

In this chapter, we are reporting the preparation and characterization of a multi-component integrated nanocomposite consisting of PANI, MWCNTs and Starch composite material and that was characterized by UV-Visible spectroscopy, FTIR, Raman, XRD, SEM, TEM, BET-Surface area, Conductivity, TGA, DSC and Cyclic Voltammetry techniques.

5.1 Introduction:

In recent years, conducting polymers have drawn a remarkable attention due to their wide applications in transistors, electrochromic devices, sensors, light-emitting diodes, capacitors, organic solar cells, anti-corrosive materials, batteries, controlled released application, radar application and others (Harun et al. 2007). In general, the composite materials of conductive polymers show improved physical and chemical properties. A variety of Polyaniline (PANI) based composite materials have been extensively studied along with other conductive polymers owing to Polyaniline's high electronic conductivity, redox activity, ion exchange properties, excellent environmental stability, inexpensive monomer and easy fabrication ability to design unique composite systems. PANI exists in oxidation states varying from the completely oxidized state called "Pernigraniline form" to completely reduced state called "Leucoemeraldine form" including the partially oxidized state known as "Emeraldine form". PANI can be switched to the conducting Emeraldine Salt (ES) form (conductivity $>1 \text{ Scm}^{-1}$) on protonation, while for obtaining insulating Emeraldine Base (EB) form (conductivity $< 10^{-10} \text{ Scm}^{-1}$), deprotonation is practiced. Conducting polymers have conjugated system and there is delocalization of electron charge due to the presence of additives and dopants. Doping allows the exchange of charge along the polymer chain resulting in exalted electrical, electrochemical and optical properties of the material. Presence of different types of dopants

in the PANI matrix changes the microstructure and grain boundary fetching various important properties of the composite. Applications of PANI and composites based on it have been extensively reported in the literature (Syed et al. 1991; Molapo et al. 2012; Gospodinova et al. 1998; Sapurina et al. 2008).

Carbon nanotubes (CNTs) have excellent electrical, thermal and mechanical properties. Incorporation of nanomaterials within polymer matrix results in synergy, leading to enhanced properties. Multi-walled carbon nanotubes (MWCNTs) within polymer matrix induces better electrical and thermal conductivity, tensile strength, chemical resistance, electrochemical behavior, optical and catalytic properties to a great extent. It also increases thermal transition temperature and reduces thermal shrinkage of the polymer/MWCNTs composite.

CNTs have the *p*-conjugative structure with a highly hydrophobic surface responsible for p-p electronic and hydrophobic interaction with many organic compounds. Carbon nanotubes (CNTs) are considered as a perfect filler with polymeric material due to their exceptional mechanical and electrical properties. They also have very high aspect ratio. With such exotic properties no wonder a large number of review articles have been reported in the literature related to carbon nanotubes based composites synthesised using various methods and exhibiting improved and synergic properties for interdisciplinary applications (Song et al. 2013; Valentin et al. 2004; Liu et al. 2014; Song et al. 2013; Khare et al. 2005; Swain et al. 2010; Tiwari et al. 2009).

Starch is a white, granular, soft and tasteless organic compound. It is a polysaccharide comprising of glucose monomers joined in α 1,4 linkages having chemical formula $(C_6H_{10}O_5)_n$. Starch-based hybrid materials have been extensively used both in biological and non-biological applications. Earlier reports have attested that PANI-starch

composite material is not only biodegradable and conductive in nature but also less toxic and biocompatible (Saikia et al. 2010; Janaki et al. 2012). Combinations of materials having contrast properties definitely provide an easy way/opportunity for designing advanced single hybrid nano-composite material which have the emergence of superior and synergic effects. Down this line, Tiwari and Singh have reported the preparation of a three component system i.e. PANI/PAA/MWCNTs in two different acids quoting improvement in the electrical conductivity (Tiwari et al. 2012).

Realizing the unique properties domains covered separately by the three materials i.e. PANI, MWCNTs and Starch, while simultaneously realizing the potential to tailor novel properties by composite formation, the present work aims to meticulously study three components composite materials based on PANI/MWCNTs/Starch, which to our knowledge has not been reported elsewhere. Motivated by the success of three component system and realizing the scope of research in this domain, we have prepared, characterized and compared three component system (system-4: PANI/MWCNTs/Starch) with one component (system-1: PANI) and two-component systems (system-2: PANI/MWCNTs, system-3: PANI/Starch). An in-depth discussion on the interaction of three materials has been reported which differ from their individual properties when they are combined together as an integrated composite system. The idea of combining a naturally occurring biocompatible, non-toxic polymer with a synthetic conducting functional polymer along with nanosized template material can be a new direction for the preparation of advanced multifunctional composite materials.

5.2 Experimental:

5.2.1 Materials:

Aniline and Hydrochloric acid (HCl) were received from Qualigens Fine Chemicals. MWCNTs were prepared via Chemical vapor deposition technique [NANOCTC 7000, FRAHNHOFFER IPA, July 2013, MRTIRMATIS]. MWCNTs were purified by boiling them with concentrated HCl. Aniline was distilled under vacuum at 182°C before using it for polymerization. Starch was purchased from Merck India Ltd. and other supplementary chemicals were of AR grade and used without further purification. All solutions have been prepared in double distilled water. The Aniline-MWCNTs complex was obtained by ultrasonicing 0.0002g MWCNTs with 4ml aniline for one hour, followed by mixing with 100 ml 0.5 M HCl. Subsequently, PANI/MWCNTs/Starch composite (system-4) was prepared by in-situ chemical oxidative polymerization of aniline in a reactive mixture containing starch and MWCNTs by dropwise addition of 100 ml oxidizing agent in an ice bath (0-5°C). The monomer to oxidizing agent molar ratio was 1:1.25 and w/w ratio of aniline to starch was 1:1. The reaction mixture was continuously stirred for 2 hours and left undisturbed for 24 hours for the completion of polymerization. A good degree of polymerization was achieved and the blackish green precipitate was recovered by filtration. The Precipitate was washed three times with 0.1 M HCl followed by final washing with Acetone until the filtrate turned colorless. The obtained material was dried in the vacuum oven and was kept in a vacuum desiccator. To perform comparative analysis we have prepared three more materials viz. system-1: PANI; system-2: PANI/MWCNTs and system-3: PANI/Starch by adopting same procedure and a similar ratio of monomer and an oxidizing agent.

5.2.2 Characterizations:

All the prepared composite materials were obtained as dark green colored powder and they were characterized by several instrumental techniques. FT-IR spectra were obtained using Perkin Elmer Spectrum Version 10.03.05 with a range of 4000-500 cm^{-1} with potassium bromide (KBr) pellets at room temperature. Optical absorption spectrum was observed using Varian Carry 100 Bio dual beam Spectrophotometer, in the wavelength region 200 to 800 nm with a scanning speed of 400 nm/min. The molecular structure and the presence of functional groups were studied using a Raman spectrometer (Micro-Raman setup, Renishaw Gloucestershire, UK) equipped with a microscope from Olympus (Model: MX50 A/T; Olympus, Hamburg, Germany) with the range of 1700-400 cm^{-1} . The crystalline properties of materials were recorded by Ultima IV X-ray diffractometer with Cu $K\alpha$ radiation. Further, Scanning Electron Microscope (SEM) observations were carried out using Quanta 200 Company- FEI of USA (SEA) PTE Ltd., Singapore at suitable voltages and magnifications. Transmission Electron Microscopy (TEM) analysis of material was performed on Tecnai 20G2 Company-FEI. The surface area and porosity were determined from nitrogen adsorption/desorption isotherms with a Micromeritics ASAP-2020 Physisorption Instrument using the BET equation to estimate the overall surface area, AC conductivity measurement was done by Wayne Kerr 6500P High Frequency LCR meter and electrochemical experiments were carried out with an electrochemical analyzer CH-630C series, CH instruments, USA. Composite material modified carbon paste electrode was used as the working electrode, a Pt wire as the auxiliary electrode and Ag/AgCl (saturated 3 M KCl) as the reference electrode. Thermal analysis has been carried out on a TA instrument by heating

the specimen from ambient temperature to 350 °C under a constant heating rate of 10 °C/min, in the inert atmosphere of nitrogen.

5.3 Results and Discussion:

5.3.1 Mechanism of the Formation of the Composite Material:

The MWCNTs based composite should have uniform dispersion of nanotubes. Dispersion of MWCNTs within pure water is not very suitable because they are hydrophobic and has high surface energy which leads to their accumulation. To overcome the problem of dispersion, we sonicated bundles of MWCNTs within vacuumed distilled Aniline which prevents sticking of MWCNTs. As a result, we obtained a well-dispersed suspension of MWCNTs in Aniline. Aniline and MWCNTs both have pi electrons and there is possibility for the presence of weak forces owing to pi-pi interactions between them. (Huang et al. 2003; Zareh et al. 2011) Ultrasonication of the reaction mixture containing 4ml Aniline-MWCNTs complex and starch in 100 ml 0.5 M HCl aqueous solution gives a blackish grey color suspension. Further ultra-sonication for 1hr was performed that resulted in homogeneous mixing of three components. Synthesis of Polyaniline depends upon many experimental parameters which control its properties and morphology. Oxidation of aniline and conductivity of oligomer/polymer greatly depends on the acidity (pH) of the solution. Conducting polymer was obtained in a reaction mixture of pH < 2.5 whereas mildly acidic/neutral/alkaline systems result in nonconducting oligomers as major products. Polymerization of aniline starts by dropwise addition of ammonium peroxydisulphate (APS) into the reaction mixture under continuous stirring condition. As the polymerization of aniline is an exothermic reaction, the process was accomplished at lower temperatures (4°C)

in an ice bath, in order to maintain the proper reaction conditions. The progress of the reaction can be monitored by recording, change in temperature or acidity. Higher molar mass green color material was produced containing conducting PANI macromolecules of regular structure. More than 95 % of aniline monomers are linked in head-to-tail para positions and a small fraction of molecules are linked via orthocoupling. The mechanism for the polymerization of Aniline monomers is well reported in the literature (Sapurina et al. 2008). Starch contains about 30 % amylose, 70 % amylopectin and less than 1 % lipids or proteins from plants. There is a possible interaction of NH group of aniline with the hydroxyl group of starch (Zareh et al. 2011). As a result of possible mutual interactions among different components, an integrated, coupled, cross-linked and conducting composite material based on PANI/MWCNTs/Starch was obtained.

A small amount of the material was sonicated in 2 ml distilled water for about 15 minutes to break the bigger particles lumps into smaller ones. The obtained uniform aqueous suspension was kept undisturbed overnight so that it could settle down under gravity. The requirements of good ink formulation for screen-printed electrode is that it should be easily suspended in the carrier solvent and have stable suspension ability for a long time ensuring better processing ability and uniform spreading or deposition of the prepared ink formulation on the electrode substrate. The photographs of the sonicated aqueous suspension of four materials were taken after 5 minutes and 24 hours. Figure 5.1 attests the required dispersion ability. We observed that the aqueous suspension of PANI/MWCNT/Starch (system-4) has better dispersion ability than others due to the nano-effect of MWCNTs (confirmed by SEM analysis) and presence of numerous hydroxyl groups due to Starch (as confirmed by FTIR and Raman analysis). PANI/MWCNTs (system-2) have higher density and compactness in

the morphology as a result of which it completely settles down within 24 hours whereas PANI/Starch (system-3) remains partially suspended.

5.3.2 Suspension Ability of the Material:

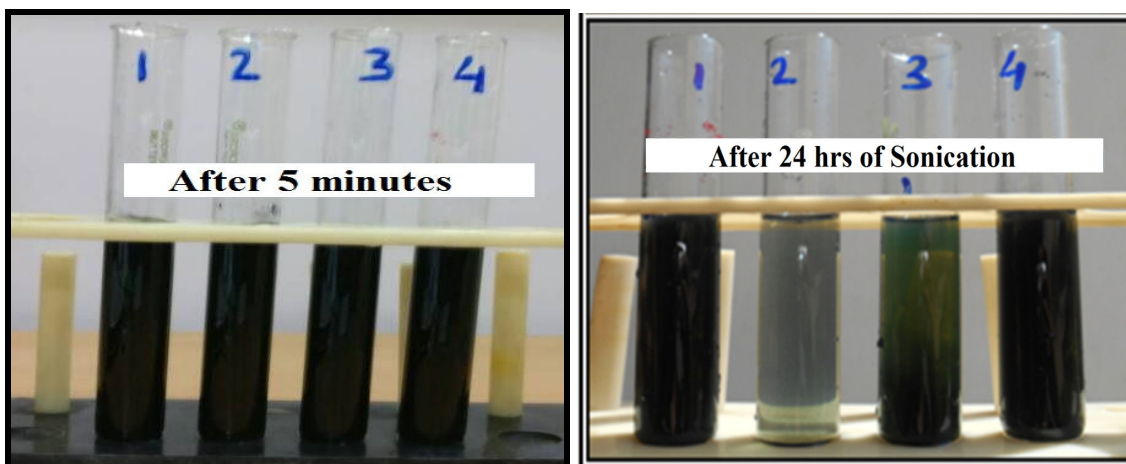


Fig. 5.1 Stability of aqueous suspension of four systems after 5 minutes and after 24 hours

5.4 Spectroscopic Analysis:

5.4.1 FTIR Analysis:

Bending, twisting, rotating and vibrational motion associated with functional groups present in molecule gives significant information about the molecular structures, functionalities, configurations, and interactions. The FTIR spectra for the four different systems viz. system-1: PANI, system-2: PANI/MWCNTs, system-3: PANI/Starch and system-4: PANI/MWCNTs/Starch composite have been shown in fig. 5.2. The comparative analysis of important peaks is listed in Table-1 (*c.f. AI*). With the influence of a dopant, there is a marked change in the frequencies and intensity of the peaks. We herein compared peaks of four systems in the different spectral regions with the reported values (Kostic et al. reported theoretical vibrational spectra of the Leucoemeraldine form of neutral reduced Polyaniline)

(Kostic et al. 1992). FTIR spectrum of PANI provides detailed information about the relative amount of different groups present in it. Previous reports suggest the characteristics peaks in the FTIR spectra of pure PANI at frequencies 3500, 2400, 1561, 1490, 1292, 1160 and 800 cm^{-1} (Ghatak et al. 2010; Arasia et al. 2009). FTIR spectra of all composites consist of broad and sharp bands in different regions lying between wave numbers 4000-500 cm^{-1} . The region around 1000 to 1600 cm^{-1} contains certain signature bands of PANI system, especially the peaks around 1478 and 1566 cm^{-1} exhibit clear presence of benzenoid (N-B-N) and quinoid ring (N=Q=N) vibration indicating the oxidation state of Emeraldine salt of PANI. FTIR Spectra for pure starch have characteristic bands at 3345, 2926, 2094, 1646, 1426, 1370, 1237, 1158 and 524 cm^{-1} (*c.f. A1 B*) as reported in the literature (Zareh et al. 2011; Kostic et al. 1992; Ghatak et al. 2010; Arasia et al. 2009).

We observed peaks due to N-H stretching, strong H-bonding, C=C sharp stretching and strong asymmetric stretching. Broadband in the region 3000-3600 cm^{-1} of all samples is attributed to the OH stretching mode, which overlaps with the N-H stretching in the same region. FTIR spectrum of starch-based composite material absorbed in hydroxyl and aliphatic ranges and shows an intensive broadening of the band at 1027 cm^{-1} , which signatures C-O-C bond. 2930 cm^{-1} is attributed to an asymmetric stretching vibration of the C-H band in paranooids ring (Zareh et al. 2011). The marked difference is observed between several absorption bands from 828-1158 cm^{-1} , which is attributed to the interactions of various functional groups, such as C-O and C-O-C of starch with N-H Group of PANI. The medium strong band around 1600 cm^{-1} is observed due to pure PANI and PANI/MWCNTs/Starch blend owing to C-C, C-N, N-H stretching. A system prepared by a combination of many materials may have complex interactions among its individual components. As a result, there

is marked variation in the spectrum of three components system in comparison to a two-component system. PANI/MWCNTs/Starch is a three component system and possesses many types of possible interactions i.e. MWCNTs and PANI can interact through aromatic structures of PANI and the basal plane of graphitic surfaces interact via π - π stacking. Quinoid ring of the PANI and the MWCNTs have effective site-selective interactions which facilitate charge-transfer processes between the two components and effective degree of electron delocalization (Yijun et al. 2005). In case of functionalized MWCNTs, there are strong interactions between amino groups of aniline monomers and carboxylic acid/acyl chloride groups of functionalized MWCNTs (Abdulla et al. 2012). There are possible interactions of NH group of PANI with the hydroxyl group of amylose and amylopectin (Zareh et al. 2011). There is shifting of the peaks due to the addition of MWCNTs and starch in the final material (PANI/MWCNTs/Starch) confirming the formation of the complex. PANI has a tendency to strongly interact with both the counter materials i.e. MWCNTs and starch. Incorporation of starch increases the O-H functionality of the composite system, resulting in more hydrophilicity and biocompatibility. Observation of strong bands at 3409 cm^{-1} , 3789 cm^{-1} is assigned to the vibration of O-H group.

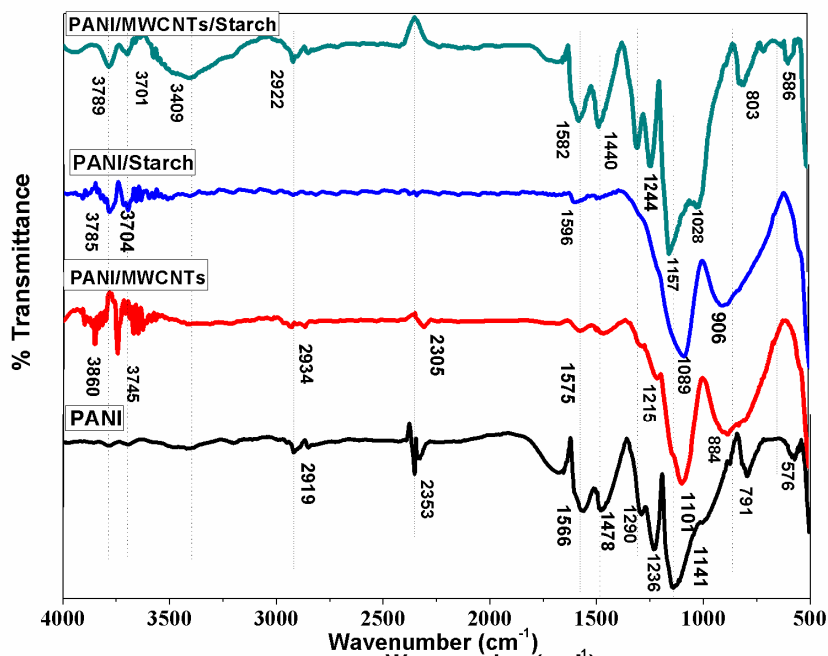


Fig. 5.2 FTIR spectra of PANI, PANI/MWCNTs, PANI/Starch, PANI/MWCNTs/Starch

5.4.2 UV-Visible Spectroscopy:

UV-Vis spectroscopy was used to understand the optical properties and electronic states of PANI, PANI/MWCNTs, PANI/Starch, PANI/MWCNTs/Starch composite. The paste of composite material with Barium Sulphate (0.05g sample and 4g BaSO₄) was prepared and scanning was done over the range of 200-800 nm. The two broad absorption bands found around 287 and 703 nm in all composites were ascribed to the $\pi \rightarrow \pi^*$ transition of the amine benzenoid rings and to the polaron/exciton formation at quinoid rings, respectively (Kostic et al. 1992). $\pi \rightarrow \pi^*$ electronic transition occurs from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The relative intensity of the exciton absorption band and pi-pi transition of the benzenoid ring indicates the relative amount of benzenoid and quinoid units present in the material. From fig. 5.3 the relative

intensity for these two bands is approximately same for system-4 attributed to the emeraldine state of PANI. The characteristic peak of PANI-MWCNT shifted to longer wavelength in comparison to PANI due to interactions between quinoid rings and MWCNTs.

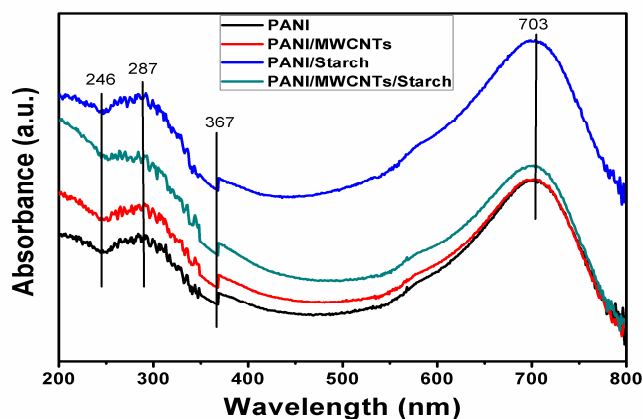


Fig. 5.3 UV-Visible Spectra of PANI, PANI/MWCNTs, PANI/Starch, PANI/MWCNTs/Starch

5.4.3 Raman Analysis:

Raman spectroscopy is an efficient tool for understanding the interaction among various components and provides information about chemical structure of different domains in the composite system. Raman Spectra of four materials have been summarized in fig. 5.4. PANI is generally represented by five structures: Leucoemeraldine, Emeraldine, Pernigraniline bases, Emeraldine salt in polaron lattice and bipolaron forms. Raman spectra have been used to obtain a quantitative characterization of PANI based composite materials using an exciting wavelength of 515.5 nm via Argon ion laser.

Doped state of PANI (conducting form) has dominant peaks in comparison to undoped state (insulating form). However, band due to an insulating form of PANI can only be observed

when conducting form is less than 1%. The higher intensity in the conducting form is due to resonating Raman Effect leading to sharp and strong peaks due to the frequency of incident radiation coinciding with the frequency of electronic transition of the sample. In conducting form of PANI, the electronic transition occurs in visible range due to π - π^* interaction in the doped form. Bands are very complicated in conducting form than in nonconducting form. We observed expected characteristic bands for PANI as reported, such as the rings C-H bending modes between 1100 cm^{-1} and 1210 cm^{-1} , rings C-C stretching modes between 1520 cm^{-1} and 1650 cm^{-1} , different C-N stretching modes (amines, imines, polarons) between 1210 cm^{-1} and 1520 cm^{-1} . The band observed in the region $1100\text{-}1140\text{ cm}^{-1}$ is the characteristic of conductive PANI and is due to the charge delocalization on the polymer backbone. A weak band at 1174 cm^{-1} has been assigned for in-plane deformation of the C-C bond of the quinoid ring of the PANI nano-fibers (Kar et al. 2013). In system 3 and 4 we observed sharp and strong band in this region. The bands at $1382, 1407, 1595\text{ cm}^{-1}$, correspond to C-N⁺ stretching, C-C stretching of the quinoid ring and ring stretching vibrations respectively. The band at 1487 cm^{-1} is assigned to the formation of bipolarons, while the band at 1247 cm^{-1} corresponds to the C-N stretching in polaronic units (Bernard et al. 2006). We observed the strong formation of bipolaron units by the addition of MWCNTs (system-2).

Shifting and appearance of bands shows a definite physical and chemical interaction among three components of composite material. Due to presence of MWCNTs, a redshift of C=C and C-C bond stretching (1600 cm^{-1}) is observed. In spectra, several bands disappeared and several new bands appeared in the composite system. Distinct oxidation states and protonation levels of PANI have different Resonance Raman conditions, as a result, the spectra differ strongly.

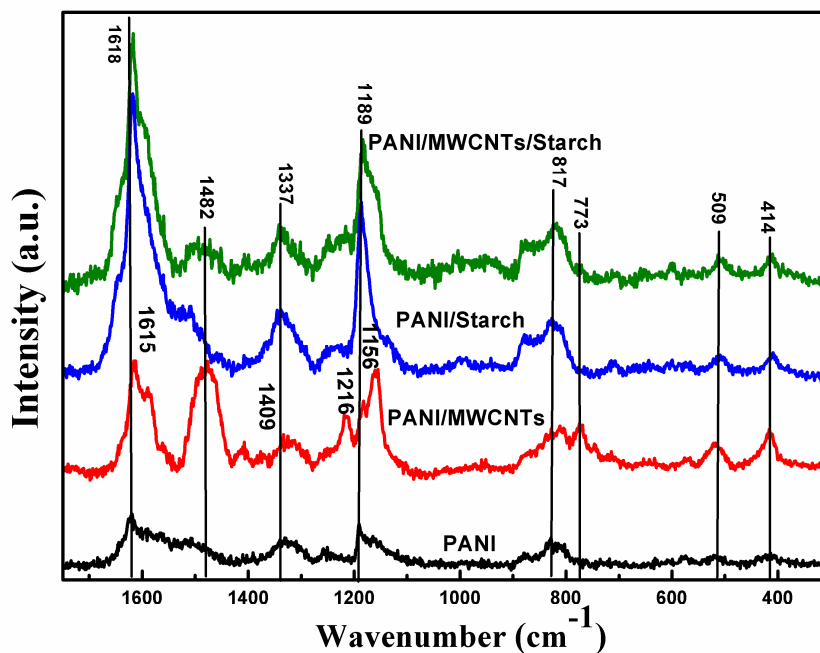


Fig. 5.4 Raman spectra of PANI, PANI/MWCNTs, PANI/Starch, PANI/MWCNTs/Starch

Four different systems differ with an intensity ratio and peak position of spectral components in the 1300-1630 cm^{-1} range. Intense bands around 1191 cm^{-1} and 1624 cm^{-1} are characteristic of p-disubstituted benzene rings. The intensity of the bands at 1615 cm^{-1} , 1482 cm^{-1} increased and some weak bands at 1408 cm^{-1} , 1337 cm^{-1} and 1212 cm^{-1} resulted owing to the formation of semiquinone radical cations i.e. the p-disubstituted benzene rings which further transformed into polarons. Increased intensity of the peak at 1189 cm^{-1} has been assigned to plane deformation of the C-C bond of the quinoid ring of the PANI. Weak band at 817 cm^{-1} in system-1 is found to blue shifted in system-2. In PANI, PANI/MWCNTs/Starch all peaks merged at 1618 cm^{-1} from others due to C=C quinoid structure. The peak at 1189 cm^{-1} has been assigned to in-plane deformation of the C-C bond of the quinoid ring of PANI.

5.4.4 XRD Analysis:

X-ray diffractograms of the PANI, PANI/MWCNTs, PANI/Starch and PANI/MWCNTs/Starch are shown in fig. 5.5. In the case of PANI, three diffraction peaks are observed at $2\theta \sim 14.87^\circ$, $\sim 20.99^\circ$ and $\sim 25.15^\circ$. We observed peaks at $2\theta = \sim 20^\circ$ and $\sim 25.8^\circ$ which attribute to periodicity in the parallel arrangement of the inter-planar spacing of PANI chains and regular repetition of monomer unit in the composite, we inferred that there is the presence of some degree of crystallinity. Semi-crystalline nature of PANI is due to the presence of planes of Benzenoid and Quinoid rings of PANI Chain (Kostic et al. 1992). Increase in intensity of the peak results (from 600 to 650 units) with the addition of MWCNTs, because they act as dopants and as a template and they guided for the deposition of PANI chains along the axis of the nanotube. The characteristic peaks of PANI shows a very slight shift at angle from 25.15° (PANI) to 25.19° (PANI/MWCNTs), 24.83° (PANI/Starch), 24.97° (PANI/MWCNTs/Starch) in the XRD pattern of B, C, D nanocomposite owing to the interactions of PANI chains with MWCNTs and Starch. X-ray diffraction studies also indicated a definite chemical interaction between MWCNTs, PANI and starch.

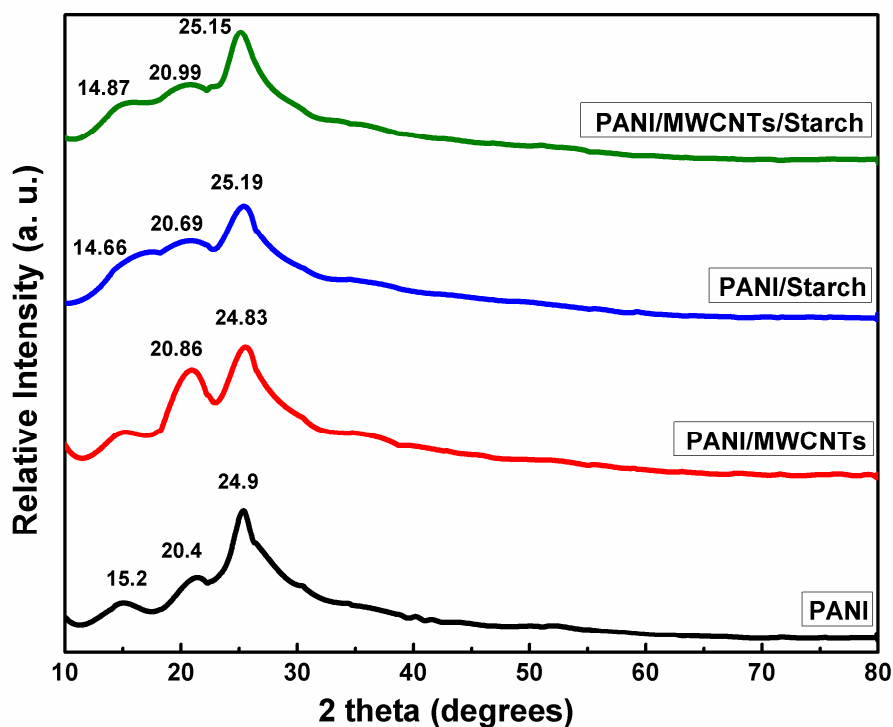


Fig.5.5 XRD pattern of (A) PANI, (B) PANI/MWCNTs, (C) PANI/Starch, (D) PANI/MWCNTs/Starch

There is a decrease in the intensity of the peaks at $\sim 15^\circ$ and $\sim 20.3^\circ$ with the addition of starch in the PANI matrix system 3 and system 4. It can be inferred that starch gets incorporated in between the PANI fibers resulting in decreased crystallinity. The Summary of XRD data of four systems is tabulated (*c.f.* 2A). MWCNTs prepared in the laboratory have been characterized by XRD showing expected characteristic peaks of CNTs at $2\theta = 26^\circ$ and 44.9° (*c.f.* 2B).

5.5 Morphological Studies:

5.5.1 SEM Analysis:

Scanning Electron Microscopy is a good technique to investigate the surface morphology. SEM images of MWCNTs, PANI, PANI/MWCNTs, PANI/Starch and PANI/MWCNTs/Starch composite material have been shown in fig. 5.6 (A, B, C, D E, F, G and H). SEM micrographs at two different resolutions are shown in fig. 5.6 A and B. We observed that MWCNTs have interconnected fibrous porous network like morphology having average size more than 500 nm shown in fig. 5.6 B. We observe similar morphology for MWCNTS as reported earlier (Granska et al. 2013). SEM images of PANI (system-1) at two different resolutions shown in fig.5.6 C and D attest compact coarse granular homogenous nature similar to the previously reported work (Granska et al. 2013) whereas in system-2 there is the incorporation of MWCNTs in PANI matrix. We observed there are fibrous noodles like structure, where MWCNTs acts as filler in a composite system and a template for alignment of polymer chains along a nanotube axis, as a result, random-coiled geometry to a more elongated one, so as to maximize their pi-pi interactions with the hexagonal lattice of CNTs and there is a higher proportion of quinoid rings. PANI fibers have overgrown wrapping around MWCNTs, resulting in nano size fibril structure (shown in fig. 5.6 E and F) similar to other reported work (Tiwari et al. 2012; Yijun et al. 2005).

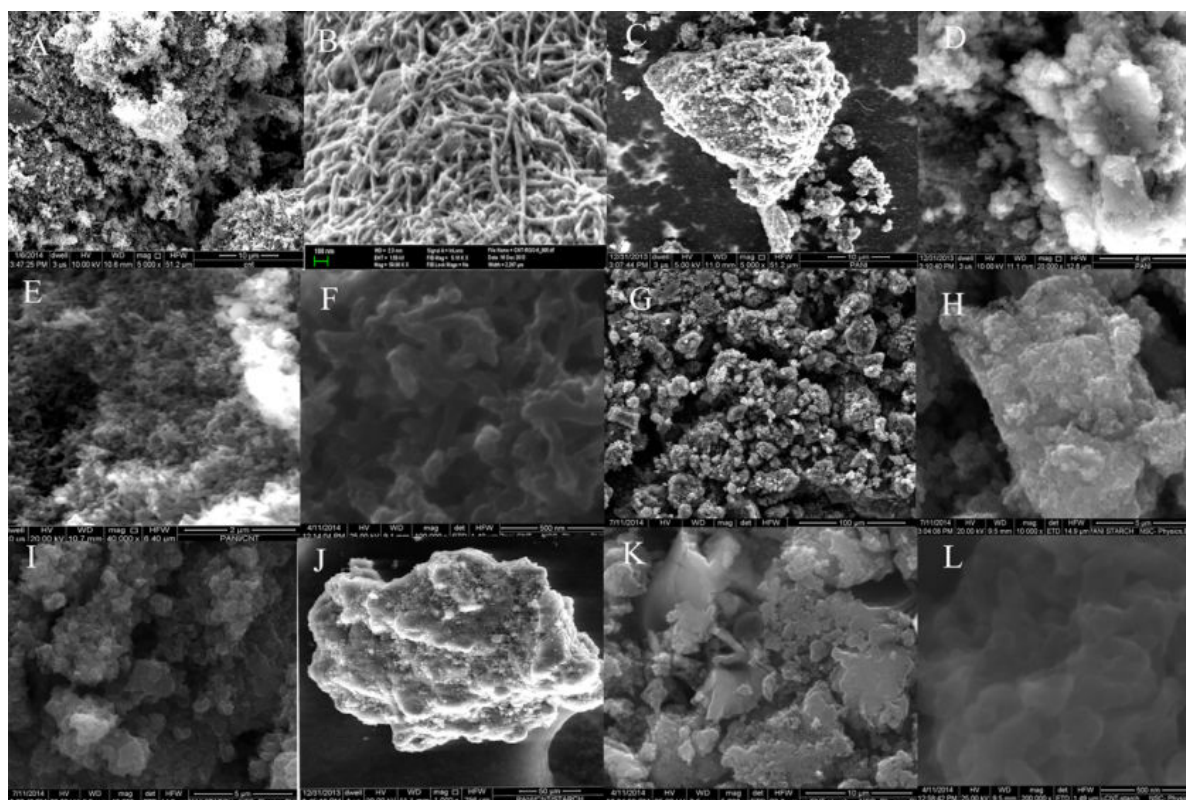


Fig. 5.6 SEM images at different magnification MWCNT (A, B), PANI (C, D), PANI/MWCNTs (E, F), PANI/Starch (G, H, I), PANI/MWCNTs/Starch (J, K, L)

It has been reported that pure starch has the irregular granular shape of size $10\mu\text{m}$ to $60\mu\text{m}$ (Saikia et al. 2010). Template behavior of starch and interactions among two polymeric chains leads to an integrated composite system (Saikia et al. 2019; Zareh et al. 2011). We get a composite system where starch granules are stuck in between the PANI fibrous structure (shown in fig. 5.6 G, H, I). We observe that PANI/MWCNTs/Starch have compact morphology, consisting of nanosized irregular fiber-like structure (shown in fig. 5.6 J, K, L at different resolution). The composite material has entirely different morphology than pure Starch, MWCNTs, and PANI.

5.5.2 TEM Analysis:

Morphological study for system-4 was done with TEM analysis shown in fig. 5.7, which confirms the formation of the homogeneous interconnected composite system. TEM images of system-4 (PANI/MWCNTs/Starch) at three different resolutions 1 μ m, 200 nm, and 100 nm were analysed. We observed porous nanosize turmeric shape structure (nanorod size~200nm in length and < 50nm in width) with uniform interconnected distribution.

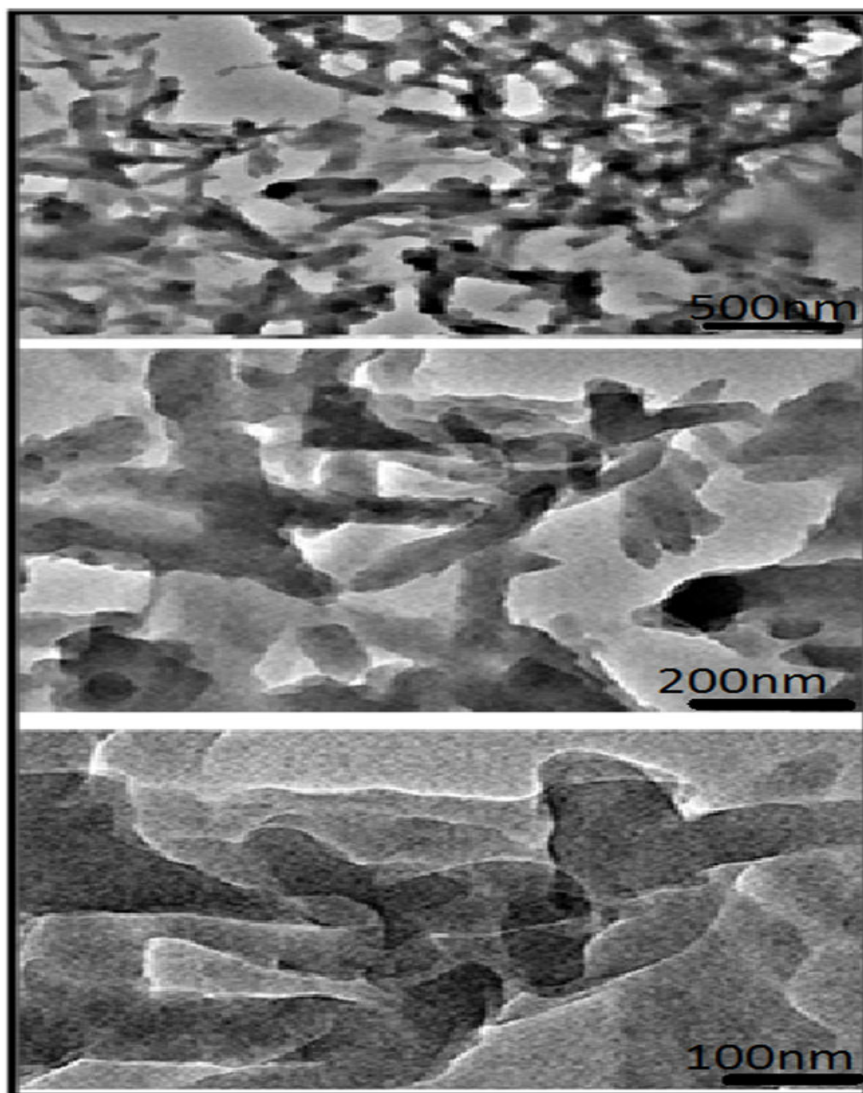


Fig. 5.7 TEM micrograph of PANI/MWCNTs/Starch composite material at different resolution

5.5.3 BET-Surface Area:

The prepared composites obtained after drying were in the form of a lump of dark green color. The big lumps are manually ground by using mortar and pestle to make fine powder for BET surface analysis. The adsorption-desorption plots and summarized data obtained from BET analysis of four different systems available as supplementary material (*c.f.* 3A and 3B). We observe that with the addition of MWCNT in PANI matrix, single point surface area of PANI/MWCNTs (system-2) composite increased by 62.90%, single point total pore volume increased by 163.6% and the average pore width decreased by 95% in comparison to pure PANI (system-1), which is attributed to the induction of nano-effect of MWCNTs on the polymer matrix in the composite material. With the addition of Starch, single point surface area increases by 17.69%, single point total pore volume decreased by 31.1% and average pore width decreased by 96% than pure Polyaniline. With the addition of both MWCNTs and Starch single point surface area decreased by 66.28%, single point total pore volume decreases by 64.45% and average pore width increased by 5.43% than pure Polyaniline. PANI/MWCNTs (system-2) have the maximum surface area and pore volume whereas system-4 has minimum surface area and maximum pore size. The results showcase that PANI/MWCNTs/Starch (system-4) is a compact, nanosized material with comparatively less porosity.

5.5.4 Thermal Analysis:

Thermal behavior of four materials viz. PANI, PANI/MWCNTs, PANI/Starch, PANI/MWCNTs/Starch was studied by TGA and DSC Analysis under nitrogen is shown in

fig. 5.8 and 5.9. It has been well reported that polyaniline starts degrading at temperatures above 400 °C, so we measured % weight loss up to 350°C to measure the trapped moisture or loosely bounded volatile species/functional groups present in the composite materials. In fig. 5.8, we observed single step decomposition in case of system-1 and system-2 whereas two steps in weight loss at below 100°C and above 200°C in system-3 and system-4 due to evaporation of moisture trapped inside the polymer matrix or bound to the polymer backbone and some small dopant molecules. The second step loss in system-3 and system-4 is due to loss of hydroxyl group present in large number in starch. The % wt. loss is higher in system-3 and system-4 than system-1 (30%) and system-2 which indicates that it has higher amount of trapped moisture and hydroxyl functionalities which again proves that system-3 and system-4 are more hydrophilic in nature than system-2. This fact is supported by the DSC measurement shown in fig. 5.9 as a sharp endothermic peak is observed at about 75°C. We have designed the said materials for considering their application in the area of biosensors. Generally, biocatalytic devices are used at ambient conditions. Hence, from the TGA and DSC analyses we can conclude that the prepared material is a promising electrode material which does not only act as stable host at ambient temperature but also has enough captured water molecules and hydroxyl groups (which provide biocompatible environment for the immobilized biocatalyst).

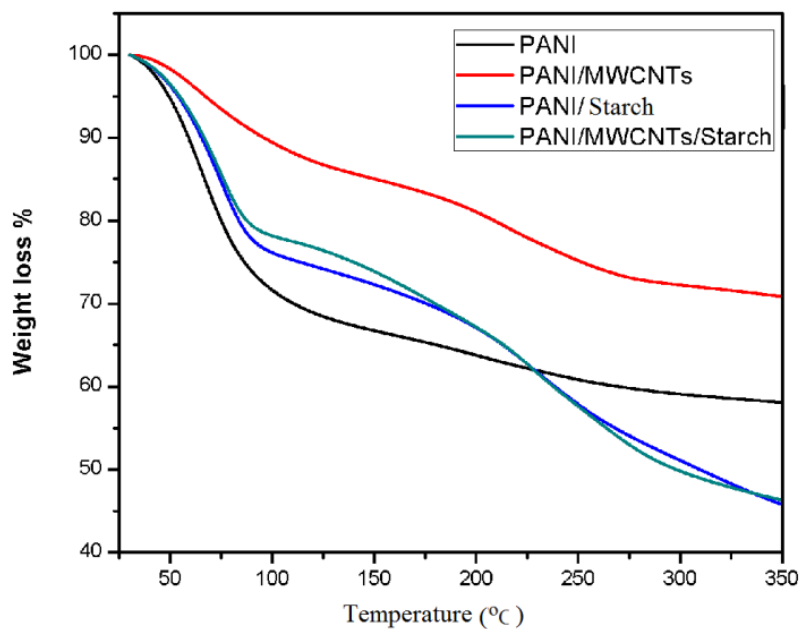


Fig. 5.8 TGA of PANI, PANI/MWCNTs, PANI/Starch, PANI/MWCNTs/Starch

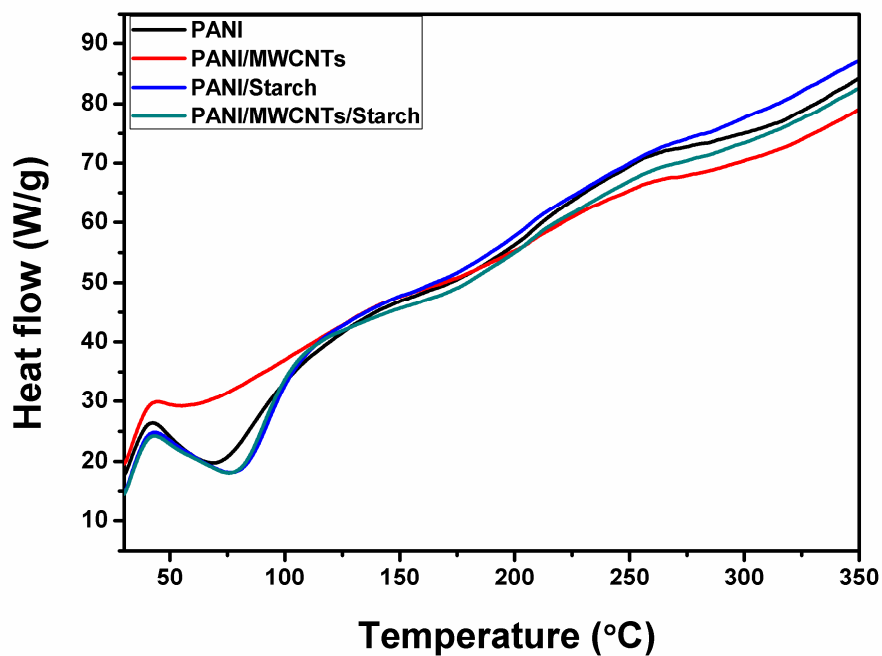


Fig. 5.9 DSC of PANI, PANI/MWCNTs, PANI/Starch, PANI/MWCNTs/Starch

5.6 Electrical Properties:

Polyaniline has ionic as well as electronic conductivity. Comparative analysis of conductivity for composite systems provides an insight understanding of conduction mechanism and the effect of additives on charge delocalization and hopping process of an electron between nearest neighbouring redox sites in a Polyaniline chain. The conductivity of Polyaniline and its composite is due to the presence of a p-conjugated chain of the polymer. Delocalization of p-electrons along with polymeric chain lead to a sequence of alternating double and single bonds. It has been reported that generally at the room temperature DC and AC conductivities are same however, there are some deviations at lower temperatures which are characteristics of a variable range of hopping. Conductivity of conducting polymer-based composites depends upon morphology, type of monomers, doping level and degree of crystallinity. Temperature and frequency dependence of AC conductivity for four materials are shown in fig. 5.10. Significant variations due to the presence of additives are clearly seen in the conductivity of PANI and its composites. It is inferred from the conductivity data that the four different systems based on Polyaniline may follow different conduction mechanisms because of variation in their chemical composition. Conductivity variation with temperature and frequency provides information regarding charge carriers and transport mechanism. The three materials viz. Polyaniline, MWCNTs and Starch differ in the electrical conductivity significantly. Polyaniline may act as insulator, semiconductor or metal based on the level of doping and its oxidation state. Starch is an insulating material and MWCNTs have good conductivity. Reinforcement of MWCNTs in a Polymer composite increases the bulk conductivity of the material. Similar trend is observed for system-2 and system-4. At high temperature, there is facilitated movement of charge under the influence of external field and

Chapter 5

as a result conductivity increases with temperatures for PANI and its composites. The maximum conductivity range for four systems was observed at different temperature i.e. for system-1 260°C, system-2 160°C, system-3 190°C, and system-4 230 ° C. For system-1 conductivity increases with the increase in frequency shown in fig. 5.10 because at low frequency there is ionic polarization whereas at higher frequency there is electronic polarization and hopping of electronic charge fluctuates across the interface and thus causes intrinsic conduction in the material.

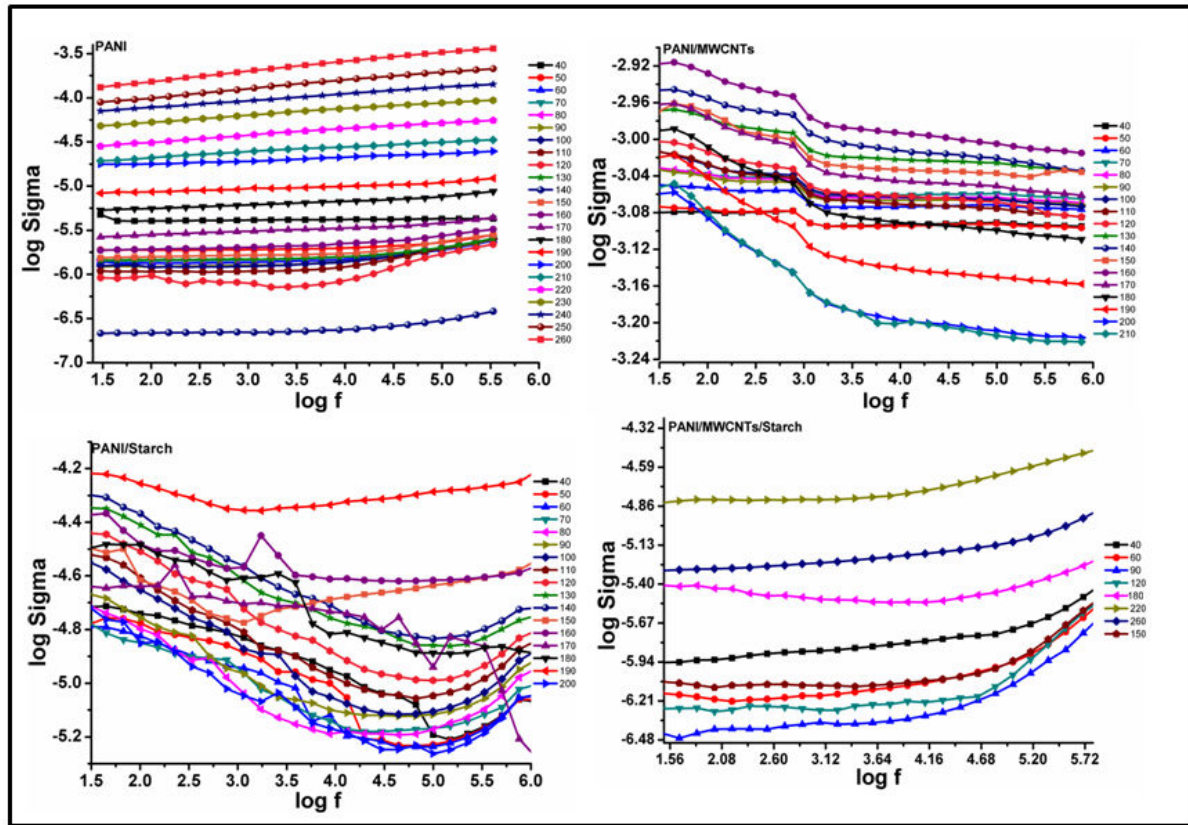


Fig. 5.10 Temperature and frequency dependence of AC conductivity for four materials

In system-2, conductivity falls down sharply at a higher temperature than at low temperature with an increment in frequency. PANI/MWCNT composite has higher

conductivity than Polyaniline. We here in propose that the addition of MWCNTs changes the conduction mechanism by providing additional current leakage centres within the composite material. At high-temperature activation energy increases the electronic charge to overcome the barrier and it diffuses to some alternative path, as a result drop in conductivity is higher at elevated temperature. PANI/MWCNTs (system-2) have higher conductivity at low frequency whereas System-1 and system-4 have higher conductivity at higher frequencies. In system-3 conductivity drops initially and then increases to an extent whereas in system-4 conductivity is independent of a certain frequency after that it increases. Further studies about the variation in the conductivity of PANI based composite is under investigation.

5.7 Cyclic Voltammetric Analysis:

Cyclic Voltammetry is a popular electrochemical analytical technique in the potentiodynamic mode to study electrochemical behavior and to understand redox reaction of an electroactive species. The cyclic voltammogram of the four materials were taken with 0.1M HCl as an electrolytic solution using CH instrument electrochemical workstation with potential sweeping between -200 mV and 800 mV up to 50 mV/s scan rate (shown in fig. 5.11). Graphite paste was prepared by using micro-sized 68 mg graphite and 2 mg composite material along with 10 μ l of nujol oil. The paste was filled in a polycarbonate electrode body. We inferred from the cyclic voltammogram of four materials that there is significant variation in peak separation and peak current for different systems. The peak separations ($\Delta E = E_{pa} - E_{pc}$) at different scan rates for PANI, PANI/MWCNTs, PANI/Starch and PANI/MWCNTs/Starch-modified composite electrodes are shown as tabulated form (*c.f.*

A4). We observed anodic peak shifts towards positive direction and cathodic peak towards negative direction. The potential of cathodic and anodic peaks are affected by the presence of additives/dopants in the PANI matrix. Bulky polymeric materials which have negative charge centres generally act as counter charged dopants and maintain the stability of the positive charge present on Polyaniline chains.

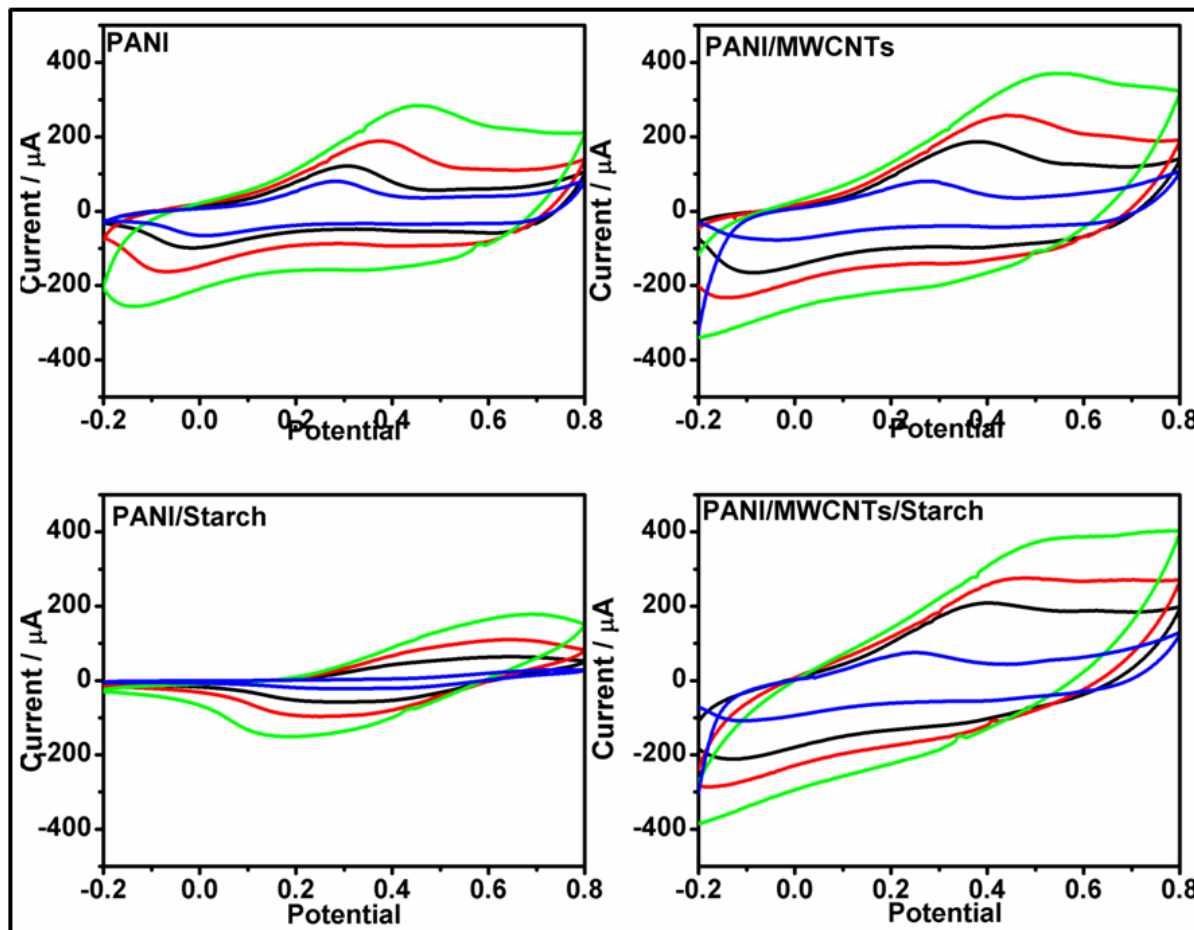


Fig. 5.11 Cyclic voltammograms of PANI, PANI/MWCNTs, PANI/Starch and PANI/MWCNTs/Starch using graphite paste electrode in 0.1M HCl

Such bulky dopants improve the conductivity and maintain electroactivity at higher pH. There is an increase in anodic and cathodic current because of the improvement in

conductivity due to the presence of MWCNTs in system-2 and system-4. Starch reduces the peak current and also broadening of peak separation is seen. The relation between scan rate and peak current provides information about the mechanism of electrochemical reaction (whether it is surface confined process or diffusion controlled process). With the increment of scan rate, there is a significant increase in the oxidation and reduction peak currents. The prepared material system-4 shows better electroactivity in terms of the higher magnitude of anodic and cathodic current than that observed for system 1, 2 and 3 at four scan rates 5, 10, 15 and 50 mV/s. We can conclude, from lower oxidizing and reducing peak potential for system-4 that PANI/MWCNTs/Starch is a suitable material for the fabrication of screen-printed carbon paste electrode. It can not only act as a mediator to shuttle electron during a redox reaction at lower potential but also as a hydrophilic biocompatible conducting host matrix for stable immobilization of biological/ sensitive elements. It is well reported in the literature that Polyaniline based materials act as good electrocatalyst for the detection of many important analytes and biomarkers. Fabrication of the screen printed biosensor by immobilizing suitable enzyme within the proposed material is under investigation.

5.8 Conclusion:

Extensive studies of four materials provide an insight on the interaction of three materials in an integrated composite system. PANI/MWCNTs/Starch-based composite materials were prepared by in-situ chemical oxidative polymerization. While the Starch improves the biocompatibility, biodegradability and hydrophilicity of the composite system, MWCNTs alongside increase the bulk conductivity of the material. Starch interacts with PANI whereas MWCNTs act as a template for PANI-Starch chains, resulting in a PANI and starch complex

Chapter 5

wrapped around nanotubes. Integration of nano level template effect of MWCNTs and interaction of polyaniline and starch architectures an integrated material system which has improved and synergic properties. System-4 has definite turmeric shape with porous, amorphous, interconnected morphology having amine/imine and hydroxyl functionality. This empowers the composite material with the higher surface area, conductivity, hydrophilicity, better electroactivity and thus attests itself as a potential material for biosensor and other biomedical applications.