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Preparation and Characterization of Graphene-grafted Chitosan/ polypyrrole Composite for Thermal, Mechanical and Electrical Properties

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Abstract: Nowadays graphene based composites were developed due to their unique structure and excellent properties. Present study involves the preparation of graphene grafted chitosan (CS) and polypyrrole (PPY) (F-GE-CS-PPY) composite through solution casting method for electrical conductivity. The prepared composite was characterised by FTIR, TGA, XRD and Conductivity analysis. The formation of F-GE-CS composite was confirmed by FTIR and XRD studies through the shifting of peak values from Chitosan to F-GE-CS composite due to strong interaction between the compounds. Thermal stability of the sample was analysed by TGA curves. The electrical conductivities of F-GE-CS-PPY increased with the increase of F-GE content.

Keywords: Graphene, Chitosan, PPY, F-GE-CH-PPY Composite,

I. INTRODUCTION

Graphene, the starting material for all the carbon nanostructures has attracted strong scientific and technological interest in recent years. It has shown great promise in many applications, such as electronics, energy storage and conversion (super capacitors, batteries, fuel cells, solar cells, and bioscience/biotechnologies). Graphene is a zero-gap semiconductor material, which is electro active and transparent [1-4].

The functionalized graphene acts as efficient nano filler in polymer composites to improve its engineering properties and a small quantity of polymer functionalized graphene improve the mechanical, electronic, optical, thermal and magnetic properties significantly. The living radical polymerizations on graphene surface can also produce diverse polymeric architecture promoting graphene from a laboratory to important nanotechnological applications. The conjugated polymer functionalized graphene exhibits typical bistable electrical switching and a nonvolatile rewritable memory effect, with a turn-on voltage of about -1 V and an ON/OFF-state current ratio of more than 10^3 because of strong π - π interaction. Some conjugated polymer functionalized graphene like polythiophenes or its derivative composites are widely used in photovoltaic devices and lightemitting diodes etc. Conducting polymers like polyaniline, polypyrrole functionalized graphene composites have a potential application in super capacitors in various field [5-8]. Polymer functionalized graphene reinforced into the matrix polymer with molecular level dispersion and fine interfacial interaction enhances the strength, stiffness, toughness of the composite. These types of composites materials may have potential applications in aerospace and naval engineering. Till now, the applications of polymer functionalized graphene composites are not very abrupt and thus it is extremely required of this type of novel materials for stepping forward together with computational studies. We believe that the exploration of polymer functionalized graphene research will bring us much surprise in the future.

Polypyrrole, is typical electrode materials among many kinds of conducting polymers for supercapacitors. The as-prepared graphene/PPy nanocomposites have been successfully characterized in terms of composition, morphology, and electrochemical properties. It was found that the chemically modified graphene nanosheets and in-situ polymerized PPy layers formed uniform nanocomposites with homogeneous PPy layers intercalated between the graphene substrates[9]. Therefore, recent research on conducting polymers is directed towards hybrid supercapacitor systems following doping with metal oxides or other carbon materials for enhanced electrochemical performances.

Chitosan is a modified natural carbohydrate polymer derived from chitin which has been found in a wide range of natural sources such as crustaceans, fungi, insects and some algae [10]. Chitosan is insoluble in water but soluble in acidic solvents below pH 6. Chitosan is a non toxic, biodegradable polymer of high molecular weight. Chitosan is widely employed in many biomedical fields [11]. Like alginate, chitosan has the characteristic of forming gels in addition to possessing viscosity-related properties, complete biodegradability, and even anti-tumor influence bacteriostatic and fungistatic properties are particularly useful for wound treatment.

Furthermore, chitosan possesses bioadhesive properties which make it of interest in bioadhesive sustained release formulation required [10].

In the present communication, we have described the synthesis and characterization of PPY with F-GE grafted with chitosan fabricated by in situ polymerization. The nanocomposites were characterized by a number of techniques including Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermal gravity analysis and electrical conductivity.

II. EXPERIMENTAL

A. Materials

polypyrrole were purchased from Aldrich. graphene used in this study was purchased from Cheap Tubes (USA, 10– 20 nm diameter). Other reagents like ammonium persulfate (APS), hydrochloric, sulfuric, and nitric acid (Sigma Chemicals) were of analytical grade.

B. Oxidation of GE

0.5 g of GE was dispersed in 40 ml of concentrated H_2SO_4 and HNO_3 with a volume ratio of 3:1 using an ultrasonicator for 10 min. The mixture was stirred at $60^\circ C$ for 24 h and then washed several times with deionized water until the p^H reached 7. The resulting acid-functionalized GE was filtered with $0.2 \mu m$ PTFE membrane filter and dried in a vacuum at $70^\circ C$ for 24 h. This treatment produced carboxylic acid groups ($-COOH$) on the surfaces of GE at their defects and shortened the length of the tubes.

C. Preparation of PPY/F-GE nanocomposites

Each of 2 and 5 wt% F-GE (based on the weight of PPY) was dispersed in the solution of 0.015 mol PPY in 100 ml of 0.1 M HCl by ultrasonication for 10–15 min. Then, the solution of 0.015 mol APS in 50 ml of 0.1 M HCl was added drop by drop into the previous solution which was stirred constantly in an ice bath in a period of 30 min to initiate the polymerization. The reaction was kept for 24 h. Acetone was then poured into the reaction mixture to stop polymerization and to precipitate the PPY/F-GE nanocomposite [9]. The purification and drying procedures were the same as those for the synthesis of the bare polymer.

D. Synthesis of F-GE-chitosan Derivative

F-GE-COCl (400 mg) was reacted with CS (2 g) in 100 mL 2% acetic acid at $75^\circ C$ for 24 hours while stirring. After the reaction was stopped, the product was washed three times with 2% acetic acid to remove unreacted chitosan.

E. Synthesis of F-GE-chitosan-PPY Derivative

Synthesis of F-GE-CS Grafted Derivative—GE-CS (0.1 g) was reacted with $K_2S_2O_8$ (0.02 g) PPY in 2% acetic acid solution at $75^\circ C$ for 2 hours. Product was centrifuged at 20,000 rpm and washed twice with water before drying at $90^\circ C$. Hereafter, the product will be referred to as GE-CS- PPY , schematically presented in figure.1 [12].

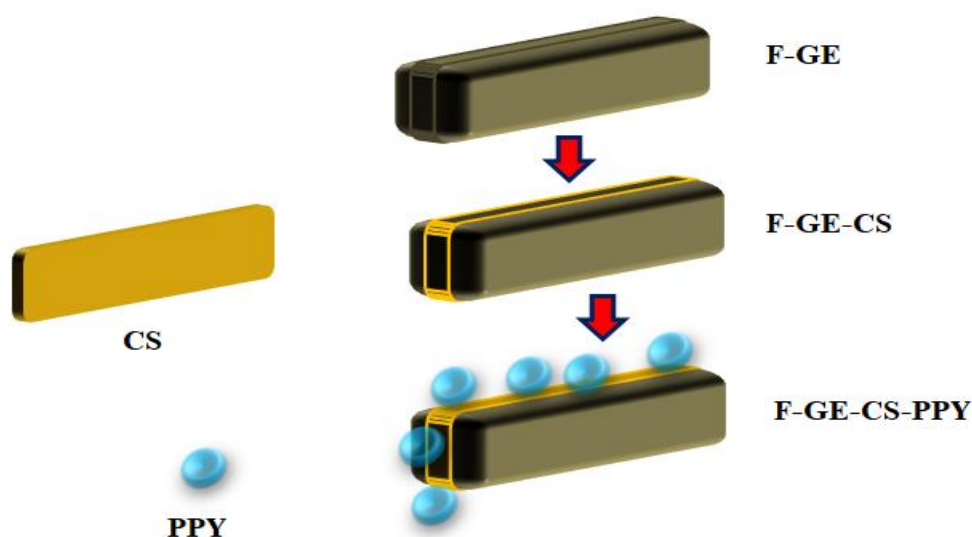


Figure 1. Schematic structure of the F-GE-CS-PPY nanocomposite film

III. MEASUREMENT

A. IR spectra

IR spectra The Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 8700 spectrometer, in the range 400–4,000 cm^{-1} .

B. XRD

X-ray diffraction (Rigaku, D/Max, 2,500 V, Cu- α radiation: 1.54056 \AA) experiments were carried out on both the plain PoPD and the composite samples. Wide-angle X-ray diffractograms were recorded at temperature of 30 $^{\circ}\text{C}$ after isothermal crystallization at this temperature for 1 h .

C. TGA

TGA was performed on a thermal analyser (TA Instruments, SDT Q600) from 40–800 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere.

D. Mechanical properties evaluation:

Tensile strength of the samples was measured according to the ASTM D638 standard. Samples were prepared with 0.01-0.02 mm width for F-GE-chitosan tensile strength was determined with a mechanical testing machine (zwick-1446) at a crosshead speed of 5 mm/min.

E. Electrical conductivities

The electrical conductivities of all nanocomposite samples were measured by four-point probe methods [8] . The four-point probe method, a four-point resistivity probing fixture (Signatone probe S-302-4 with a SP4 probe head) was used. The relative humidity in the moisturizing chamber was controlled by a humidity controller with an accuracy of $\pm 5\%$ RH.

IV. RESULT AND DISCUSSION

A. FT-IR Spectrometry

FTIR spectrum of pure compound CS, F-GE, F-GE/CS and F-GE/CS-PPY composite was shown in Figure 2 and table 1. The C=O stretching of NHCO (amide I) and N-H bending of NH_2 (amide II) for pure CS was observed at 1661 cm^{-1} and 1572 cm^{-1} , the similar value was observed at 1682 cm^{-1} and 1521 cm^{-1} for F-GE-CS composite. The shifting of bands to lower values indicates the strong interaction between CS and F-GE during grafting and also with PPY during composite formation [13-15].

The C-O stretching vibrational bands of CS and F-GE was overlapped with PPY [16-18]. CS and F-GE showed its C-H, C=C and C-C stretching vibrations at 2821 cm^{-1} , 2953 cm^{-1} , 1429 cm^{-1} , 1361 cm^{-1} respectively as shown in table. Figure shows a small peak of OH stretching vibration of PPY and CS at 3600 cm^{-1} . This less intense peak indicates that the OH group of both the compound was involved in weaker Hydrogen bonding.

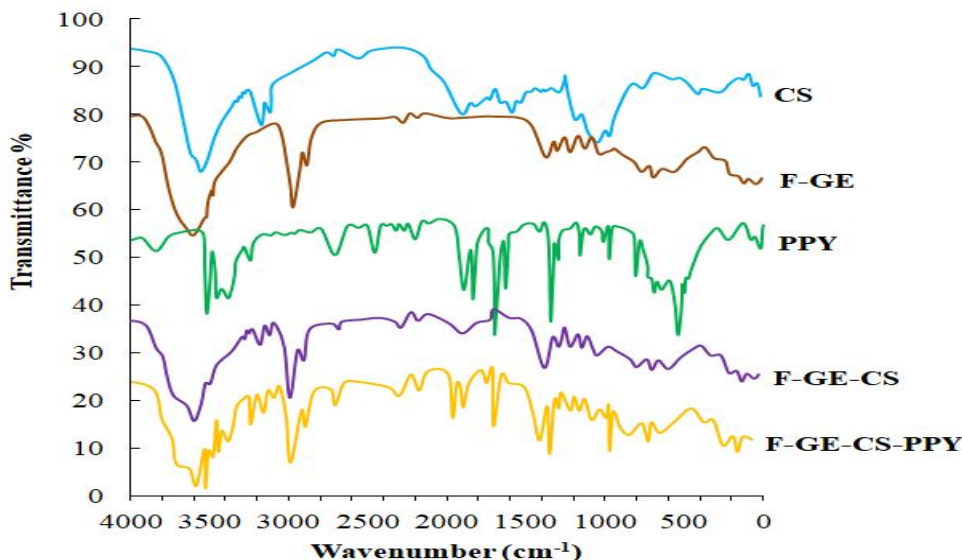


Figure 2. FTIR spectrum of CS,F-GE,PPY,F-GE-CS, F-GE-CS-PPY nanocomposite

Table.1 FTIR values for pure chitosan, OPD, grapheme and F-GE/CH/OPD

Groups	CS	PPY	F-GE	Composites
OH -str	3492	3532,3446	3452	3452
N-H str	3329			3433
C-H str	2943,2852		2921,2839	2953,2821
C-H def	1461,1381	1554,1423	1451,1471	1429,1361
N-H def	1572			1516
C=O str	1732,614		1721,1646	1743,1661,1619
C-O str	1732,614		1032	1045
PO ₄	1155,042	1134,1256		1035

B. XRD

Figure 3 shows the XRD patterns of pure CS, F-GE, PPY and the prepared F-GE/CS composite. Pure CS was shown at 16.5°, F-GE at 16.2° and F-GE/CS at 9.25° and 16.63°. In F-GE/CS/PPY was found broadened peak at around 9.65° which are the diffractions of (211), (300), (202) at an angle of 9.3°, 15.2°, 31° respectively [19, 20]. The broadness of a peak indicates the partial demineralization of PPY and low crystallinity of the F-GE/CS composite [21-22]. The pure CS shows characteristic peaks at 16° (Crystalline structure) . The broadness of the first peak was decreased and the second peak was shifted and overlapped with F-GE (10°) peak due to the strong interaction of CS with OPD and F-GE [23, 24].

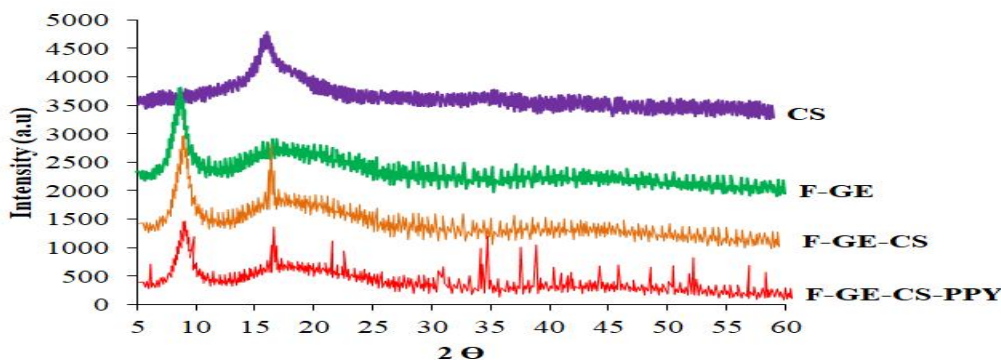
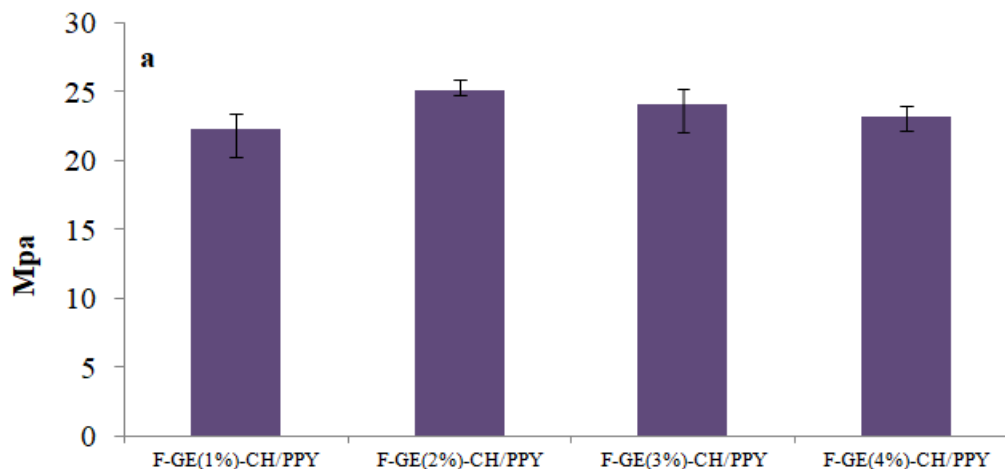


Figure 3. XRD spectrum of CS,F-GE,PPY,F-GE-CS, F-GE-CS-PPY nanocomposite

C. Tensile strength

Figure. 4a and b shows the tensile strengths of F-GE, F-GE/CS, and F-GE/CS/PPY composites films. The results indicate change in mechanical properties with the increase in F-GE concentration up to 2% (26 ± 32 MPa and 28± 52MPa). The results is also supported by XRD data analysis where it was identified that with the increase in F-GE concentration, there was a subsequent increase in intermolecular hydrogen bonding and thereafter there was a decrease in intermolecular hydrogen bonding.



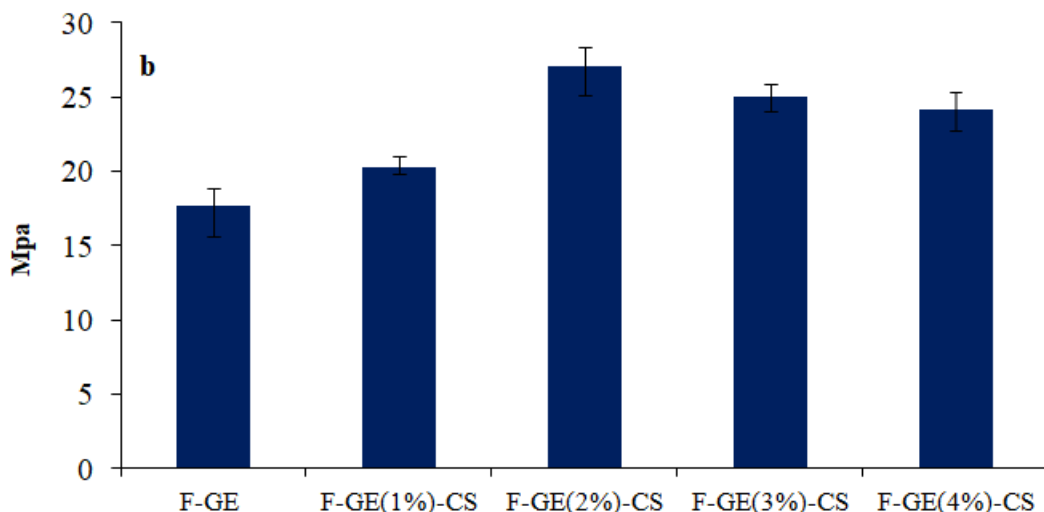


Figure 4. Tensile strength of CS,F-GE,PPY, F-GE-CS-PPY nanocomposite

D. Thermal Analysis

The prepared F-GE/CS-PPY composite was subjected to TGA and DTG Analysis. TGA thermogram of prepared F-GE/CS-PPY composite (Figure 5) showed the various stages of decomposition. The weight loss occurred between 33-225^oC showed two derivative peaks at 47.27^oC and 208.47^oC. The peak one indicates desorption of adsorbed water molecules and peak two indicates the release of crystalline water of PPY [24]. The weight loss occurred at this temperature is very less (9.12%) and it co-insides with FTIR spectra of the composite, confirming the existence of weaker hydrogen bonding. A major weight loss of 18.73% was observed between 270^oC - 425^oC, which corresponds to the degradation of the glucosamine in CS and it was indicated by a derivative peak of 300^oC [25]. The weight loss between 438^oC and 425^oC attributed to the combustion of carbon present in F-GE and CS [26]. The decomposition of PPY was observed at 682^oC shown by the DTG curve. The TGA analysis confirms the presence of all the three compounds and their decomposition temperatures. The thermal stability of the prepared composite was not increased as expected.

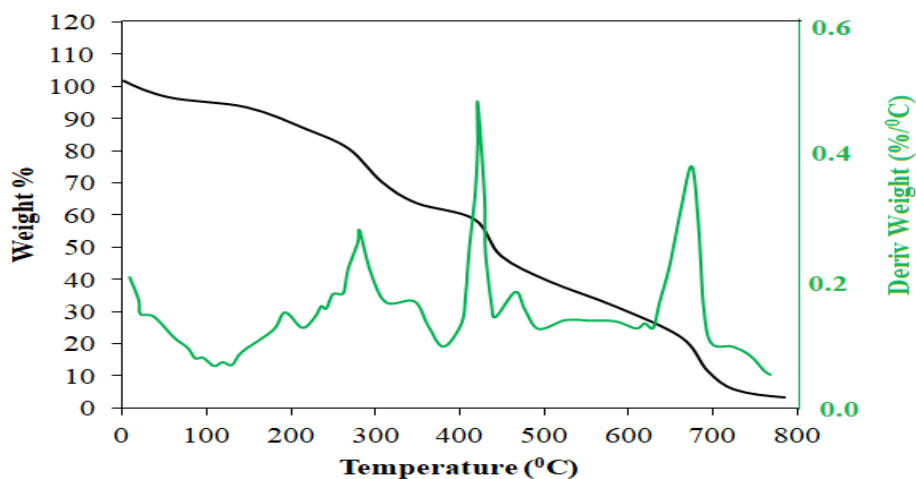


Figure 5. TGA and DTG of CS,F-GE,PPY, F-GE-CS-PPY nanocomposite

E. Conductivity of F-GE-CS-PPY

The electrical conductivity of F-GE-CS-PPY composites with weight of F-GE was measured using four-probe method shown in Figure. 6. The conductivity of PPY synthesized in the presence of hydrochloric acid at room temperature is of 1.11×10^{-4} S/cm. Meanwhile, by the addition of 2 wt% F-GE into PPY, the conductivity at room temperature increases from 1.11 to 8×10^{-4} S/cm. The reason for improvement in conductivity is the $\pi-\pi^*$ interaction between the surface of F-GE and the quinoid ring of the copolymer chain, which effectively improves the degree of electron delocalization between the two components, as confirmed by FTIR.

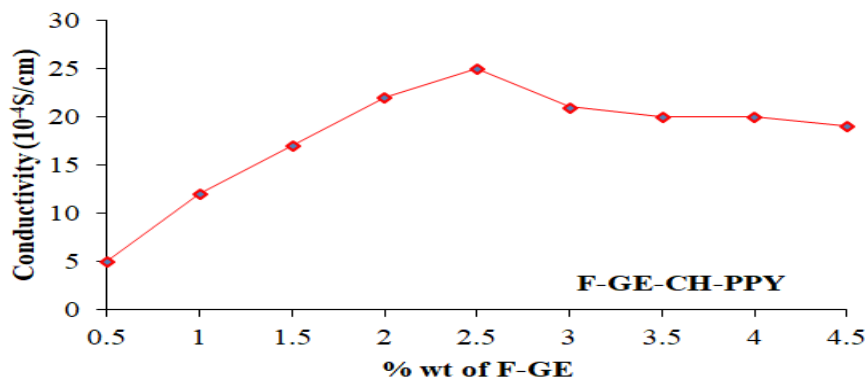


Figure 6. Conductivity of F-GE-CS-PPY nanocomposite by four probe method

V. CONCLUSION

F-GE grafted CS and PPY composite was successfully prepared by solution casting method. XRD and FTIR evidenced the strong interaction among the precursors. TGA studies of the prepared F-GE-CS composite confirm the grafting of F-GE through Hydrogen bonding with CS and PPY.

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