

Preparation of Polyaniline (Pani): It's Composites with Functionalised Multi Walled Carbon NanotubesKarina Khan¹, Monika Trivedi¹, Anil Kumar²¹ Jayoti Vidyapeeth Women's University, Jaipur, Rajasthan, India,²Lovely Professional University, Phagwara, 144411, India.**Abstract**

In the present study a polymerization route for the synthesis of polyaniline (PANI) salts adopted. Polyaniline synthesized by solvent free technique i.e. chemical oxidative polymerization method using HCl as dopant and ammonium peroxodisulphate (APS) as oxidizing agent. The fabrication of multiwalled carbon nanotubes (MWCNTs)/PANI composites membrane by a filtration and flash welding method. MWNTs are treated with acid i.e. functionalisation of MWCNT to acquire better distribution in the composite membranes. PANI-nanofibers with a unique electrical property are obtained by chemical oxidative polymerization of aniline. PANI and PANI/MWCNT characterized by XRD, FTIR, UV-vis, SEM, TGA, I-V Curve. The electrical conductivity is found to be increased in PANI/MWCNT composites than pure PANI. These results indicates that the further more improvement in material consistency and reduction in defect states, for further use the PANI/carbon nanotubes material can be used to fabricate organic electronic devices.

Keyword: PANI, XRD, FTIR, MWNT, TGA, Carbon.**1. Introduction**

Generally polymers possess insulating nature, but a new class of polymers introduced which can conduct electric current and are known as conducting polymers. In 2000, the three scientists Heeger, MacDiarmid and Shirakawa were awarded by the Nobel Prize in chemistry for their tremendous discovery and development of conducting polymers [1-3].

Conducting polymers have various applications such as light emitting diode [4], sensors [5], data storage [6], rechargeable batteries [7], catalyst supports [8], solar-cell devices [9], field-effect transistors [10], corrosion protection [11], actuators [12] and many more.

The most popular polymer among the class of conducting polymer is polyaniline (PANI). Among the three oxidation states of PANI, emeraldine which is the partially oxidized polymer is the most attractive form due to its adaptive states: emeraldine salt (ES) and emeraldine base (EB). ES is the conductive salt form of PANI. It can be synthesized by various chemical and electrochemical methods [13]. Proton doping is done when the emeraldine films dipped in acid and acid in the form of gas passes over them to protonate the imine nitrogen atoms in the polymer. Emeraldine salt can be converted into insulating emeraldine base by treating it with aqueous alkali. The emeraldine base contains number of alternating amine units and imine units which are repeated along the chain [14,15]. Mostly HCl is used as protonic acid unlike any other strong acid for the protonation occurs at the nitrogen in imines. The -NH- group is only group in the polyaniline and present in its backbone, responsible for the creating interest in chemistry and physics [16]. PANI can be synthesized by various methods. One of them is solvent free method used for synthesis of PANI a wet grinding solid-phase reaction produces superior conductivity 27 S/cm [17] and another is chemical oxidative polymerization method (COP) adopted for

the preparation of PANI which gives better yield by using oxidizing agent like ammonium peroxodisulphate (APS) [18]. In the present study this method adopted for synthesized PANI.

The composites of conducting polymer may have significantly improved electrical and mechanical properties as compared to the pure conducting polymers. Several studies have been done on the various aspects of polymer- carbon nanotubes (CNTs) composites. (CNTs) due to its exotic properties like high electrical conductivity, high tensile strength, high thermal conductivity, good electron field emitters etc. used to form composites with polymers. The properties of nanotubes depend on atomic arrangement, morphology, and nanostructure. CNT are classified into two: first one is single walled carbon nanotubes (SWNTs), consist of single sheet of grapheme rolled to form a cylinder of order of 1nm. Another is multi-walled nanotubes (MWNTs), consist of an array of such cylinders formed concentrically which is separated by 0.35 nm [19]. CNT's behaves as a metal or as a semiconductor, confiding on its chirality [20]. Flash welding method is used for synthesis the CNT/PANI composites [21].

But CNTs tend to aggregate and entangled spontaneously. The poor chemical compatibility limits their application that's why the fuctionalizations of CNTs are required. Refluxing is the appropriate method for the functionalization of CNTs [22].

The aim of this study is to provide a report about the development in the different methods of synthesis of PANI, CNT/PANI composites and functionalized CNT/PANI composites.

2. Experimental

2.1 Materials and Method

Double Distilled Aniline (Merck, $C_6H_5NH_2$, $M=93.13$ g/ mol, 99%), Ammonium peroxodisulphate (APS) (Merck, $(NH_4)_2S_2O_8$, $M=228.20$ g/mol, $\geq 98\%$), Hydrochloric acid (Merck, HCl , $M=36.46$ g/mol, 37%), Multi Walled Carbon Nanotubes (ISHU interMWCNTs, $< 2\%$), Conc. Sulfuric acid (H_2SO_4 , $M=98.08$ g/mol, 98%), Conc. Nitric acid (Qualige, HNO_3 , $M=63.01$ g/mol, 0.01%), functionalized CNTs, Dimethyl sulfoxide (HI Media, DMSO, C_2H_6OS , $M=78.13$ g/mol, 99.5%).

(a) Chemical oxidative polymerization method: PANI synthesized by using APS as an oxidizing agent. Firstly APS added into the 100 ml solution of DI water and HCl (4:1) taken into the titration flask over a water bath maintaining temperature below $5^\circ C$. Then pre distilled aniline was added drop wise into the solution upto 30 minutes with vigorous stirring. After the completion of the addition of aniline it kept for stirring for further 3 hours in the same air tight flask. After 3 hrs this solution was kept for 10-15 hours at room temperature in the same air tight flask for complete polymerization of aniline. A dark greenish precipitate was obtained and it followed by filtering and washing it 2-3 times by DI water and 2-3 times by acetone and dried at $80^\circ C$ in incubator. Polyaniline powder is formed which was grinded into fine powder and kept in vacuum desiccators [18]

(b) Functionlisation of CNT: Firstly a solution of conc. H_2SO_4 and conc. HNO_3 was prepared in 3:1 (H_2SO_4 ; HNO_3) molar ratio. Then pristine MWCNTs added into it then this solution was sonicate at $40^\circ C$ for 6 hours. 1L D.I water added into it and keep it for rest for overnight. The MWCNTs settled down into the beaker. Now centrifuge this by adding more DI water till this solution become neutral. After that the MWCNTs was poured into Petridis and dried at $55^\circ C$ for 12hrs [19].

(c) PANI/MWCNT composite: Functionalized MWCNTs of different weight percent (0.5 wt.%, 1.0 wt.%, 1.5wt% and 2.0wt%) was added into the 5 ml DMSO solution and sonicate it for 2 hours at room temperature. After sonication PANI added into the solution of MWCNTs and kept for stirring till 1hour. Then this solution was filtered and followed by washing for 3-4 times using DI water and methanol then dried at 55°C for 12hrs in incubator [23]. After this lightly grinded functionalized PANI/MWCNT put in air tight Eppendorf tube.

3. Results and Discussion

3.1 Fourier Transform infrared (FTIR) Spectroscopy Anal

Fig 1(b) shows the FTIR spectra of PANI/MWCNT nanocomposite. It shows that the typical characteristic bands in 3433.85 cm⁻¹, 2922 cm⁻¹, 1466.72 cm⁻¹, 1293.20 cm⁻¹, 1118.08 cm⁻¹, 790 cm⁻¹, which represents combination of the FTIR bands of acid-treated MWCNTs and those of PANI-nanofibers. The composites of different wt. % MWCNT doped PANI shows that band at the same position but differ in intensity, which may be due to the interaction of MWCNTs with the polymeric chains [21].

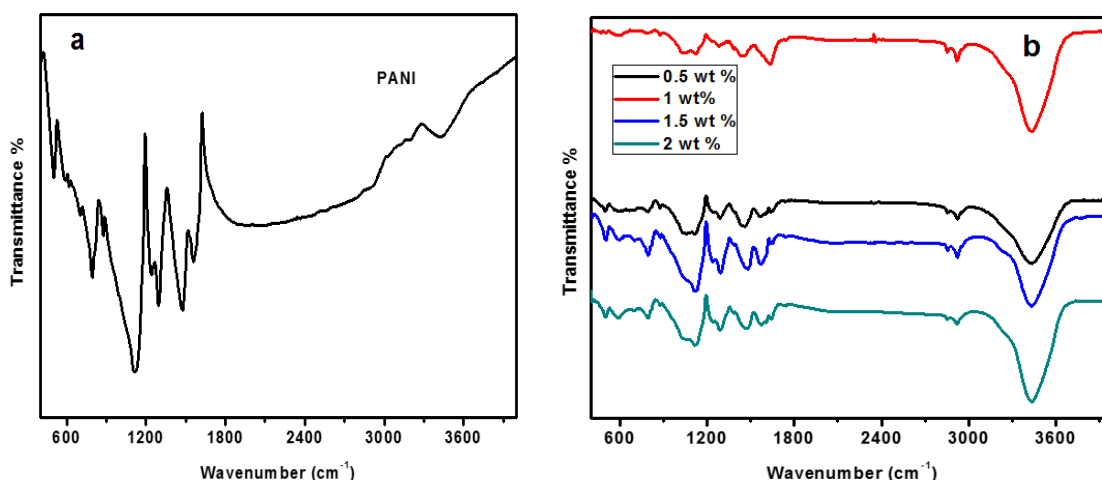


Fig 1: FTIR spectra of (a) pure PANI and (b) PANI/MWCNT nanocomposite

3.2 Ultraviolet-Visible (UV-Vis) Spectra Analysis:

Fig. 2 represents the absorption spectra of pure PANI and PANI/MWCNT nano-composites. **Fig. 3a** shows the absorption peak at ~332 nm is due to the excitation of benzenoid rings in PANI and the peak at ~635 nm is due to the is related to the doping level and formation of polaron of the conducting form and due to exciton absorption of the quinoid rings [1]. A broad hump starting from 605 nm is related to the doping level and formation of polarons of the conducting form. It can be seen from the graph the band gap of pure PANI is found to be 3.21 eV (**Fig.4c**). While, the **Fig. 3b** shows the absorption spectra of PANI doped MWCNTs which shows the two characteristic bands at 332 nm in visible corresponds to inter ring charge transfer ratio of benzenoid to quinoids and at 635 nm in UV corresponds to π - π^* transition along the polymer chain [24], it indicate that the synthesized emeraldine salt is in doped position. The intensity of the absorption band decrease with the 2wt% of MWCNT which indicated that the strong interaction between the quinoid rings with the MWCNTs.[25], while the additional band observed in the 2 wt. % MWCNT due to the polar functional group i.e.

MWCNT-COOH. The band gap of the nanocomposites is found to be (i) 0.5 weight % MWCNT(ii) 1 weight % MWCNT (iii) 1.5 weight % MWCNT (iv) 2 weight % MWCNT are 3.14 eV, 3.17 eV, 3.03 eV and 3.11 eV respectively

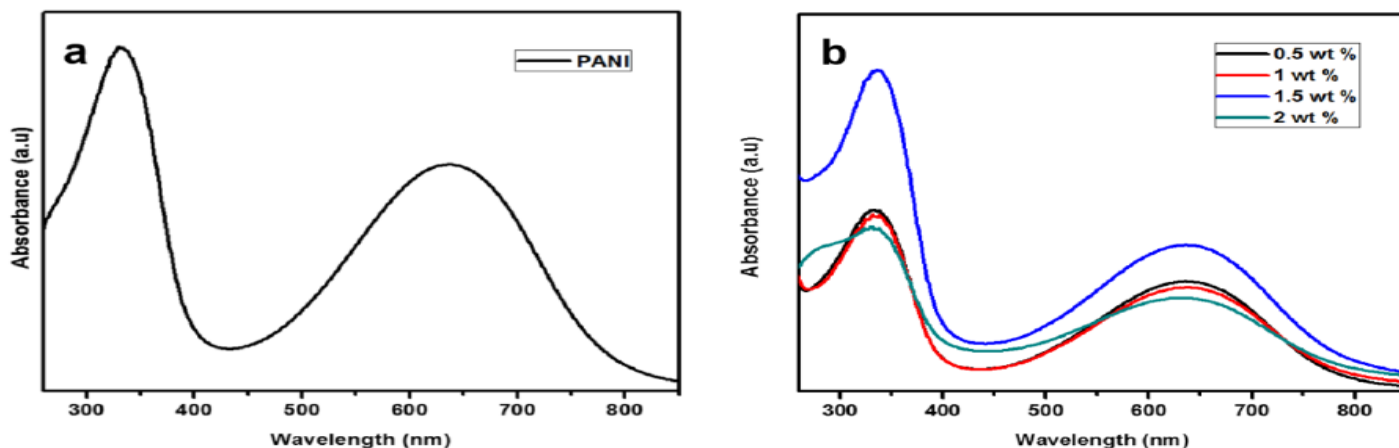
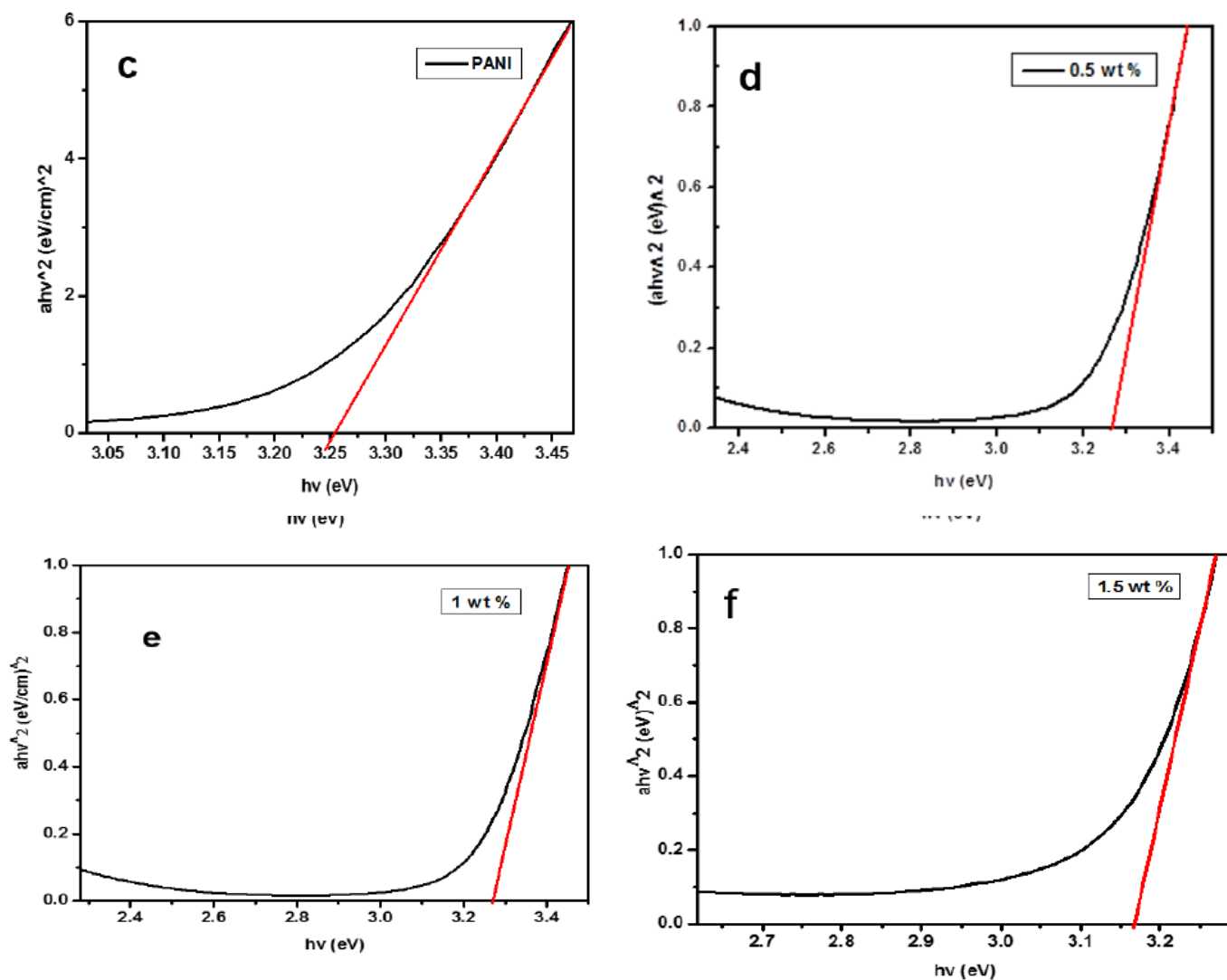


Fig 3 (a) Absorption spectra pure PANI and (b) PANI/MWCNTnanocomposites



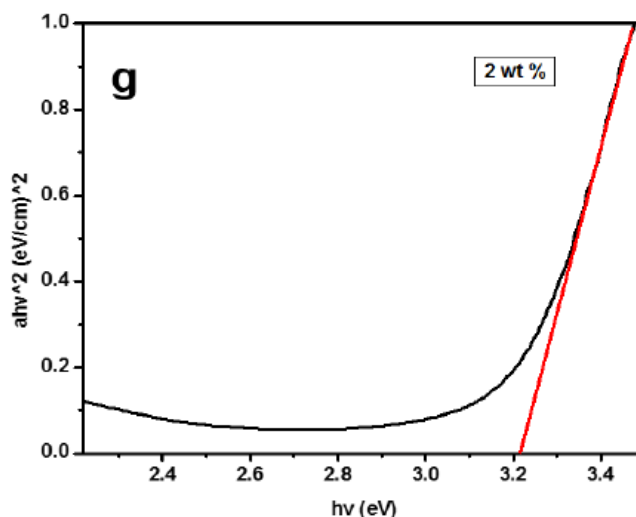


Fig 4 : Optical band gap of (c) pure PANI (d) 0.5 wt% MWCNT+PANI (e) 1.0wt% MWCNT+PANI (f) 1.5 wt% MWCNT+PANI (g) 2.0 wt% MWCNT+PANI

3.3 Current-Voltage (I-V) Curve Analysis:

I-V characteristic of the pure PANI and PANI/MWCNT composites is shown in **Fig. 5.**, From **Fig. 5a** it is to be found that the conductivity of pure PANI is about 0.2 S/cm. While with the doping of different wt. % of MWCNT into the PANI it is to be observed that the conductivity of PANI nanocomposite is increased for 0.5wt% MWCNT, 1wt % MWCNT, 1.5 wt% MWCNT and 2wt% MWCNT were calculated as 9.98×10^{-4} S/cm, 78.4×10^{-4} , and 33.3×10^{-4} and 47.37×10^{-4} S/cm respectively **Fig. 5b**. The conductivity of the composites increases up to 1wt. %MWCNT.

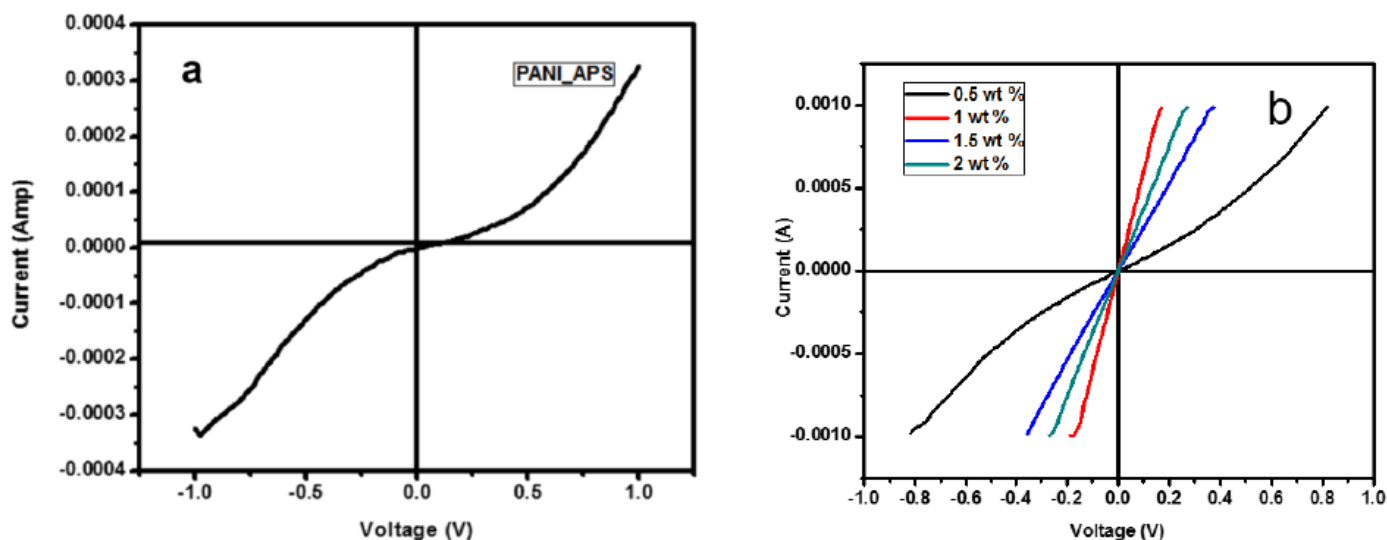


Fig 5: I-V characteristic of (a) pure PANI (b) PANI/MWCNT nanocomposites

3.4 X-ray diffraction (XRD) Analysis:

Fig 6 shows the XRD pattern of HCl doped PANI and the PANI/MWCNT nanocomposite. The XRD patterns of these sample have sharper peak ranging 2θ from 10° to 60° shows the presences of high crystallinity in these sample resolved the diffraction of emeraldine salts. The number of crystalline peak increases with increasing weight percent of MWCNT.

From XRD pattern (a) for pure PANI peak at $2\theta=14.85^\circ$ and 20.56° arises due to the amorphous nature of PANI and the peak at $2\theta= 25.60^\circ$ is the semi crystalline peak [26]. From XRD pattern of PANI/MWCNT the diffraction peaks were observed at $2\theta = 14^\circ \sim 25^\circ$ are similar to pure PANI and in pattern of 1.5 wt. % and 2.0 wt.% $2\theta = 41.02^\circ$ and 49.76° indicate incorporation of MWCNT over the PANI and also additional peaks indicates that the semi-crystalline order has been introduced [27].

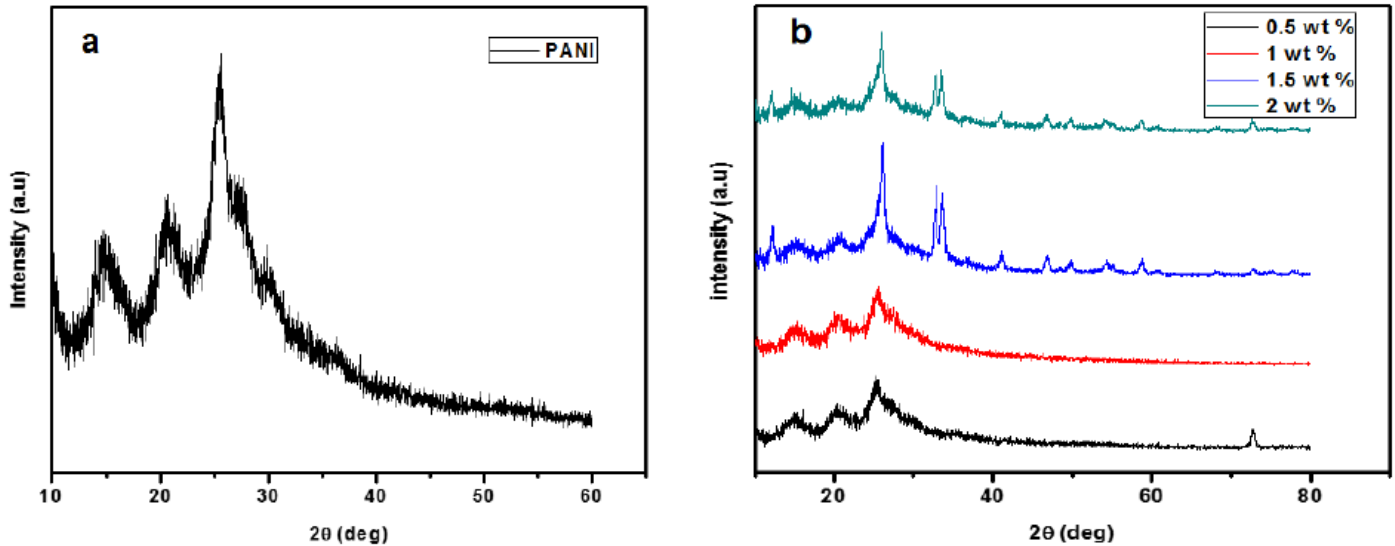


Fig. 6: XRD patterns of (a) pure PANI and (b) PANI/MWCNT nanocomposites

4.5 Scanning Electron Microscopy (SEM)

Fig 7 (a&b) shows the morphology of the pure PANI and MWCNT doped PANI. From the SEM images it is to be observed the fibular morphology of the PANI. It is to be observed from fig. 7b the presence of MWCNT along with PANI fibers.

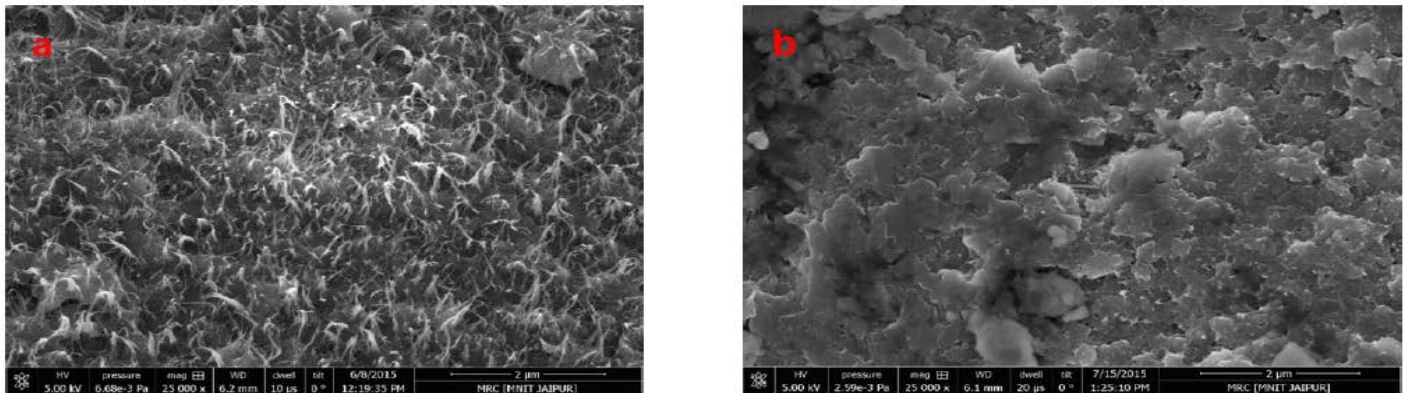


Fig 7 (a) SEM image of pure PANI (b) SEM image of PANI/MWCNT nanocomposites

4.6 Thermogravimetric Analysis (TGA)

TGA of the pure PANI and MWCNT doped PANI shows in Fig 8. Initially the mass loss of the PANI because of the water molecules starts from the $50^\circ-110^\circ\text{C}$, while the loss near about 210°C is due to the degradation of HCl occur and continue loss of mass observed between $400^\circ- 600^\circ\text{C}$ due to the oxidative degradation of the polymers.

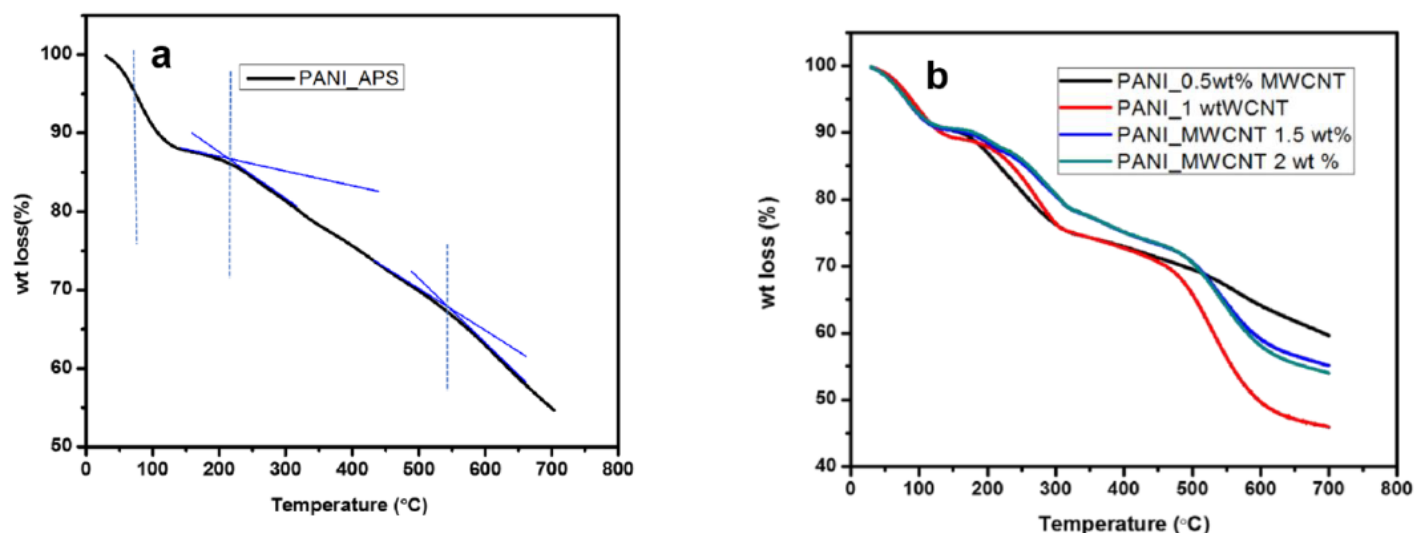


Fig 8 TGA curve of (a) pure PANI and (b) PANI/MWCNT nanocomposites

Similar behavior does not show by PANI/MWCNT nanocomposites. Fig. 8b shows with the addition of different wt. % MWCNT in PANI the stability of nanocomposite is increased as compared to the pure PANI [27].

Conclusion

PANI and PANI/MWCNT nanocomposites are prepared by the chemical oxidative polymerization method. The characterization was done by the XRD, FTIR, UV-Vis, SEM, TGA and Two-probe method. XRD pattern of PANI and MWCNT doped PANI shows the semi-crystalline nature. From UV-Vis spectra band gap of PANI 3.21 eV and of the nanocomposite are found to be 3.14 eV, 3.17 eV, 3.03 eV, 3.11 eV. Conductivity of PANI/CNT composites increases with increasing weight percent but exceptional increase in conductivity observed in the 1 wt %. Morphological analysis of PANI observed the fibular morphology, MWCNT was also observed with the nanofiber of the polyaniline.

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