

Synthesis and characterization of functionalized single - walled Carbon nanotube/ Chitosan/Polyaniline nanocomposite

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ABSTRACT: In this work the synthesis of polyaniline/chitosan/functionalized single- walled carbon nanotube nanocomposite is carried out. For this purpose, single -walled carbon nanotubes were reacted with thionyl chloride to change the hydroxyl to acyl chloride groups for improving the react ability. In other step, aniline monomers and chitosan were polymerized in the presence of Iron (III) Chloride to synthesize the chitaline copolymer. The synthesized chitaline then reacted with functionalized single- walled carbon nanotube to prepare chitaline-single walled carbon nanotube nanocomposite. The synthesized nanocomposite was also characterized to evaluate the structure and morphology by Fourier infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and thermo gravimetric analysis (TGA). The results showed that the formation of the composite in nano scale can be good carbon materials with high adsorption capacity in porous surfaces for improving the properties as a good candidate such as nano bio filter for removing the organic and inorganic wastes from water.

Keywords: Chitosan; Chitaline; Functionalized single- wall Carbon nanotube; Nanocomposite; Polyaniline; SEM.

INTRODUCTION

Chitosan has received much attention for its interesting properties such as nontoxicity, biocompatibility and biodegradability. However, chitosan has low solubility and poor mechanical properties which limit its wide applications [1]. Grafting onto chitosan is a common way to improve its properties such as increasing the solubility. Among various methods, graft copolymerization is most attractive because it is a useful technique for modifying the chemical and physical properties of natural polymers [2, 3]. Chitosan bears two types of reactive groups that can be grafted: first, the free amino groups on deacetylated units and secondly, the hydroxyl groups on the C₃ and C₆ carbons on acetylated or deacetylated units. Grafting onto chitosan allows the formation of functional derivatives by covalent binding of a desired molecule onto chitosan backbone [3]. Polyaniline (PAni) is one of the most extensively used polymers for grafting. It has attracted considerable

attentions due to its high hydrophobic nature, good environmental, thermal and chemical stability and low cost [4,5]. The grafting of chitosan with aniline in aqueous conditions enables the introduction of polyaniline side chains at amino groups to chitosan. This can help the improvement of the solubility in water [6]. Some initiators such as: ammonium persulphate (APS), potassium persulphate (PPS), ceric ammonium nitrate (CAN), thiocarbonation potassium bromate (TCPB), 2, 2'-azobisisobutyronitrile (AIBN) and ferrous ammonium sulfate (FAS) have been developed to initiate grafting copolymerization reaction [7]. Carbon nanotubes (CNTs) have attracted recent attentions as reinforcing materials for polymer matrices, since their discovery in 1991. Their nanometer size, high aspect ratios, excellent mechanical, electrical, thermal and conducting properties make them potentially useful in a wide variety of applications [8]. The grafting of CNTs onto polymers through covalent functionalization appears to be one of the most attractive and effective ways to achieve homogeneous dispersion of CNTs in polymer matrices. This technique has been used to synthesize CNT-polymer nanocomposites [9-11]. CNTs

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can be found in single-walled carbon nanotubes (SWCNTs) and multi walled nanotubes (MWCNTs) forms [12]. SWCNTs were discovered in 1993 and have a diameter close to 1 nm. SWCNTs have a wide range of properties such as mechanical, electronic, thermal, optical, pharmaceutical and very large surface area [13, 14]. Functionalized nanotubes are also typically easier to disperse in organic solvents and water which can improve the dispersion and homogeneity when reacting with a polymer. To our knowledge, most of them were obtained by non covalent interactions such as bending, layer-by-layer, self-assembly, surface deposition, crosslinking and electrochemical deposition on the surface of CNTs [15-17]. Also chitosan has been used to modify carbon nanotubes in order to improve dispersion stability in aqueous solutions and its biocompatibility [18]. The covalent grafting of chitosan

and chitosan- MMA to CNTs has been reported [19]. Also covalent functionalization of multi-walled carbon nanotubes with a low molecular weight chitosan has been investigated [20]. Chemical linkage of chitiline onto functionalized single-walled carbon nanotube by this method was not reported before, so the advantage of this work are the synthesis of biocompatible conductive polymer with SWCNTs as a good carbon materials with high adsorption capacity in porous surfaces of nanocomposite for improving the properties as a good candidate such as nano bio filter for removing of organic and inorganic wastes from water that is being studied in our research group and the results will be published soon. In Fig. 1, Strategy for the synthesis of the polyaniline-chitosan-functionalized single walled carbon nanotube nanocomposite is shown [20].

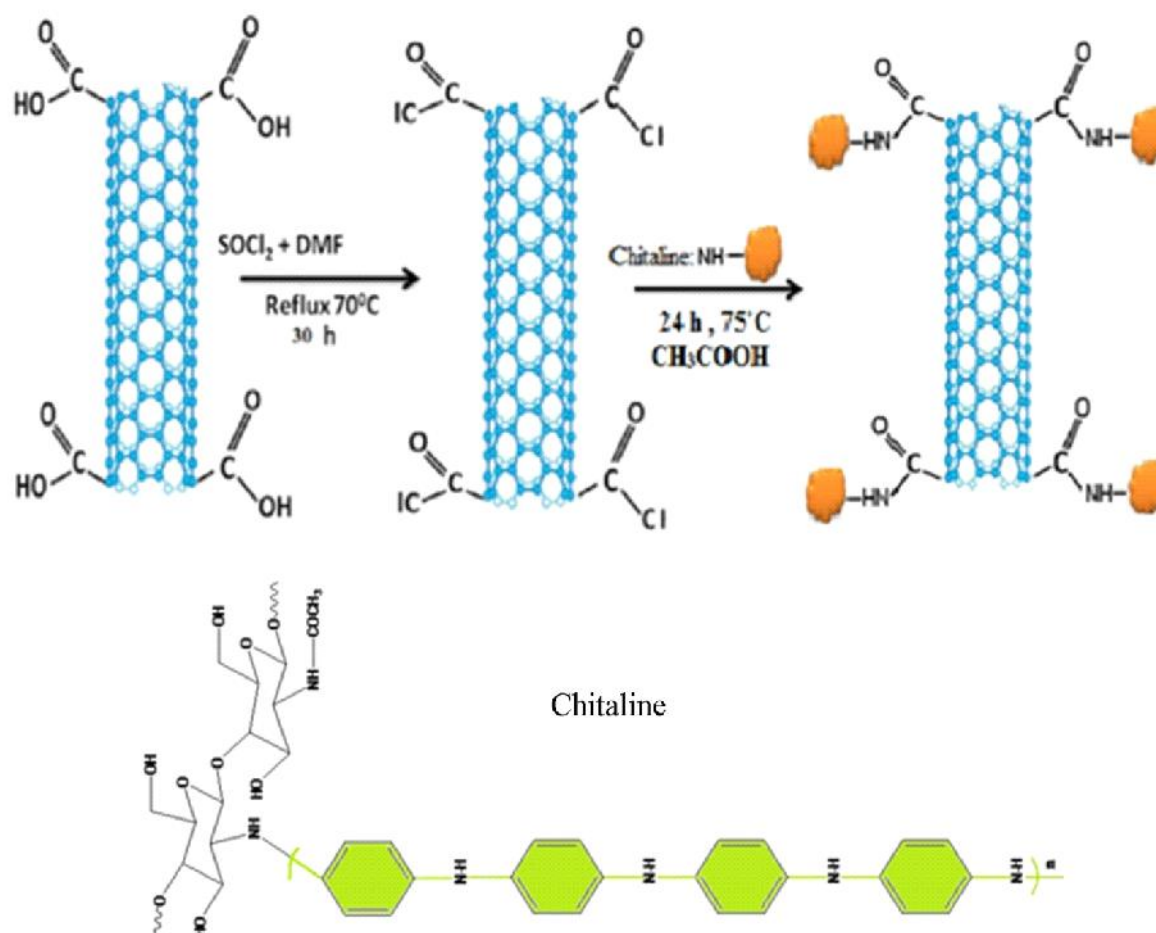


Fig. 1: Strategy for the synthesis of the polyaniline-chitosan-functionalized single walled carbon nanotube nanocomposite.

EXPERIMENTAL

Material

Chitosan, thionyl chloride, aniline, acid functionalized single walled- carbon nanotube, acetic acid (CH_3COOH), Hydrochloric acid (HCl), Iron (III) Chloride hexa hydrate, Chloroform (CHCl_3) and *N, N* dimethyl formamide were purchased from Sigma Aldrich and used as received.

Instrumentation

Infrared spectra in the range of $400\text{--}4000\text{ cm}^{-1}$ were recorded using Perkinelmer100 spectrum to confirm the presence of functional groups in chitosan and SWCNTs derivatives. Dried samples and dried potassium bromide (KBr) were used to prepare pellets. Scanning electron microscopy (SEM) was performed using sigma IGMA/VP. The sample was prepared on a carbon coated copper grid by just dropping a very small amount of the sample on the grid. Thermal stability was analyzed in thermo gravimetric analyzer (TGA) S -1500 scinco. The temperature scanned from $30\text{ }^\circ\text{C}$ to $800\text{ }^\circ\text{C}$ and at a heating rate of $20\text{ }^\circ\text{C}/\text{min}$ and at nitrogen atmosphere.

Synthesis of polyaniline

One ml of freshly distilled aniline was dissolved in 30 ml of hydrochloric acid (1 M) and the mixture was brought to $0\text{--}4\text{ }^\circ\text{C}$ in ice bath. Then a certain amount of iron (III) chloride hexahydrate (0.5M) were added to hydrochloric acid (1M) and stirred. The prepared solution were added to the previous solution drop by drop and stirred for 5h. The product were washed with hydrochloric acid (1 M) and filtered and were dried at $50\text{ }^\circ\text{C}$ for 24h.

Preparation of Chitaline

0.02 grams of chitosan were dissolved in one ml of 2% acetic acid and stirred for 1h. Then a certain amount of Iron (III) chloride hexahydrate were added to the solution and stirred. Freshly distilled aniline was added to the solution drop by drop and stirred for 12h. The product was washed with 10 ml of 2% acetic acid, filtered and dried at $60\text{ }^\circ\text{C}$ for 6h.

Synthesis of acyl chloride functionalized single walled carbon nanotube

0.01 grams of CNTs – COOH were reacted with 1.5 ml of thionyl chloride for 30h at $80\text{ }^\circ\text{C}$ while refluxing. Then the mixture was cooled, centrifuged and washed to remove excess reactants and dried at $60\text{ }^\circ\text{C}$ for 6h.

Synthesis of the polyaniline-chitosan-functionalized single- walled carbon nanotube nanocomposite

CNT – COCl (20 mg) were reacted with 0.1 gr of chitaline in 5 ml of 2% acetic acid for 24h while stirring. The product was then washed three times with 10 ml of 2% acetic acid to remove excess reactants.

RESULTS AND DISCUSSION

FT-IR analysis

FT-IR analysis of chitosan: FT-IR absorption peaks for chitosan were shown in Fig. 2. The strong band between $3200\text{--}3600\text{ cm}^{-1}$ was attributed to overlapping -OH and -NH stretching. Other peaks include: absorption bands at 1055 cm^{-1} due to asymmetric stretching of the C-O-C Bridge (1,4) glycosidic bonds and 2900 cm^{-1} due to -CH stretching and bending of - CH_3 . The absorption band at 1595 cm^{-1} was also attributed to -NH bending.

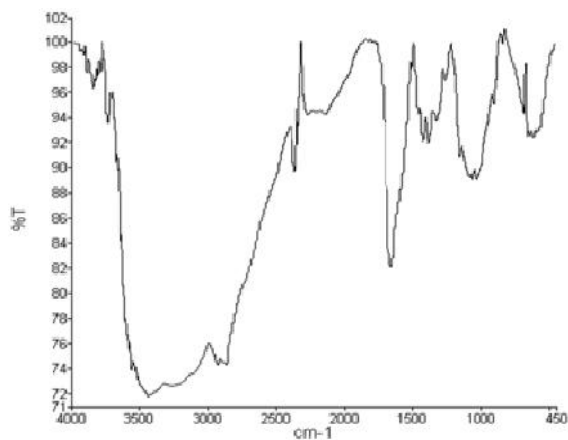


Fig. 2: FT-IR spectrum of chitosan.

FT-IR analysis of polyaniline (PAni): The spectrum of polyaniline is shown in Fig. 3 and exhibits an absorption band at 3460 cm^{-1} that could be attributed to NH_2 stretching mode. The spectra also shows the main bands in 1566 cm^{-1} and 1477 cm^{-1} corresponding to the stretching vibrations of the quinoid and benzenoid rings of aniline. The band between $1566\text{--}1601\text{ cm}^{-1}$ corresponds to bending vibration of N-H and the peak at 1293 cm^{-1} corresponds to the symmetric C-N stretching.

FT-IR analysis of chitaline: In Fig. 4 the broad and strong band between $3200\text{--}3600\text{ cm}^{-1}$ was attributed to overlapping between -OH in chitosan and -NH

stretching in PANi. Other peaks which were characteristic of chitaline included absorption bands at 2900 cm^{-1} due to $-\text{CH}$ stretching in $-\text{CH}$ and 1605 cm^{-1} due to $-\text{NH}$ and 1443 cm^{-1} due to stretching vibration of $\text{C}=\text{C}$ and $\text{C}=\text{N}$. When PANi is grafted onto chitosan, the peak at 1073 cm^{-1} disappears and a noticeable peak near 1100 cm^{-1} appears which indicates the presence of chitaline.

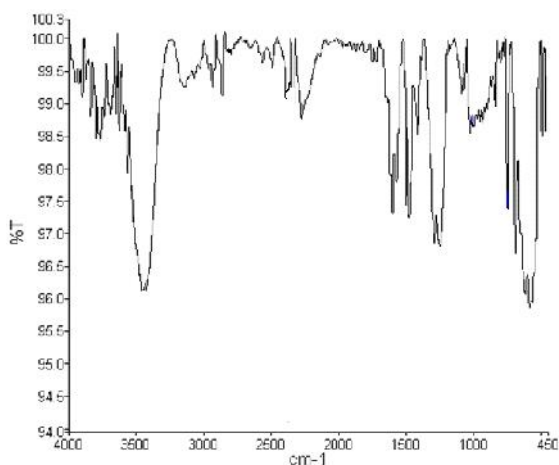


Fig. 3: FT-IR spectrum of PANi.

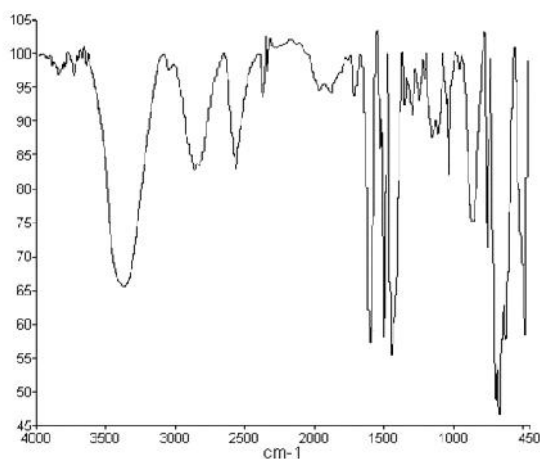


Fig. 4: FT-IR spectrum of chitaline.

FT-IR analysis of SWCNT-COOH: The spectrum of SWCNT-COOH in Fig. 5 shows a sharp absorbance at 1617 cm^{-1} which refers to the $\text{C}=\text{O}$ stretching in COOH . The broad and strong band at 3467 cm^{-1} was attributed to OH stretching in COOH .

FT-IR analysis of SWCNT-COCl: The FT-IR spectrum of synthesized SWCNT-COCl in Fig. 6 shows a sharp absorbance at 610 cm^{-1} which refers to the $\text{C}-\text{Cl}$ band in COCl . The absorption band at 1706 cm^{-1} was attributed to $\text{C}=\text{O}$ stretching in COCl and indicates the presence of Cl .

FT-IR analysis of polyaniline-chitosan-functionalized single walled carbon nanotube nanocomposite: In Fig. 7 the peaks are observed in the area of 1594 cm^{-1} and 1156 cm^{-1} . The 1594 cm^{-1} attributed to $\text{N}-\text{H}$ stretching vibration. The 1156 cm^{-1} attributed to $\text{C}-\text{N}$ stretching. These peaks attributed to presence of $-\text{C}=\text{O}$ and $-\text{C}-\text{N}$ of $-\text{NHCO}-$. The spectrum of the CNT-chitosan-polyaniline indicated the $-\text{COCl}$ of SWCNT were reacted mainly with the $-\text{NH}_2$ of chitosan and turned into $-\text{NHCO}-$.

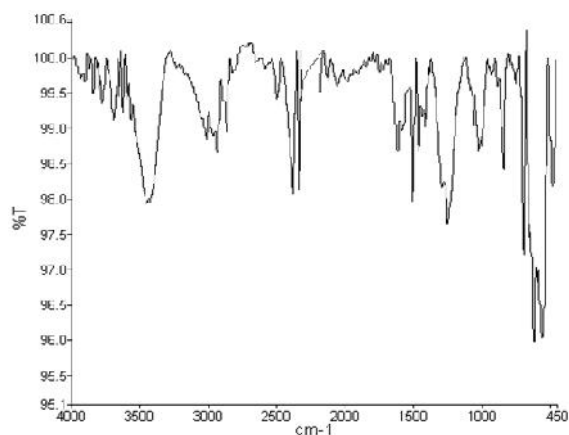


Fig. 5: FT-IR spectrum of SWCNT-COOH.

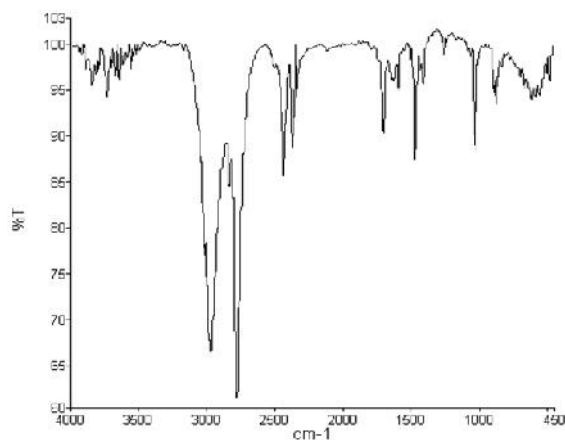


Fig. 6: FT-IR spectrum of SWCNT-COCl.

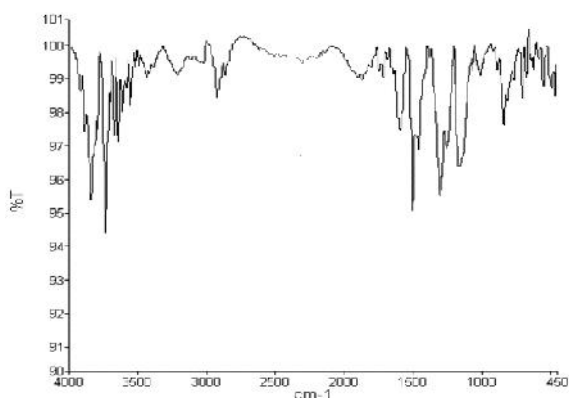


Fig. 7: FT-IR spectrum of polyaniline-chitosan-functionalized single walled carbon nanotube nanocomposite.

Morphology

SEM micrograph of chitaline: Morphology of the synthesized compounds were studied using scanning electron microscopy (SEM). In Fig. 8. SEM micrographs are shown which are related to: a) chitosan, b) CNTCOOH, c) CNTCOCl, d) polyaniline, e)chitaline and f) polyaniline-chitosan-functionalized single walled carbon nanotube nanocomposite. In SEM image of chitaline the attachment of chitosan to the polyaniline is indicated by the thin strings in Fig. 8e which results from covalent bond formation. After functionalization of SWCNTs, it was observed that the diameter of functionalized SWCNTs were more than that of pristine SWCNTs which indicates the presence of chloride atoms that are shown in figures 8 b and c.

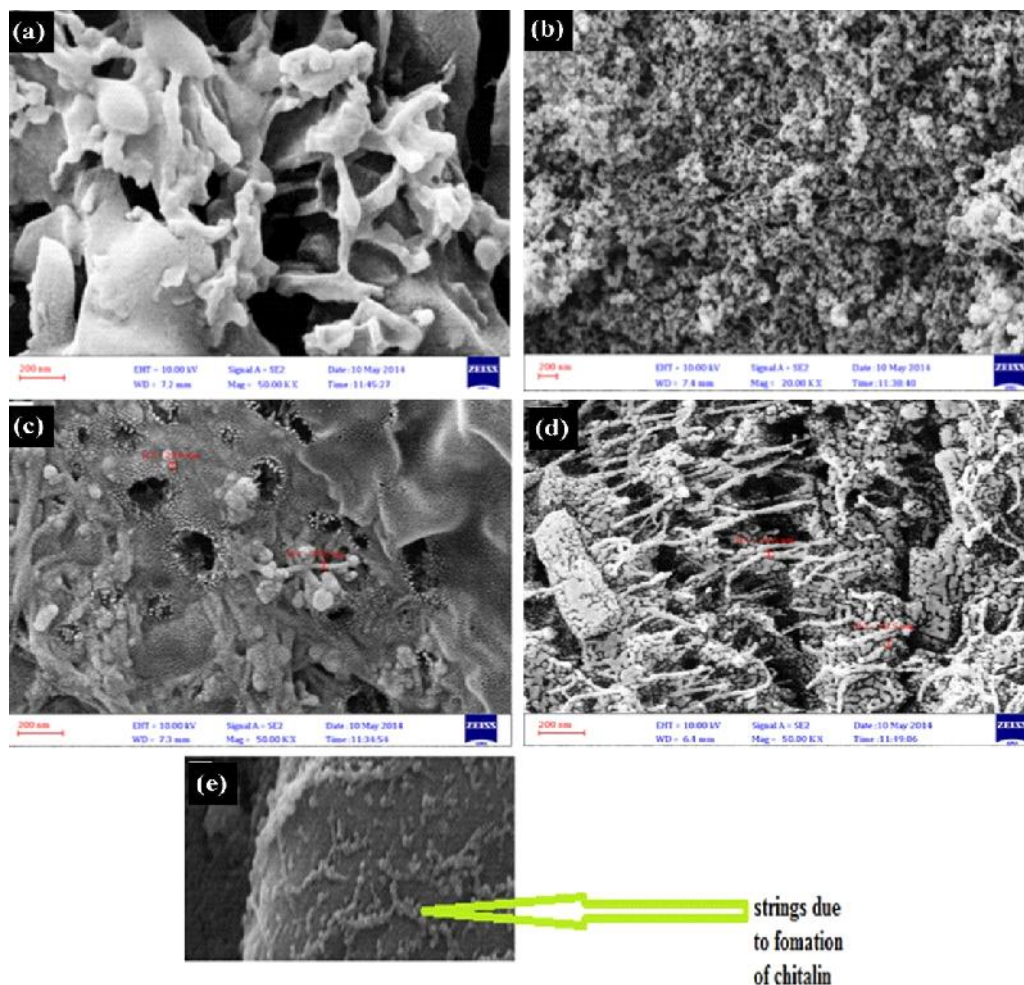


Fig. 8: SEM micrograph for a) chitosan, b) CNTCOOH, c) CNTCOCl, d) polyaniline, e) chitaline, f) polyaniline-chitosan-functionalized single walled carbon nanotube nanocomposite.

SEMized single walled carbon nanotube nanocomposite: To investigate the effect of different factors, SEM observations were carried out on the morphology of polyaniline-chitosan-functionalized single walled carbon nanotube nanocomposite. The SEM micrograph in Fig. 8-f shows the synthesized nanocomposite consisting SWCNTs and chitaline which are attached by covalent bondings and shown whit strings in the figure. SWCNTs, chitosan and polyaniline and the attachments are also indicated in this figure.

Thermo gravimetric analysis (TGA-DSC): The thermal stability of chitaline and polyaniline-chitosan-functionalized single walled carbon nanotube nanocomposite were analyzed using thermo gravimetric analysis (TGA). The nanocomposite, begins to soften from the temperature about 45 °C. This issued by the loosening of connections between PANi, chitosan and SWCNT. Heating process was started from 30 °C and continued to 800 °C. There

are endothermic areas and exothermic areas in these curves. Exothermic areas are due to degradation and gas formation that is along with heat production. The Fig. 9 indicates that at between 100-200 °C weight losses in case of SWCNT-chitosan-polyaniline nanocomposite is around 5% and for the chitaline it is around 10%. This may be due to the absorbance of water vapor by the sample. In SWCNT-chitosan-polyaniline nanocomposite the weight loss is 18% at 400 °C and for the chitaline it is around 25%. In SWCNT-chitosan-polyaniline nanocomposite the weight loss is 58% and for the chitaline it is around 48% at 800 °C which can be attributed to the structure of nanocomposite and breaking the covalent bonds. This degradation appears to be delayed in SWCNT-chitosan-PANi which confirms the formation of covalent bond and formation of the thermal stable nanocomposite and this is the reason of disappearing the second exothermic peak at 600 °C in chitaline as shown in Fig. 10.

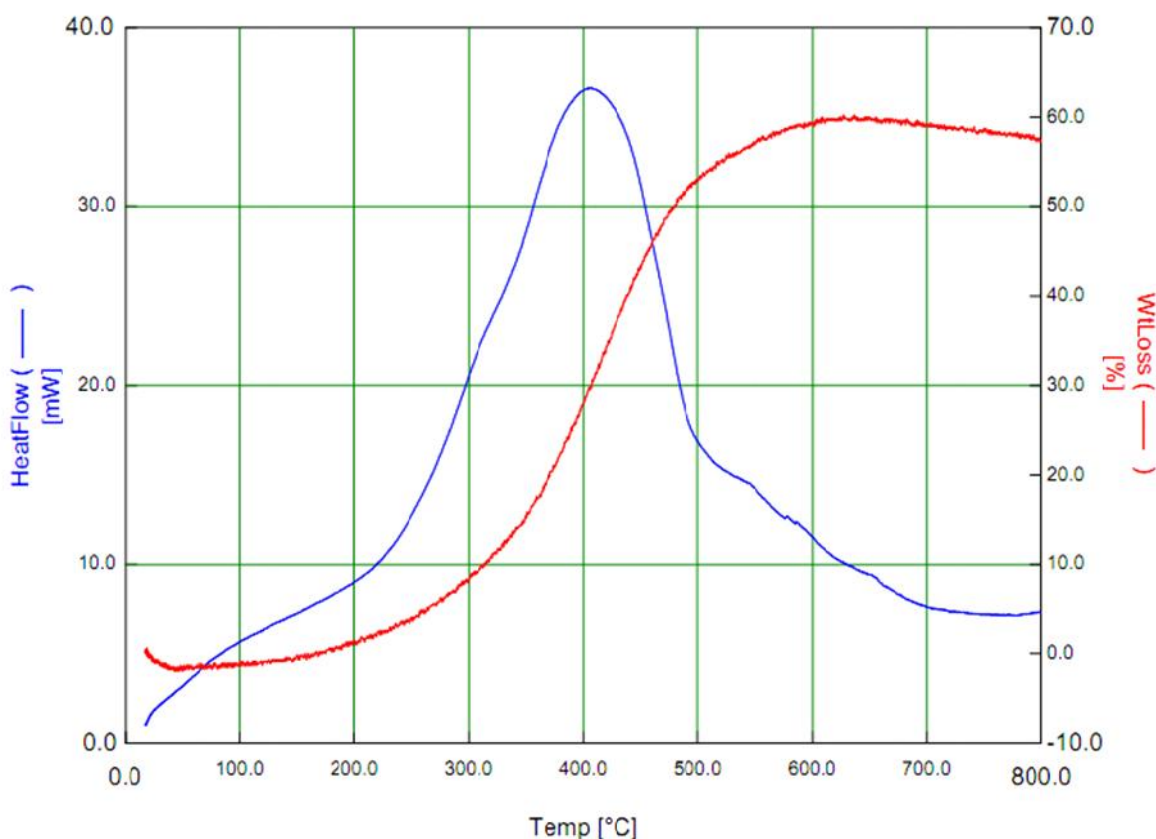


Fig. 9: TGA spectrum of polyaniline-chitosan-functionalized single walled carbon nanotube nanocomposite.

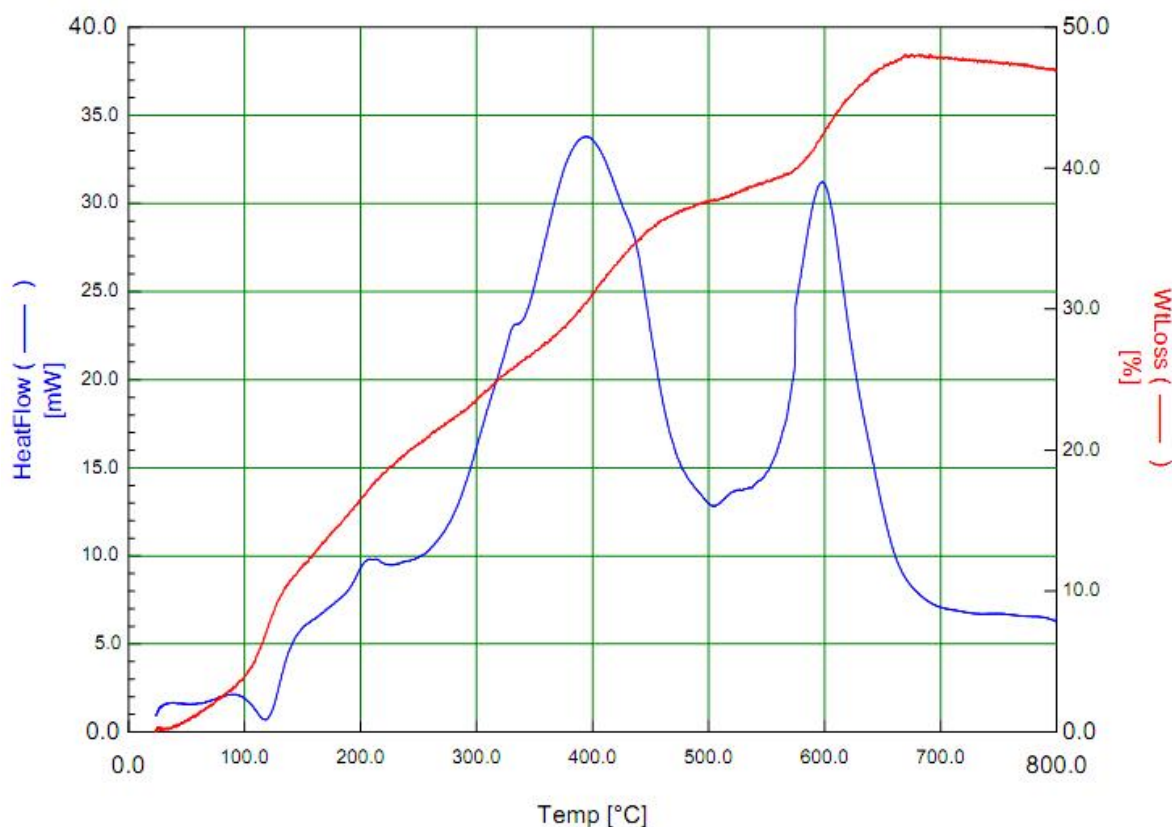


Fig. 10: TGA spectrum of chitaline.

CONCLUSION

The synthesized nanocomposite was characterized to evaluate the structure and morphology by further infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and thermal gravimetry analysis. The SEM for CNTs indicated the attachment of SWCNTs to the chitaline and further attachment between SWCNTs-chitosan-polyaniline were confirmed. Also TGA confirmed the thermal stability of the synthesized nanocomposite by chemical grafting process. The results showed that the formation of the composite in nano scale can be good carbon materials with high adsorption capacity in porous surfaces for improving the properties as a good candidate such as nano bio filter for removing the organic and inorganic wastes from water.

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