



## Study of doping of polyaniline composite with HCl in situ polymerization

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### Abstract

In the present research field polymerization way for the synthesis of polyaniline (PANI) This research paper reported the doping of polyaniline with single walled and multiwall carbon nanotubes by chemical oxidation method in situ polymerization. Here we use HCL as a dopant and APS (ammonium peroxy disulphite) as an oxidizing agent . The MWCNT were ultrasonicated to obtain uniform dispersion within the PANI matrix. The molecular structure is determined by forier transform infrared spectroscopy (FTIR)which show the peaks of pure PANI comparing with its composite .Structural information can be obtained from X – Ray diffraction study (XRD).TGA (Thermogravmetric analysis ) is use to identify the stability of composite at certain temperature .

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### Introduction

Since the discovery of conductive polyacetylene (PA) by iodine doping, [1] other p-conjugated polymers such as polypyrrole (PPy), polyaniline (PANI) and polythiophenes(PTH) have been reported as conducting polymers (CPs)[2] A polymer-Carbon nanotubes (CNTs) composite is a combination of polymer matrix with CNTs that possess properties that are unique and cannot be obtained with each material acting alone. CNTs with unique electrical, thermal and mechanical properties has become a potential candidate for wide range of applications in nanoscience and nanotechnology, suitable to serve as conducting filler in polymer nanocomposite. As carbonaceous nanofillers, CNTs play a very promising role due to their better structural and functional properties such as high aspect ratio, high mechanical strength, and high electrical properties etc. than other fillers [3]. The conducting polymers receive much attention because of their wide application range. Among the several conducting polymers, Polyaniline (PANI) has been studied extensively due to its high electrical conductivity, abundant raw materials, easy synthesis, good environmental stability, cost effectiveness and simple redox chemistry [4]. The PANI-CNT nanocomposite is one of the versatile nanocomposite due to the numerous applications such as Biosensor [5], Super capacitor [6], Solar cell [7], Fuel cell [8], Corrosion protection [9], etc. On the other hand, carbon allotropes including fullerene, Single/multiwall carbon nanotubes (CNTs), graphite, diamond and Graphene have attracted considerable attention over the last two decades because of their excellent properties and wide applications[10].

**Experimental****Materials**

Commercial aniline, Ammonium peroxodisulfate (APS), methanol and corporation company while hydrogen chloride (37%) and acetone were supplied from Savita chemicals (INDIA). MWCNT was supplied from TECHINSTRO Company with diameters 10–50 nm, length 10  $\mu\text{m}$  and number of layers nearly 4–8.

**Nano-PANI-composites preparation**

The MWCNT-acid-doped PANI composites were created via in situ chemical polymerization. In a typical PANI technique, 150 ml of distilled water was combined with 5 mol of aniline monomer, and the mixture was agitated in an ice bath at 3 °C for 1 h; MWCNT composite core was taken in at 0.15 wt%. After being dissolved in 20 ml of 1.0 M HCl solution and being sonicate in an ultrasonic bath for three hours, the weighted composite core was mixed with aniline-HCl solution using a magnetic stirrer. The suspension was then mixed with 60 ml of an aqueous solution containing 5 mol of APS, and the combination was agitated at 0 to 5 °C for two minutes. . Subsequently, the samples were kept at 3°C to complete polymerization process. Ppt in a green colour appeared. To remove any contaminants, the products were filtered, cleaned with HCl 1 M, acetone-methanol, and then cooled at 50 °C for two hours in a Petri dish to prevent PANI nanoparticle aggregation. According to PANI/composite ratios, the synthesized composites are organized.

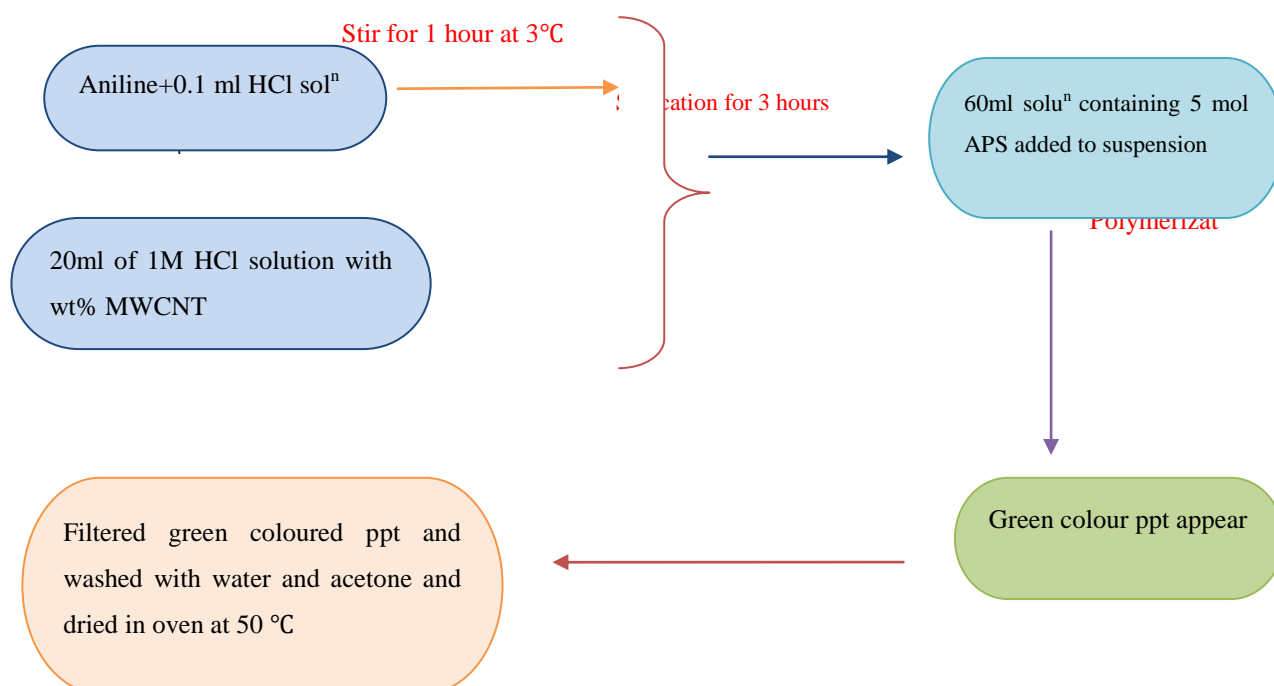


Table 1 PANI/composites ratio

No.	Sample	Composite core (wt %)
1.	MWCNT /PANI	0.15

## Instrumentation

X-ray diffraction (XRD) analysis was performed on an X-ray diffractometry from PANI analytical company model BRUKER-binary V3 with 2 $\theta$  from 10 to 90 and conditions 40 mA, 40 kV and wavelength of Copper Ka1 at 1.54 Å. The Fourier transform infrared spectroscopy (FTIR) spectrum (400–4000 cm<sup>-1</sup>) was measured. Using PerkinElmer Spectrum Version 10.4.00, the sample was mixed with pure KBr as the background, and then the mixture was dried and compressed into a transparent tablet for measurement. XRD patterns were recorded on a Bruker's model D<sub>8</sub> advance system using nickel filtered Cu-K $\alpha$  radiation as the X-Ray source. The thermal stability was assessed by thermal gravimetric analysis (TGA) (SDT Q600 V20.5 Build 15) in the temperature range of 10–900 °C (10 °C/min) under a nitrogen atmosphere.

## Results and discussion

### a) Fourier Transform infrared characterization (FTIR)

FTIR technique for analysis of various conducting polymer composites is renowned to be appropriate to characterize functional groups, chemical bonds, and the components of anonymous sample mixtures. The recorded spectra are in the range of 4000–400 cm<sup>-1</sup> spectrum.

The characteristic absorption band found in FTIR represented in figure confirms the conductive emeraldine salt state of polyaniline [11]. The two bands observed in vicinity of 1564.70 cm<sup>-1</sup> and 1488.13 cm<sup>-1</sup> are assigned to the stretching vibration mode of quinoid (C=N) rings and benzenoid rings, respectively. These two bands surely reveal that the polymer is formed of imines and amine units. Furthermore, the peaks at 3436.11 ~ 3425.62 cm<sup>-1</sup> and 1292.20 ~ 1292.78 cm<sup>-1</sup> attribute to stretching vibration mode of N-H bond and C-H bond, respectively. A band noticed at 796.44 ~ 800.33 cm<sup>-1</sup> is responsible for out of plane bending of C-H.

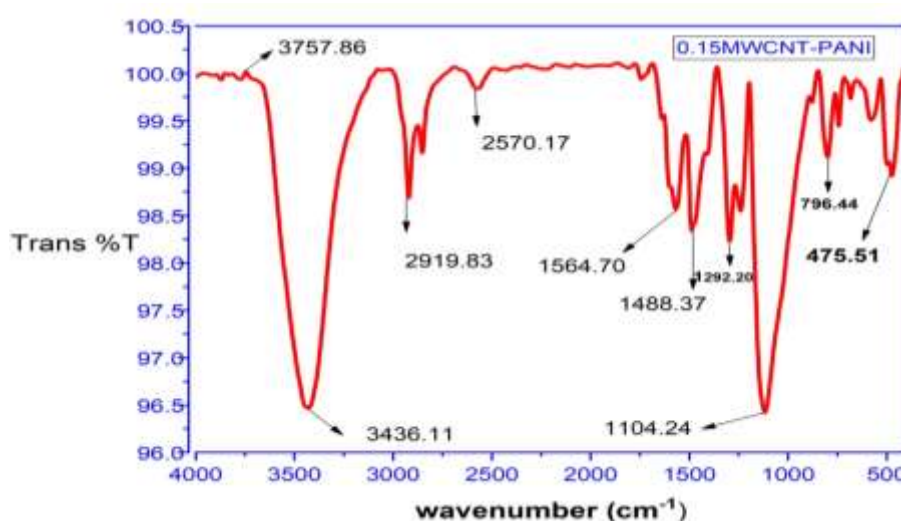
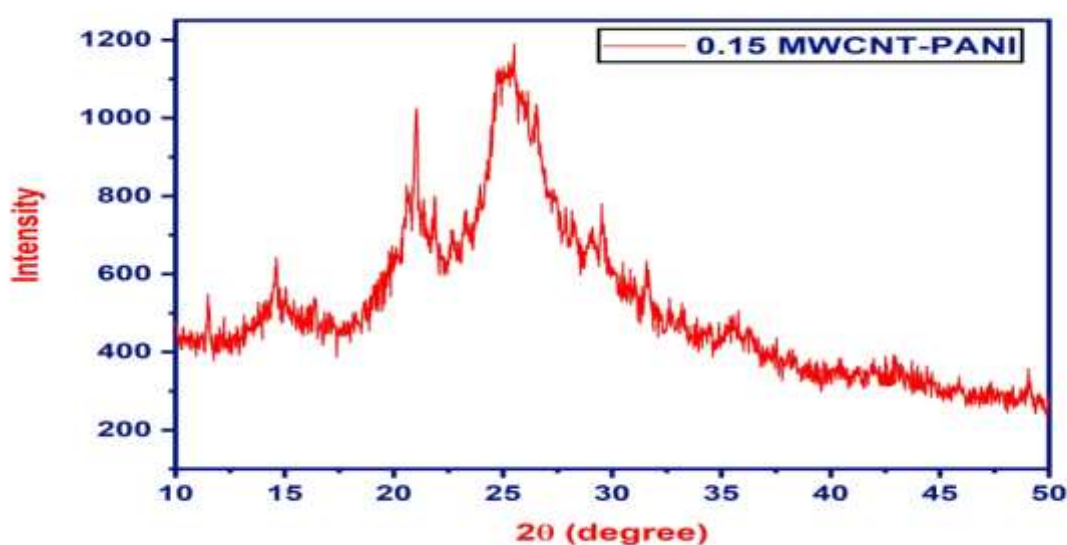


Figure 1: FTIR Graph of MWCNT-PANI

**b) X-Ray diffraction study (XRD)**

The typical XRD pattern of MWCNT –PANI in figure .Two peak diffracted at the angle of  $2\theta=20.5$  and  $25.37$  corresponding to (010) and (200) crystal planes, respectively, of represented the presence of polyaniline [12]

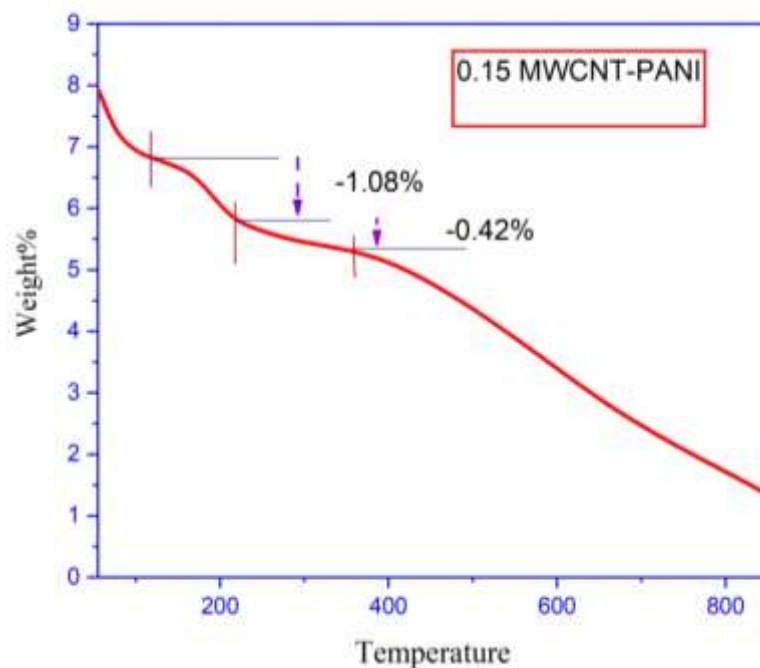
The broad bump observed in XRD pattern confirms the semi crystalline characteristic of polyaniline [13]which is due to the repetition of quinoid and benzenoid rings in polymer matrix.XRD spectrum indicating no additional crystalline order had been introduced to the PANI. The intensity of (200) reflection was enhanced by increasing the wt%.



**Figure 2: XRD Graph of MWCNT-PANI**

**c) Thermal Examination****Thermogravimetric Analysis (TGA)**

The thermal stability of synthesized PANI –MWCNT nanocomposite was studied using Thermogravimetric analysis (TGA) figure ().Taken in an atmosphere of nitrogen with the range of 50 to 500 C at the scanning temperature range of  $10\text{ C min}^{-1}$ .the weight of the sample was used 2.088 mg. The weight loss observed in TGA curve of PANI –MWCNT in three step .The loss of mass in 1st step begins at approx.  $130^{\circ}\text{C}$  C and keeps going until temperature reaches to  $230^{\circ}\text{C}$ . A significant weight loss of about -1.08 % is observed due to evaporation of  $\text{H}_2\text{O}$  molecule absorbed on the surface of PANI as it has extraordinary hygroscopic nature. The second steady decline in weight occurred at a temperature  $200^{\circ}\text{C}$  to  $230^{\circ}\text{C}$  specifying 0.42 % weight loss. The second weight loss attributed to the decomposition of acid dopant confined to the PANI.A rapid loss of weight was observed after  $250^{\circ}\text{C}$  which was due to the oxidative degradation of polymer chain. The presence of benzenoid ring in chain is responsible for better thermal stability of Polyaniline. The presence of quinoid ring in structure of PANI is accountable for the inferior stability [14].



**Figure 3: TGA Graph of MWCNT-PANI**

### Conclusion

In this work PANI/MWCNT composite were prepared via in situ polymerization .FTIR, XRD and TGA prove that, peaks FTIR show the presence of PANI. And XRD data show the semi crystalline behavior of composite, TGA show the stability after 400 °C.

### References

1. Shirakawa, H., Louis, E. J., MacDiarmid, A.G., Chiang, C.K., Heeger, A.J.: Synthesis of electrically conducting organic polymers:halogen derivatives of polyacetylene, (CH)<sub>x</sub>. J. Chem. Soc.Chem. Commun. 578–580 (1977). doi:[10.1039/c39770000578](https://doi.org/10.1039/c39770000578).
2. 2 Nalwa, H.S.: Encyclopedia of Nanoscience and Nanotechnology.CRC Press, Boca Raton (2004).
3. G. Mittal, V. Dhand, K. Y. Rhee, S.-J. Park, and W. R. Lee, "A review on carbon nanotubes and graphene as fillers in reinforced polymer nanocomposites," *Journal of Industrial and Engineering Chemistry*, vol. 21, pp. 11-25, 2015.
4. S. Palaniappan and A. John, "Polyaniline materials by emulsion polymerization pathway," *Progress in Polymer Science*, vol. 33, pp. 732-758, 2008.
5. T. H. Le, N. T. Trinh, L. H. Nguyen, H. B. Nguyen, V. A. Nguyen, and T. D. Nguyen, "Electrosynthesis of polyaniline–mutilwalled carbon nanotube nanocomposite films in the presence of sodium dodecyl sulfate for glucose biosensing," *Advances in Natural Sciences: Nanoscience and Nanotechnology*, vol. 4, p. 025014, 2013.

6. M. S. Dorraji, I. Ahadzadeh, and M. Rasoulifard, "Chitosan/polyaniline/MWCNT nanocomposite fibers as an electrode material for electrical double layer capacitors," *International Journal of Hydrogen Energy*, vol. 39, pp. 9350-9355, 2014.
7. H. Zhang, B. He, Q. Tang, and L. Yu, "Bifacial dye-sensitized solar cells from covalent-bonded polyaniline–multiwall carbon nanotubes complex counter electrodes," *Journal of Power Sources*, vol. 275, pp. 489-497, 2015 .
8. H.-F. Cui, L. Du, P.-B. Guo, B. Zhu, and J. H. Luong, "Controlled modification of carbon nanotubes and polyaniline on macroporous graphite felt for high-performance microbial fuel cell anode," *Journal of Power Sources*, vol. 283, pp. 46-53, 2015.
9. A. M. Kumar and Z. M. Gasem, "In situ electrochemical synthesis of polyaniline/f-MWCNT nanocomposite coatings on mild steel for corrosion protection in 3.5% NaCl solution," *Progress in Organic Coatings*, vol. 78, pp. 387-394, 2015 .
10. Anderson, M.R., Mattes, B.R., Reiss, H., Kaner, R.B.: Conjugated polymer films for gas separations. *Science* 252, 1412–1415 (1991)
11. Pinna, C.D.; Zappa, E.; Busca, G.; Sironi, A.; Falletta, E. Electrochemical property of polyaniline prepared by two different approaches and their applicability in force measurement . *sens. actuators B: Chem.* **2014**, 201395-401.
12. Mostafaei, A., & Zolriasatein, A. (2012). Synthesis and characterization of conducting polyaniline nanocomposite containing ZnO nanorods. *Progress in Natural Science: Materials International*, 22(4), 273-280.
13. Bi, W.; Haung, J.; Wang, M.; Jahrman, E.P.; Seidler, G.T.; Wang, J.; Wu, Y.; Gao, G.; Cao, G. (2019). V<sub>2</sub> O<sub>5</sub>-conductive polymer noncable with built-in local electric field derived from interface oxygen vacancies for high energy density supercapacitors. *J. Mater. Chem. A*, 1-9.
14. Porramezan, M., & Eisazadeh, H. (2011). Fabrication and characterization of polyaniline nanocomposite modified with Ag<sub>2</sub>O nanoparticles. *Composites Part B: Engineering*, 42(7), 1980-1986.