized MWCNTs, conductive polymer deposited MWCNTs as conductive reinforcement. 2D laminated electrically conducting C-epoxy composites were prepared with varying amounts of conductive polymers and conductive polymer/MWCNTs. The addition of conductive polymer and conductive polymer/MWCNTs improved electrical conductivity of C-epoxy composite significantly. 0.5wt% conductive moiety reinforced composite showed the best electrical conductivity among all samples which were studied, thus demonstrating the promise this conducting polymer/MWCNT loading has for improving the conductivity of electrically insulating C-epoxy composite materials.

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