5.1 Introduction

One of the major attractions of polyaniline (PANI) is that it can be easily made highly conducting through proper doping [1-4]. Making composites of PANI with suitable materials is another method to enhance its conductivity [3,5-6]. Multi Walled Carbon Nano Tube (MWNT) is one such highly pursued material due to its high electrical conductivity, mechanical strength and thermal stability [7]. Although there have been a few reports on the synthesis and characterization of Polyaniline-carbon nanotube composites [8-10], a systematic study on its temperature dependent D.C electrical conductivity, especially in the high temperature
solution used and low mass of Cl\(^-\) ions. Actually only less than 1% of the available charge carriers contributes to the conductivity of doped PANI. If all the charge carriers do contribute, the room temperature conductivity of doped PANI would be comparable to that of copper [19]. In fact PANI is only partially crystalline, with conducting metallic islands separated by large amorphous regions as evident from the X.R.D spectrum (see fig 5.7). The characteristic metallic conductivity in doped PANI is limited by strong disorder [19].

The room temperature D.C electrical conductivity of PANI(HCl)-MWNT composites increases initially with increase in MWNT loading and thereafter saturates at 28S/cm(1:0.4), almost 4 times higher than that observed for pristine MWNTs(7S/cm) used in the present work. Due to the large aspect ratio (Length is very large compared to diameter) and surface area of MWNTs, MWNTs may serve as conducting bridges between scattered PANI islands, boosting the charge delocalization [8]. There is also a possibility of charge transfer from the quinonoid unit of polyaniline to the carbon nanotubes, since carbon nano tubes are good electron acceptors and doped PANI is a good electron donor. The improved crystallanity of PANI with the addition of MWNT as evident from the XRD investigations is another reason for the increase in conductivity. Particularly the peak at 25\(^\circ\), representing the extent of \(\pi\) conjugation [1, 9, 20] becomes sharper and more intense on MWNT addition, facilitating greater charge transport due to enhanced carrier mobility. PANI (HCl)-MWNT composite
region, in doped composite samples is quite scanty. Moreover similar investigations reported earlier are centered on thin film samples and the investigations on powder samples in the form of pressed pellets of PANI or its composites are quite scarce [11-12]. In this chapter, the structural, morphological, electrical and thermal studies on PANI (HCl)-MWNT composites in powder form are described.

5.2 Synthesis of PANI and PANI-MWNT Composites

HCl doped PANI is prepared by chemical oxidative polymerization method using ammonium persulphate (APS) as oxidant at a synthesis temperature of around -10°C. Details are given in section 3.2.

For preparing HCl doped PANI-MWNT composites with different aniline to MWNT feed ratios, high pure MWNT (purchased from SUN NANO) is dispersed in 1.5M HCl solution. Freshly distilled aniline (A.R grade) is added to it. APS dissolved in water is added drop wise to the mixture with continuous stirring for 4-5 hours. The synthesis temperature is maintained at around -10°C. The precipitate obtained is filtered, washed and dried.

5.3 TEM Analysis

The morphology of PANI-MWNT composites is found out based on the TEM images. The TEM image of HCl doped PANI is shown in figure 5.1. Figures 5.2-5.3 depict the TEM images of HCl doped PANI-MWNT composites synthesized in the aniline monomer to MWNT feed ratios 1:0.1 and 1:0.5 (weight/weight) respectively. All samples are taken in pellet form.
Figures 5.2 & 5.3 clearly indicate the presence of both PANI and MWNT in the composite. The rod-like and coiled like structures of MWNT in the composite are clearly seen in the TEM images, which suggest the following possibilities. MWNTs can exist as bundles with special gaps between them. Aniline molecules occupy these gaps due to strong $\pi-\pi$ electron interaction between
the MWNTs and aniline monomers and are then in situ polymerized. As polymerization proceeds, the long chain PANI molecules would break the MWNT bundles into individual nanotubes. The MWNTs are thus dispersed individually into the PANI matrix. In addition to this, PANI macromolecules can also be adsorbed at the surface of MWNTs, forming a tubular shell of the composite [9]. Due to the large aspect ratio (Length is very large compared to diameter) and surface area of the MWNTs, they act as ‘conducting bridges’ connecting PANI domains, forming a 3D network structure[8].

5.4 SEM Analysis

The SEM images of PANI (HCl) and PANI (HCl)-MWNT (1:0.5) composite (both in powder form) are given in figures 5.4 and 5.5.

![SEM image of PANI (HCl)](image1)

![SEM image of PANI (HCl)-MWNT](image2)

The SEM images give the surface morphology of the samples. From figure 5.5, it is clear that aniline is polymerized between the wedges of MWNTs as well as on the tube surfaces, as described earlier in section 5.3.
5.5 X.R.D Analysis

The X.R.D spectrum of MWNT is given in figure 5.6 and those of PANI(HCl) and PANI(HCl)-MWNT composites with various aniline to MWNT feed ratios are given in figure 5.7. All the samples are taken in powder form.

Fig. 5.6 X.R.D spectrum of MWNT

Fig. 5.7 X.R.D spectra of PANI (HCl) and PANI (HCl)-MWNT composites
PANI shows amorphous peaks at around $8^0$ and $20^0$ and somewhat sharper peaks at $15^0$ and $25^0$. MWNT has a highly crystalline peak at $25^0$ which is much more intense and sharper than that of PANI at the same position. An additional crystalline peak appears at around $43^0$ with reduced intensity [8-9]

PANI-MWNT composites show the crystalline peaks of MWNT at $25^0$ and $43^0$ with high intensity and sharpness. The amorphous peaks of PANI at $8^0$ and $20^0$ appear sharper in the XRD spectrum of PANI-MWNT composite, confirming the formation of the composite. The appearance of the graphite-like diffraction peak at $25^0$[9], which is common to both PANI and MWNT, indicates the presence of long range $\Pi$ conjugation, in both the samples. This peak is very much sharper in MWNT because of the much enhanced $\Pi$ conjugation in MWNT. The crystallinity of PANI-MWNT composite increases drastically with increase in MWNT content in the feed ratio of aniline to MWNT as evident from figure 5.7. All these point towards enhanced $\Pi$ conjugation in PANI-MWNT composite compared to PANI.

5.6 Raman Analysis

The Raman spectra of PANI (HCl) and PANI (HCl)-MWNT (1:0.5) composite is shown in figure 5.8.
Fig. 5.8 Raman spectra of PANI (HCl) and PANI (HCl)-MWNT (1:0.5) composite

All the characteristic Raman frequencies of PANI (HCl) and PANI (HCl)-MWNT composite are observed in the spectra [9, 13-14]. The characteristic D-mode and G-mode vibrations of MWNT are observed in the composite at 1574cm\(^{-1}\) and 1345cm\(^{-1}\) respectively, confirming the formation of the composite.

5.7 FTIR Analysis

A comparison of the FTIR spectra of PANI (HCl) and PANI (HCl)-MWNT (1:0.5) composite is shown in figure 5.9.
Fig. 5.9 FTIR spectra of PANI (HCl) and PANI (HCl)-MWNT composite (1:0.5)

The two spectra resemble each other closely with only small shifts in absorption wave numbers. Both the spectra show all the characteristic vibrations of HCl doped PANI. [4] However, it is observed that the NH stretching vibration occurs at around 3500cm\(^{-1}\) in HCl doped PANI, whereas the NH stretching vibration seems to have shifted to 3000cm\(^{-1}\) in HCl doped PANI-MWNT composite. This could be due to the interaction of MWNT with the lone pair electrons of nitrogen. Since the characteristic C=C vibrations of MWNT are more or less in the same frequency range as those in HCl doped PANI, the presence of MWNT in the composite cannot be clearly established from the FTIR spectra. But the TEM, SEM, XRD and Raman investigations, described earlier clearly establish the formation of PANI(HCl)-MWNT composite.
5.8 D.C electrical conductivity studies

The temperature dependence of D.C electrical conductivity of HCl doped PANI and HCl doped PANI-MWNT composites is shown in figure 5.10. All the samples are taken in the form of pressed pellets, applying uniform pressure. Measurements have been taken using 4-probe technique.

![Conductivity vs Temperature Graph](image)

**Fig. 5.10** Temperature dependent D.C electrical conductivity plots of PANI (HCl) and PANI (HCl)-MWNT composites with various aniline to MWNT feed ratios

All the samples exhibit negligible variation of electrical conductivity with temperature, characteristic of highly conducting samples [1,15-18]. HCl doped PANI shows a flat temperature dependence of D.C electrical conductivity (room temperature conductivity is 2.17S/cm). The reasonably high electrical conductivity of HCl doped PANI is attributed to the high molarity of dopant acid
solution used and low mass of Cl⁻ ions. Actually only less than 1% of the available charge carriers contributes to the conductivity of doped PANI. If all the charge carriers do contribute, the room temperature conductivity of doped PANI would be comparable to that of copper [19]. In fact PANI is only partially crystalline, with conducting metallic islands separated by large amorphous regions as evident from the X.R.D spectrum (see fig5.7). The characteristic metallic conductivity in doped PANI is limited by strong disorder [19].

The room temperature D.C electrical conductivity of PANI(HCl)-MWNT composites increases initially with increase in MWNT loading and thereafter saturates at 28S/cm(1:0.4), almost 4 times higher than that observed for pristine MWNTs(7S/cm) used in the present work. Due to the large aspect ratio (Length is very large compared to diameter) and surface area of MWNTs, MWNTs may serve as conducting bridges between scattered PANI islands, boosting the charge delocalization [8]. There is also a possibility of charge transfer from the quinonoid unit of polyaniline to the carbon nanotubes, since carbon nano tubes are good electron acceptors and doped PANI is a good electron donor. The improved crystallanity of PANI with the addition of MWNT as evident from the XRD investigations is another reason for the increase in conductivity. Particularly the peak at 25⁰, representing the extent of Π conjugation [1, 9, 20] becomes sharper and more intense on MWNT addition, facilitating greater charge transport due to enhanced carrier mobility. PANI (HCl)-MWNT composite
synthesized in the 1:0.5 ratio exhibits room temperature D.C electrical conductivity same as that of the 1:0.4 ratio composite sample.

One of the interesting observations is that, D.C electrical conductivity of PANI (HCl) and MWNT samples is almost constant with temperature. A comparatively sudden jump in conductivity with temperature, at high temperatures is observed only for PANI (HCl)-MWNT composite samples. The decrease in D.C electrical conductivity with temperature becomes sharper with increase in MWNT content in the composites. The results may be explained as follows.

For PANI (HCl) sample, the D.C electrical conductivity stays constant at 2.17S/cm up to 373K. In the temperature range 373K-378K, it exhibits a marginal drop to 1.85S/cm. Thereafter, there is a gradual (not sharp) decrease of conductivity to about 0.7S/cm at 413K. The nominal decrease in D.C electrical conductivity at higher temperatures is due to elevated charge carrier scattering at high temperatures arising from enhanced carrier mobility. The MWNT exhibits quite flat temperature dependence of conductivity up to the maximum temperature of investigation (a conductivity of 7S/cm is observed in the range 303K-413K). This is a consequence of the long range order prevailing in the MWNT system as observed from the X.R.D spectrum (fig 5.6).

For the PANI (HCl)-MWNT (1:0.1) composite, the D.C electrical conductivity stays constant at 10S/cm up to 373K. A marginal drop to
8.8S/cm is observed at 383K. Thereafter conductivity decreases to 7S/cm at 413K. The drop in conductivity with temperature is more or less gradual and not sharp and is comparable to the behaviour of PANI (HCl) sample. PANI (HCl)-MWNT composite samples with aniline to MWNT feed ratio at or above 1:0.3 exhibit a comparatively sharper drop in conductivity with temperature at high temperatures. The D.C electrical conductivity in all the above three samples, remains constant up to a particular temperature. For example, for PANI(HCl)-MWNT(1:0.3) composite sample, the D.C electrical conductivity remains constant at 15.7S/cm from 303K-408K and decreases from 15.7S/cm to 12.5S/cm in the temperature range 408K-413K. The sample with feed ratio 1:0.4 shows a much sharper decrease in conductivity within the same temperature range (from 28S/cm to 19S/cm). PANI(HCl)-MWNT(1:0.5) composite sample exhibits a sharp drop in conductivity from 28S/cm to 17S/cm at 413K.

From the TEM images, it is clear that aniline molecules are polymerized in the special gaps between the MWNT bundles. They are also adsorbed at the surface of MWNTs and subsequently polymerized. Thus MWNTs may serve as 'conducting bridges' connecting the isolated PANI islands, boosting the charge mobility. At higher temperatures, the increased mobility of the charge carriers may give rise to enhanced scattering effects from the intersections of PANI and MWNTs. As the MWNT content increases in the composites, the number of interfaces also increases leading to greater charge scattering. This can be the reason for the observed sharp drop in conductivity in
PANI (HCl)-MWNT composite samples with higher MWNT content, compared to other samples.

PANI (HCl)-MWNT composite (1:0.5 feed ratio) exhibits the highest room temperature D.C electrical conductivity of 28S/cm (almost equal to that of 1:0.4 ratio) which stays constant upto 408K. The sample with 1:0.4 feed ratio shows the same value of D.C electrical conductivity within the temperature range 303K-408K. The stable and reasonably high D.C electrical conductivity observed for the composite sample even at elevated temperatures offers prospects of applications in the fabrication of devices working at high temperatures. An almost flat response of D.C electrical conductivity with temperature has been reported earlier on MWNT and PANI(EB)-MWNT composite samples in the temperature range 27K-300K[7]. Similarly an almost constant temperature response of D.C electrical conductivity and a sharp decrease at high temperatures has been observed on the pellet samples of sulphuric acid doped PANI and its metal oxalate composites with trivalent metal ions[21]. But a similar study has not been attempted on doped PANI-MWNT composites yet.

5.9 Thermoelectric power studies

The temperature dependent thermoelectric power plots of PANI (HCl) and PANI (HCl)-MWNT composite (1:0.5) are shown in figures 5.11 and 5.12 respectively. All the samples are taken in the form of pressed pellets, applying uniform pressure.
Fig. 5.11 Temperature dependent thermo power of PANI (HCl)

Fig. 5.12 Temperature dependent thermo power of PANI(HCl)-MWNT (1:0.5) composite

The room temperature thermo power of PANI (HCl)-MWNT composite is about 6.8μV/k, which is about 8 times higher than that of
HCl doped PANI(0.8 μV/k). The positive thermo power value observed for HCl doped PANI establishes its semi metallic nature[1]. The positive and much higher thermo power value of PANI(HCl)-MWNT composite is very close to the value obtained for CSA doped PANI films showing metallic behaviour[1]. The magnitude and sign of thermo power are consistent with the results obtained for a number of partially doped p-type conducting polymers[1,22-24]. The positive sign of the thermo power agrees with the calculated band structure of the metallic emeraldine salt with a three quarter-filled π band with one hole per repeat unit[25]. PANI(HCl) shows an exponential decrease of thermo power with temperature, while PANI(HCl)-MWNT composite(1:0.5) exhibits a nearly linear response, after an initial decrease. The possible reason may be explained as follows. PANI (HCl) is mostly amorphous in nature. On the other hand, PANI (HCl)-MWNT composite is considerably crystalline. Increase in crystallinity implies increase in chain orientation. As the chain orientation increases, the temperature dependence of thermo power shifts from its U-shaped behaviour to linear nature [26]. Thus the absence of linear temperature dependence for PANI (HCl) is due to the higher degree of disorder and the formation of metallic islands which suppresses the intrinsic conductivity [1]. The D.C electrical conductivity also rises with rise in crystallinity as already observed. The thermo power results thus compliment the D.C electrical conductivity studies.
5.10 T.G.A

The thermo grams of PANI (HCl), MWNT and PANI (HCl)-MWNT composite (1:0.5) composite are shown in figure 5.13. All samples are taken in powder form.

Weight loss up to 100°C is mainly due to the evaporation of adsorbed water molecules. Loss of dopants become prominent from a temperature of 250°C. Degradation of the polymer backbone starts at around 400°C. [27]. From the thermo grams, we see that the thermal stability of PANI(HCl)-MWNT(1:0.5) composite is remarkably better compared to HCl doped PANI. For example at 300°C, weight loss of HCl doped PANI is about 50% whereas that of the HCl doped PANI-MWNT composite is only 30%. At 900°C, the weight loss for HCl doped PANI is 86% whereas that for the
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composite is only 50%. Obviously thermal stability increases with the addition of MWNT possibly due to the better thermal conductivity of MWNT [8].

5.11 Conclusions

HCl doped PANI-MWNT composites are synthesized by chemical insitu polymerization and their structural, thermal, morphological and electrical studies are carried out.

The so synthesized PANI-MWNT composites show quite high room temperature D.C electrical conductivity, very good thermal stability, a nearly flat temperature dependent conductivity response and quite high positive thermo power value comparable to doped polymers showing metallic conductivity. The present study is relevant where there is increased demand for identifying polymer/organic materials with high mobility charge carriers for the fabrication of transistors and microprocessors. The stable D.C electrical conductivity observed in the PANI (HCl)-MWNT composite even at high temperatures highlights the prospects of application of these composites in the fabrication of devices capable of operating at high temperatures.

References


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