

Preparation and Characterization of Graphene-grafted Chitosan/ Ortho-Phenylenediamine 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 fictionalized graphene grafted chitosan and ortho-Phenylenediamine (F-GE-CH-OPD) 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-CH composite was confirmed by FTIR and XRD studies through the shifting of peak values from Chitosan to F-GE-CH composite due to strong interaction between the compounds. Thermal stability of the sample was analysed by TGA curves. The electrical conductivities of F-GE-CH-OPD increased with the increase of F-GE content.

Key words: Graphene, Chitosan, ortho-Phenylenediamine, F-GE-CH-OPD Composite

Introduction

Graphene has attracted tremendous attention in recent years owing to its exceptional thermal, mechanical, and electrical properties. One of the most promising applications of this material is in polymer nanocomposites, polymer matrix composites which incorporate nanoscale filler materials. This polymer functionalized graphene acts as an efficient nanofiller 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 [1-4].

The development of a nanolevel dispersion of graphene particles in a polymer matrix has opened a new and interesting area in materials science in recent years. These nanohybrid materials show considerable improvement in properties that cannot normally be achieved using conventional composites or virgin polymers. The extent of the improvement is related directly to the degree of dispersion of the nanofillers in the polymer matrix. The most important aspect of these nanocomposites is that all these improvements are obtained at a very low filler loadings in the polymer matrix [5-8].

Ortho-Phenylenediamine, is typical electrode materials among many kinds of conducting polymers for supercapacitors. A polyaniline based supercapacitor was reported, which reached a specific capacitance of 150 F g^{-1} . The energy density and power density of the device were 5 Wh kg^{-1} and 1200 W kg^{-1} , respectively. 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 [9].

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 [43]. Its 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 OPD 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.

Experimental

Materials

Ortho-Phenylenediamine and aniline monomers 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.

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°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 $0.2 \mu\text{m}$ PTFE membrane filter and dried in a vacuum at 70°C for 24 h. This treatment produced carboxylic acid groups ($-\text{COOH}$) on the surfaces of GE at their defects and shortened the length of the tubes.

Preparation of PoPD/F-GE nanocomposites

Each of 2 and 5 wt% F-GE (based on the weight of oPD) was dispersed in the solution of 0.015 mol oPD 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 PoPD/F-GE nanocomposite. The purification and drying procedures were the same as those for the synthesis of the bare polymer.

Synthesis of F-GE-chitosan Derivative

F-GE-COCl (400 mg) was reacted with chitosan (2 g) in 100 mL 2% acetic acid at 75 °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.

Synthesis of F-GE-chitosan-OPD Derivative

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

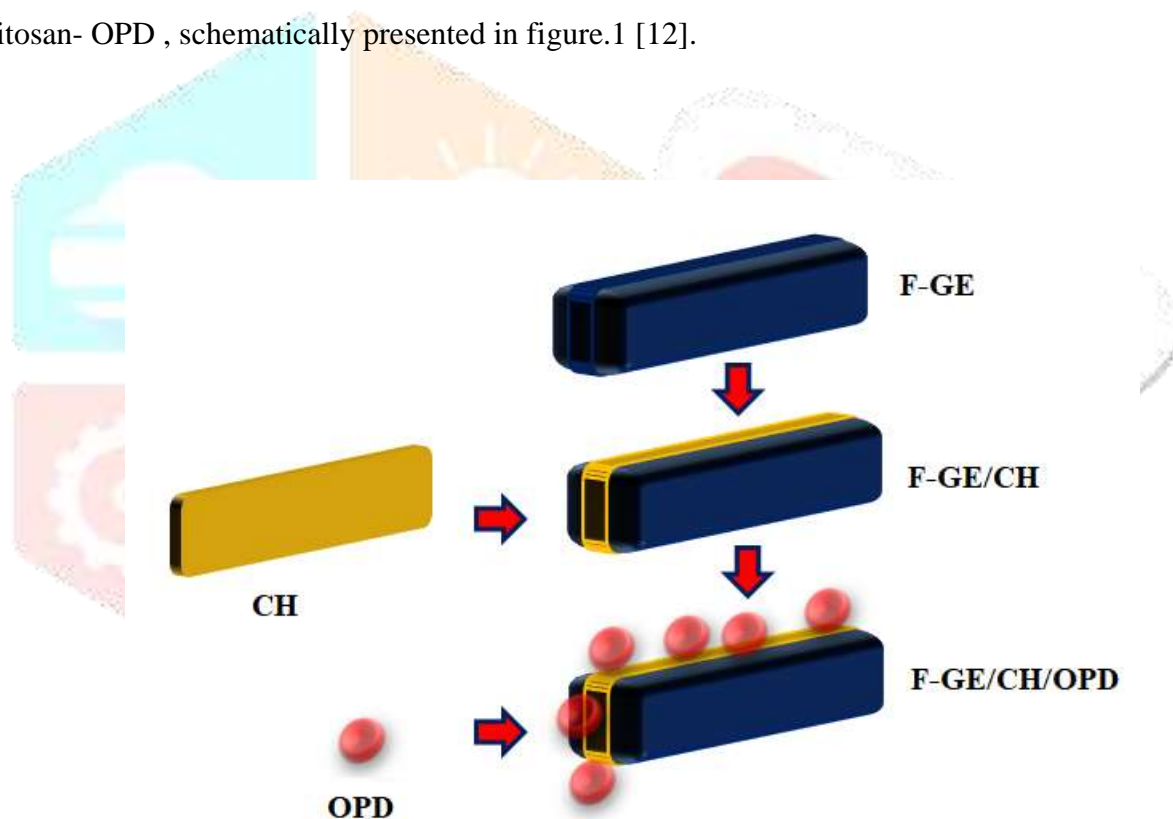


Figure.1. schematically presentation of Graphene-grafted Chitosan/ Ortho Phenylenediamine Composite

Measurement

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} .

XRD

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

TGA

TGA was performed on a thermal analyser (TA Instruments, SDT Q600) from 40–800°C at a heating rate of 10°C/min under nitrogen atmosphere.

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.

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.

Result and Discussion

FT-IR Spectrometry

FTIR spectrum of pure compound CH, F-GE, F-GE/CH and F-GE/CH-OPD composite was shown in Figure 2 and table 1. The C=O stretching of NHCO (amide I) and N-H bending of NH₂ (amide II) for pure CH was observed at 1661 cm⁻¹ and 1572 cm⁻¹, the similar value was observed at 1681 cm⁻¹ and 1526 cm⁻¹ for F-GE-CH composite. The shifting of bands to lower values indicates the strong interaction between CH and F-GE during grafting and also with OPD during composite formation [13-15].

The C-O stretching vibrational bands of CH and F-GE was overlapped with OPD [16-18]. CH and F-GE showed its C-H, C=C and C-C stretching vibrations at 2923 cm⁻¹, 2923 cm⁻¹, 1449 cm⁻¹, 1352 cm⁻¹ respectively as shown in table. Figure shows a small peak of OH stretching vibration of OPD and CH at 3500 cm⁻¹. This less intense peak indicates that the OH group of both the compound was involved in weaker Hydrogen bonding.

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

Groups	Chitosan	OPD	F-GE	Composites
OH -str	3492	3512,3456	3452	3451
N-H str	3329			3443
C-H str	2943,2852		2921.2839	2923,2872
C-H def	1461,1381	1564,1463	1451,1471	1449,1352
N-H def	1572			1526
C=O str	1732,614		1721,1646	1728,1681,1629

C-O str	1732,614		1032	1035
PO ₄	1155,042	1094,1036		1025

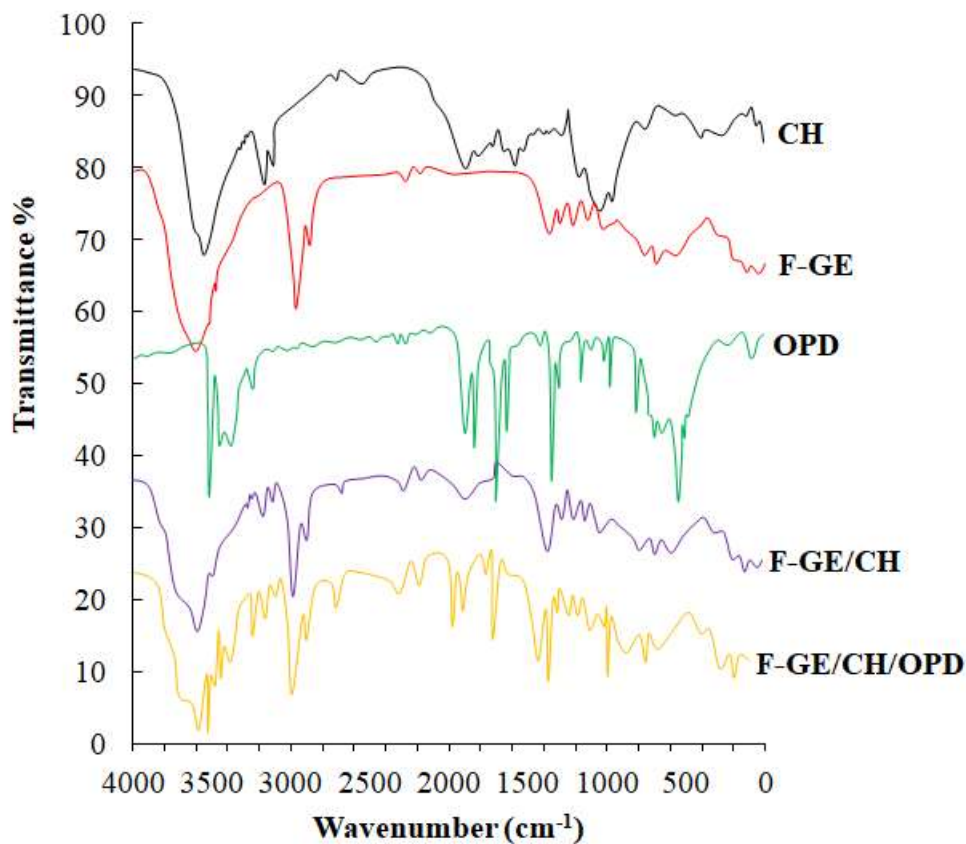


Figure.2. FTIR of CH, F-GE, OPD, F-GE/CH, F-GE/CH/OPD

XRD

Figure 3 shows the XRD patterns of pure CH, F-GE, OPD and the prepared F-GE/CH composite. Pure CH was shown at 16.2° , F-GE at 16.2° and F-GE/CH at 9.45° and 16.23° . In F-GE/CH/OPD was found broadened peak at around 9.65° which are the diffractions of (211), (300), (202) at an angle of 9.5° , 15.3° , 31° respectively [19, 20]. The broadness of a peak indicates the partial demineralization of OPD and low crystallinity of the F-GE/CH composite [21-22]. The pure CH 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 (9°) peak due to the strong interaction of CH with OPD and F-GE [23, 24].

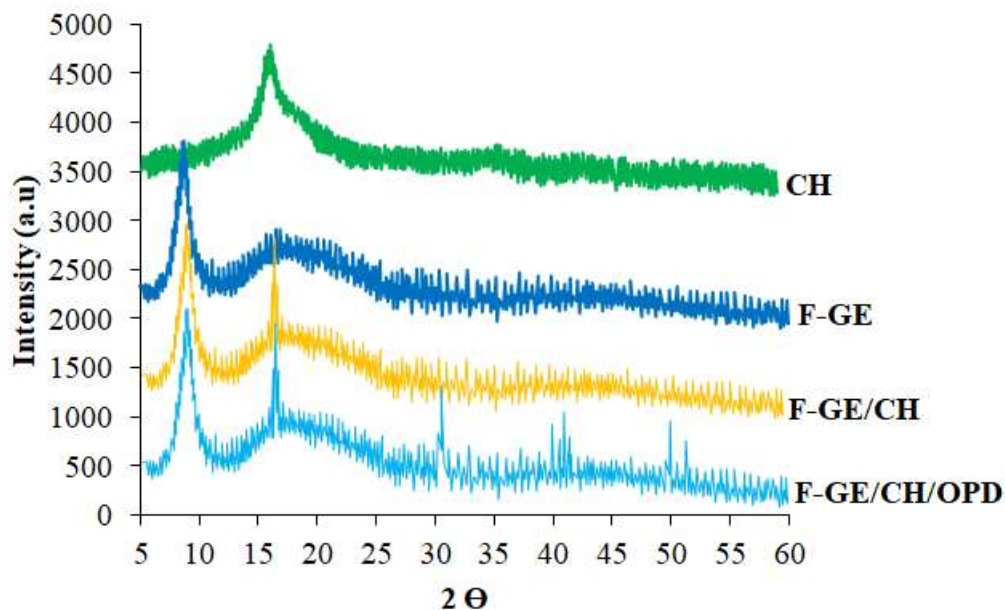


Figure-3. XRD of CH, F-GE, OPD, F-GE/CH, F-GE/CH/OPD

Tensile strength

Figure. 4a and b shows the tensile strengths of F-GE, F-GE/CH, F-GE/CH/OPD composites films. The results indicate change in mechanical properties with the increase in F-GE concentration up to 0.75g (27 ± 12 MPa and 28 ± 32 MPa). 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.

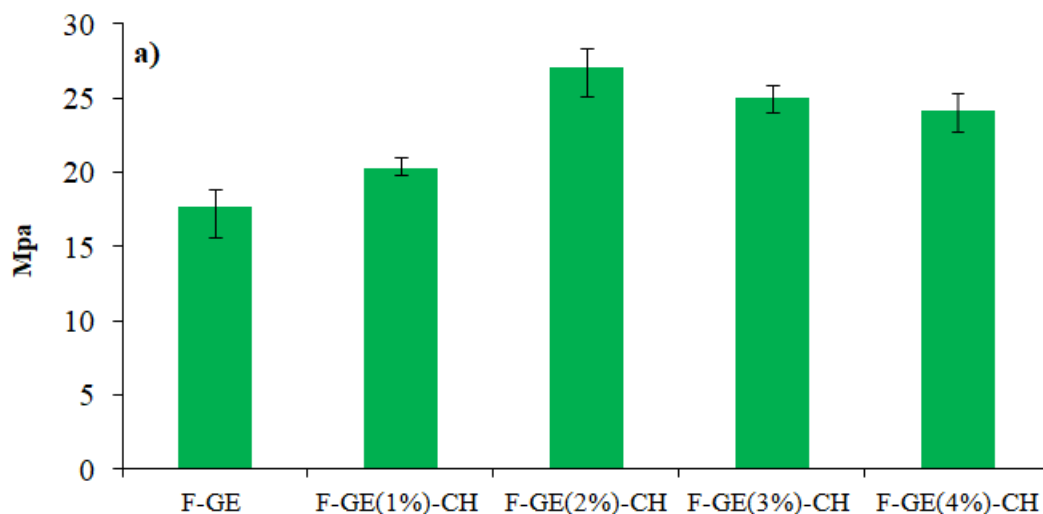


Figure.4a. Tensile strength of different percentage of grapheme with CH

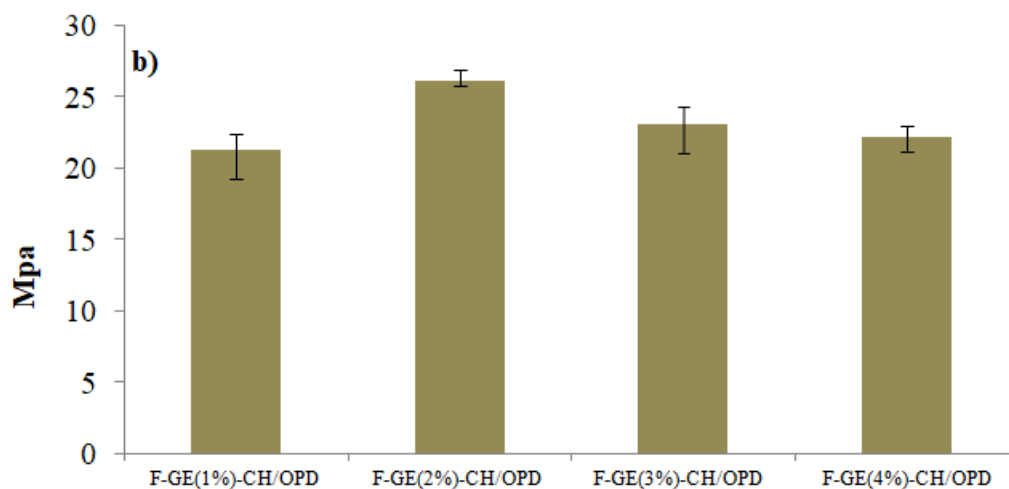


Figure.4. Tensile strength of different percentage of grapheme with CH/OPD

Thermal Analysis

The prepared F-GE/CH composite was subjected to TGA and DSC Analysis. TGA thermogram of prepared F-GE/CH composite (Figure 5) showed the various stages of decomposition. The weight loss occurred between 32-215^oC showed two derivative peaks at 46.27^oC and 206.47^oC. The peak one indicates desorption of adsorbed water molecules and peak two indicates the release of crystalline water of OPD [24]. The weight loss occurred at this temperature is very less (8.12%) 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 265^oC - 426^oC, which corresponds to the degradation of the glucosamine in chitosan and it was indicated by a derivative peak of 300^oC [25]. The weight loss between 418^oC and 435^oC attributed to the combustion of carbon present in F-GE and CH [26]. The decomposition of OPD was observed at 692^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.

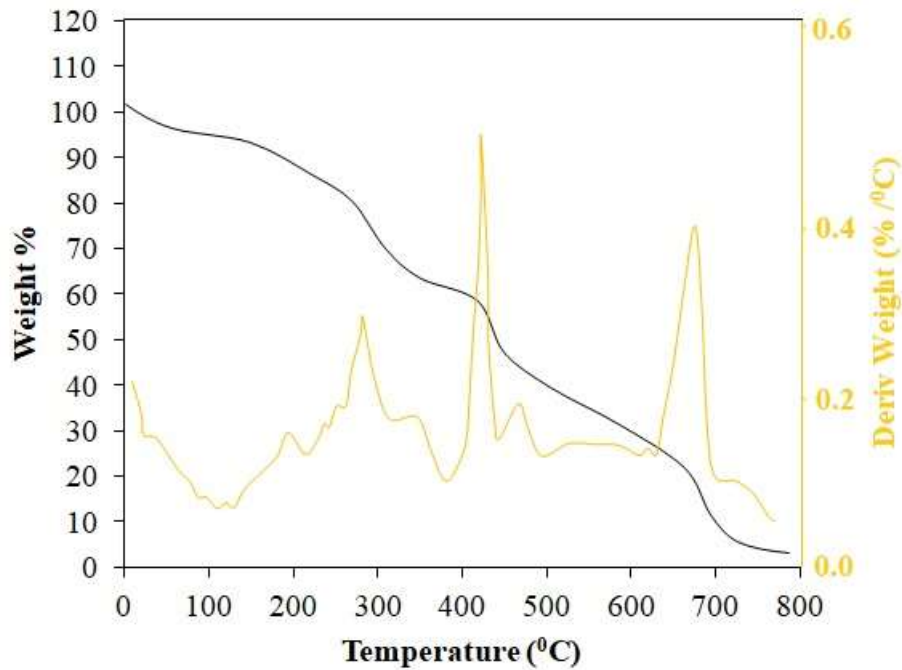


Figure.5. TGA and DTG of F-GE/CH/OPD

Conductivity of F-GE-CH-OPD

The electrical conductivity of F-GE-CH-OPD composites with weight of F-GE was measured using four-probe method shown in Figure. 6. The conductivity of OPD 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 OPD, the conductivity at room temperature increases from 1.11 to 8×10^{-4} S/cm. The reason for improvement in conductivity is the π - π^* 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.

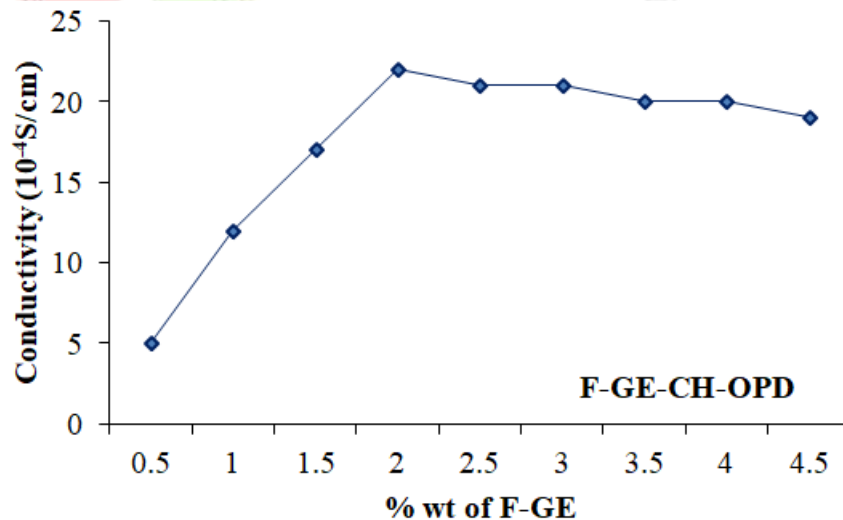


Figure.6. Conductivity of F-GE-CH-OPD

Conclusion

F-GE grafted CH and OPD 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-CH composite confirm the grafting of F-GE through Hydrogen bonding with CH and OPD.

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