Synthesis and Electrical Characterization of Polyaniline-Multiwalled Carbon Nanotube Composites with Different Dopants

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Abstract: Conductive polymers or, more precisely, intrinsically conducting polymers (ICPs) are organic polymers that conduct electricity. Such compounds may have metallic conductivity or can be semiconductors. Electrical conductivity of conducting polymers can be tuned from insulating to metallic through proper doping. Examples of conducting polymers include polyaniline(PANI),Polypyrrole, Polythiophene, Polyacetelyne etc. Amongst the family of conducting polymers, PANI is unique due to its ease of synthesis, environmental stability, and simple doping/dedoping chemistry. They can offer high electrical conductivity through proper doping.Making PANI with suitable materials is another method to enhance it's conductivity.Multiwalled Carbon Nanotube is one such highly pursued material due to its high electrical conductivity,mechanical strength and thermal stability. In the present work, PANI-MWCNT composite is prepared using Hyrochloric acid(HCL) & Camphor sulphonic acid(CSA) as dopants&compared it's d.c. conductivity with PANI prepared using HCL &CSA as dopants.The FTIR, XRD& SEM analysis of the samples were done. PANI-MWCNT composite showed good conductivity compared to PANI samples.In the case of composite, aniline molecules are polymerized in the special gaps between MWCNT bundles.They are absorbed at the surface of MWCNTs&subsequently polymerized.The MWCNT may serve as conducting bridges connecting the isolated PANI.The sample prepared with HCL as dopant showed more conductivity than that of the sample prepared using CSA. Comparatively higher d.c. conductivity of HCL doped sample may be due to the presence of lighter dopant ions ie CI—ions in HCL.The light weight CI-- ions have greater mobility than SO3--- ions in CSA.

Index Terms: Conducting polymers, PANI, MWCNT,CSA ,HCL & D.C. Conductivity

I. INTRODUCTION

A polymer is a material whose molecule contains a very large number of atoms linked by covalent bonds, which makes it a macromolecule. The fundamental repeating unit in a polymer is known as "monomer". Although the term polymer is sometimes taken to refer to plastics, it actually encompasses a large class of compounds comprising both natural and synthetic materials with a wide variety of properties.

Conductive polymers or, more precisely, intrinsically conducting polymers (ICPs) are organic polymers that conduct electricity. Such compounds may have metallic conductivity or can be semiconductors. Electrical conductivity of conducting polymers can be tuned from insulating to metallic through proper dopping. They have a conjugated structure with alternate σ and π bonds. The π bonds are delocalized throughout the entire polymer network. This results in enhanced electrical conductivity[1-2].Preparing conducting polymer composite is a clever way to improve the conductivity of conducting polymers.PANI-MWNT are widely explored nowadays[3]

In the present work,the sample polyaniline-Multiwalled Carbonnanotube(PANI-MCNT) composite is prepared using Hyrochloric acid(HCL) & Camphor sulphonic acid(CSA) as dopants& tried to compare the D.C.electrical conductivity of the composite with PANI prepared using HCL &CSA as dopants. The FTIR spectral analysis , XRD analysis&SEM analysis confirmed the presence of PANI &MWNT.The D.C.electrical conductivity of the prepared samples were measured .In both cases,the composite showed more conductivity than the PANI prepared using same dopant.

II.   EXPERIMENTAL TECHNIQUES

PREPARATION OF POLYANILINE AND PANI-MWNT COMPOSITE USING CAMPHOR SULPHONIC ACID&HCL AS A DOPANTS

Polyaniline is prepared using chemical oxidative polymerization. For this aqueous solution of one molar distilled aniline and one molar Camphor Sulphonic acid(CSA) were mixed to form a solution.Ammoniumpersulphate(APS) is used as oxidant. This solution is kept in a magnetic stirrer. After two hours of stirring the polymer is filtered, washed with dopant electrolyte solution, and dried in air oven at 60^0C. The dried polymer is finely powdered.The same procedure is repeated using HCL as dopants.

For preparing HCI doped PANI-MWNT composite high pure MWNT is dispersed in 1M HCl solution.Freshly distilled aniline is added to it.APS dissolved in water is added dropwise to the mixture with continuous stirring for 4-5 hrs.The precipitate obtained is filtered, washed and dried.The same procedure is repeated using CSA as dopant.

XRD Analysis

The XRD analysis of the sample is carried out using a fully automated Rigaker 1710 X-ray diffractometer. In our set-up, filtered Cu-K2 radiation having wavelength 1.542 Å is used for diffraction. The accelerating potential applied to the X-ray tube is 30 KV and the tube current is 20mA.

Fourier Transform Infrared Spectroscopy (FTIR Spectroscopy)

The sample powder is mixed with KBr to form very fine powder.The powder is then compressed into a thin pellet & FTIR spectrum is taken using an Avatar 370 spectrometer employing DTGS KBR detector.

SEM Analysis

Field emission SEM is used for high resolution imaging.High quality low voltage images are obtained with negligible electrical charging of samples.

Measurement of electrical conductivity

Conductivities of different samples of polyaniline were measured using four probe set-up instrument. Electrical conductivities of polymer pellets were measured with a constant - built current source accompanied with four -probe set up.

Fig 1 Four -probe set up.

The circuit used for resistivity measurements are shown in figure 2.
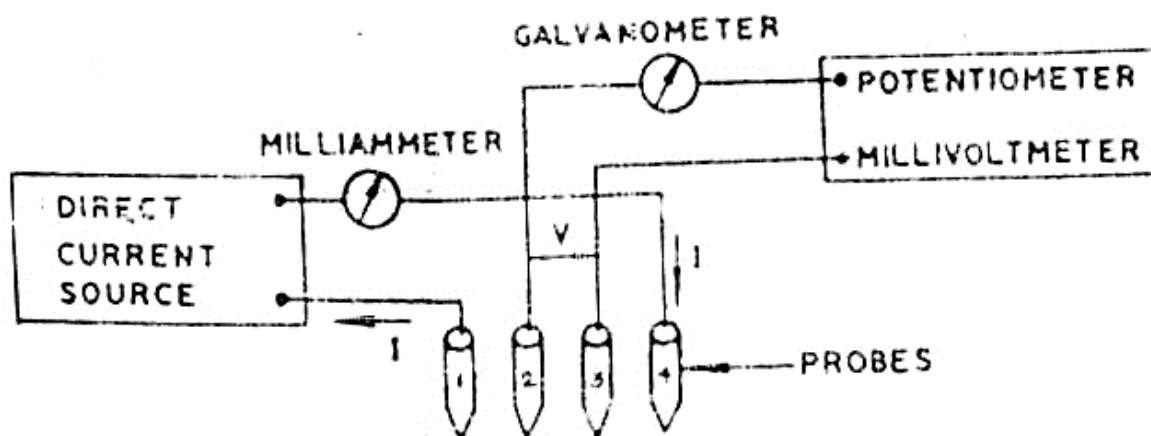

Fig 2 Circuit for resistivity measurements

Current 'I' is passed through the outer probes (1 and 4) and the floating potential 'V' is measured across the inner pair of probes(2 and 3). When the point spacings are equal i.e. $S_1=S_2=S_3=S$, the equation for resistivity for a large sample using probe technique is $\rho=2 \pi S* V/I$ .Therefore the conductivity $\sigma =I /\rho$

 The sample pellet was put on the base plate of the four probe arrangement and the four probe was gently placed on the pellet and a very gentle pressure was applied and tightens the pipe. By adjusting the milliammeter reading current was kept constant. The millivoltage was then measured. Repeat the experiment with the other side of the pellet. Again the same experiment was repeated using another pellet of the same polymeric sample.

III.   RESULTS &DISCUSSION

XRD spectrum of PANI doped with Hydrochloric acid and Camphor sulphonic acid are   shown below in   figure 3 and 4 respectively.
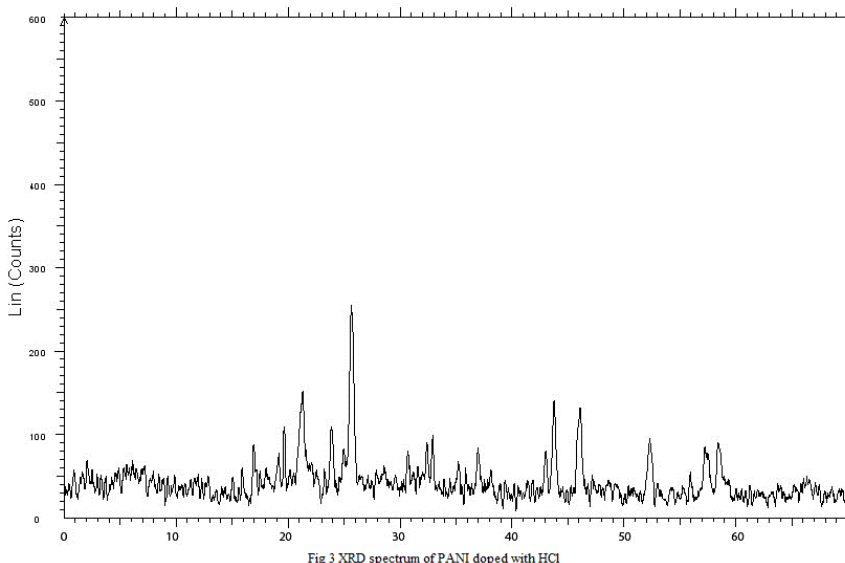

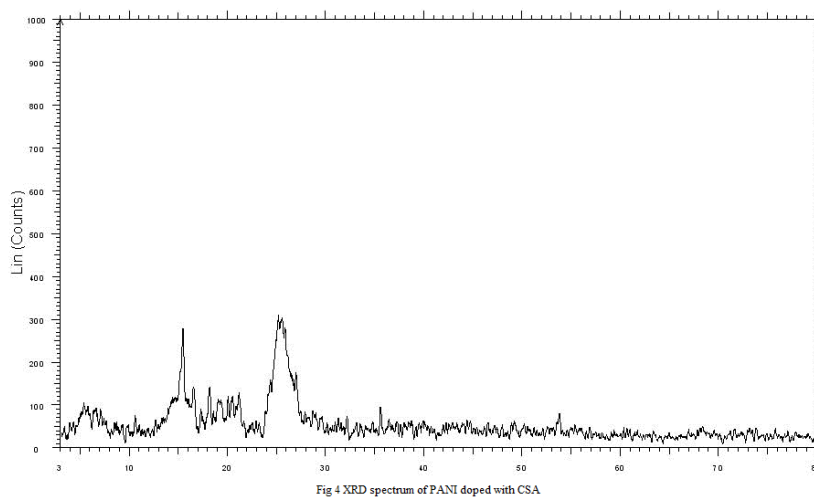Fig 3 XRD spectrum of PANI doped with HCl

Fig 4 XRD spectrum of PANI doped with CSA

The peak around 25˚ is the characteristic of π conjugation in PANI.   PANI is only partially crystalline with conducting metallic islands separated by large amorphous regions as evident from the XRD spectrum. Conductivity is limited by strong disorder. XRD spectrum of PANI(HCl)-MWNT &PANI (CSA)-MWNT composites are shown in Figures 5 and 6 below.
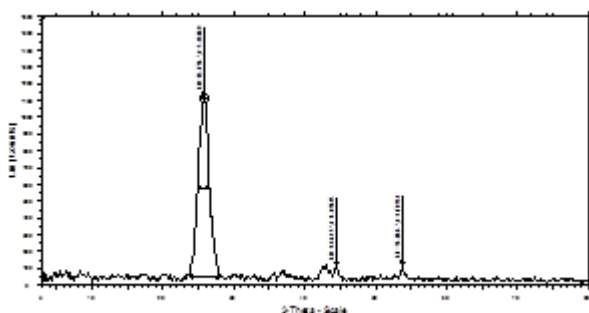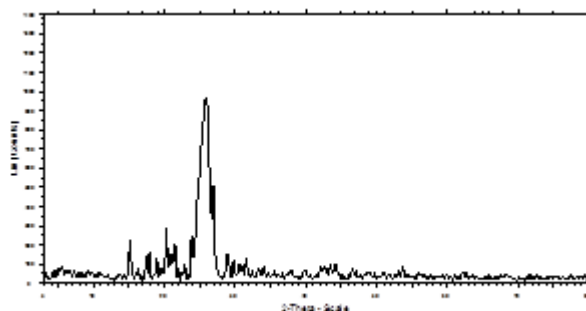

Fig 5 XRD spectrum of PANI(HCl)-MWNT composite

Fig 6 XRDspectrum of PANI (CSA)-MWNT composite

PANI-MWNTcomposite shows the crystalline peaks at 25° with high intensity and sharpness.The appearance of diffraction peak at25° which is common in both PANI and MWNT,indicate the prsence of long range –conjugation, in both samples.This peak is very much sharper in PANI-MWNT composite because of much enhanced – conjugation in MWNTs.[4-5]

FOURIER TRANSFORM INFRARED STUDIES

FTIR spectrum of PANI doped with Hydrochloric acid & Camphor sulphonic acid are given in figures 7 and 8 respectively below.
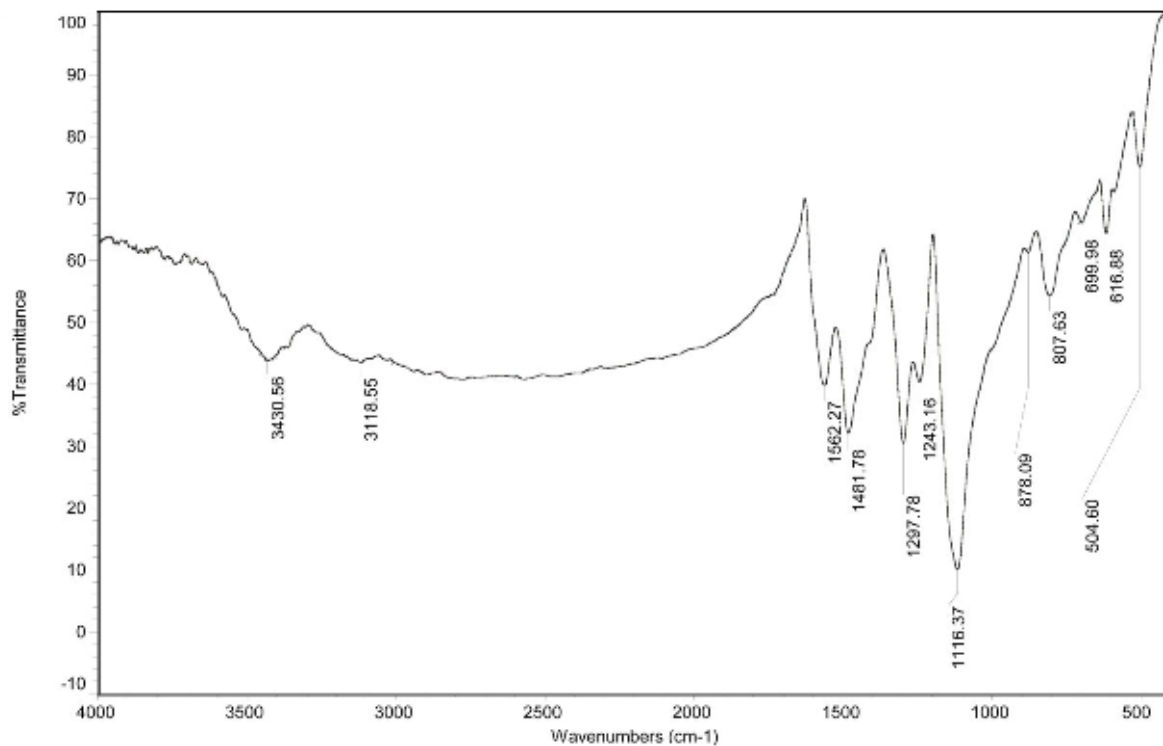

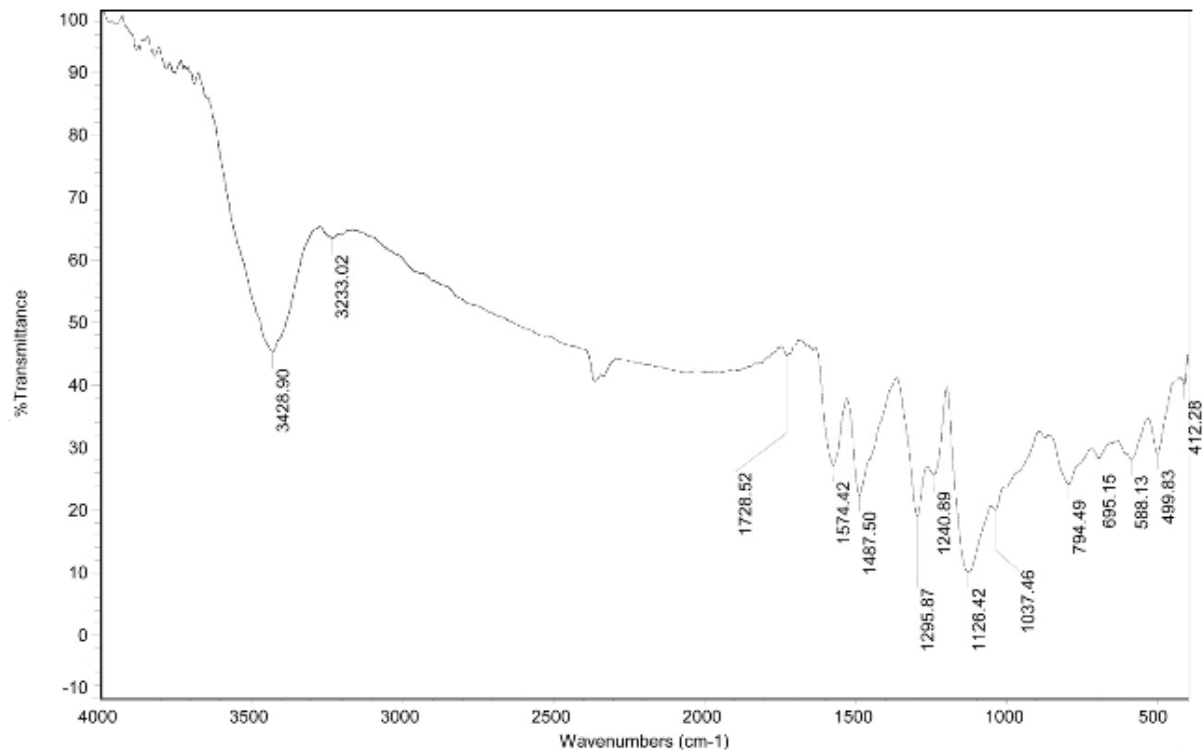Fig 7 FTIR spectrum of PANI doped with HCl

Fig 8 FTIR spectrum of PANI doped with CSA

In HCl doped PANI,the major peaks are at around 3500/cm(N-H stretching vibration),3200/cm(O-H usually broad), 1780/cm(cyclobutanone), 1570/cm(C=N strech of the quinonoid unit of PANI),1470/cm(C=C strech of the benzoid unit of PANI) In CSA doped PANI ,the major peaks are at around 3500/cm(N-H stretching vibration),2900/cm(CH stretching vibration),1570/cm(C=N strech of the quinonoid unit of PANI),1470/cm(C=C strech of the benzoid unit of PANI) and 1100/cm(quinonoid unit of vibration of doped PANI). FTIR spectrum of PANI(HCl)-MWNT &PANI (CSA)-MWNT composites are shown in figures 9 and 10 below.
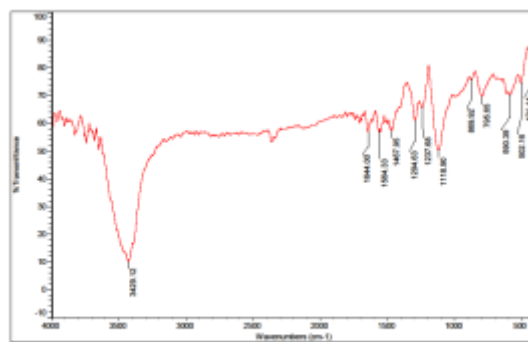

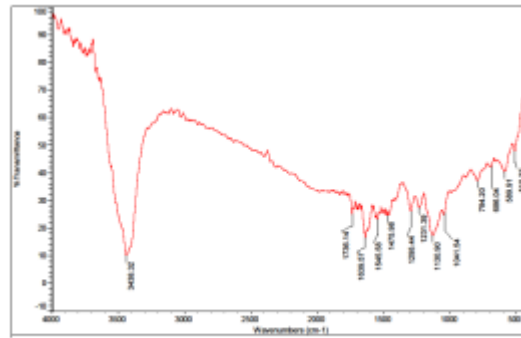Fig 9 FTIR spectrum of PANI(HCl)-MWNT composite

Fig 10 FTIR spectrum of PANI (CSA)-MWNT composite

In both cases, the two spectrum resemble each other closely with only small shifts in absorption wave numbers.Since the characteristic C=C vibrations of MWNT are more or less in the same frequency range as those in doped PANI,the presence of MWNT in the composite can not be clearly established from the FTIR spectrum.But the XRD &SEM investigations clearly establish the formation of PANI-MWNT composite.[6-7]

4 .**SEM ANALYSIS**

The SEM images of PANI(HCl)-MWNT &PANI (CSA)-MWNT composites are shown in figures 11 and 12 below

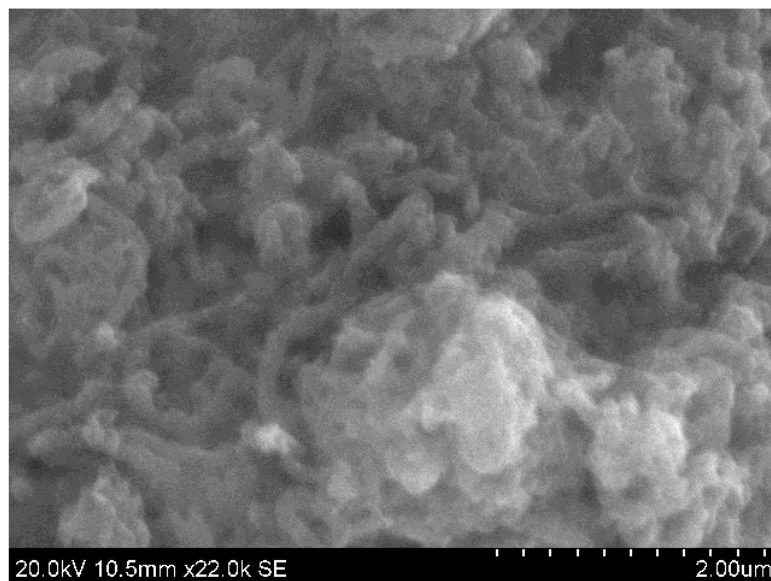20.0kV 10.5mm x22.0k SE   2.00um
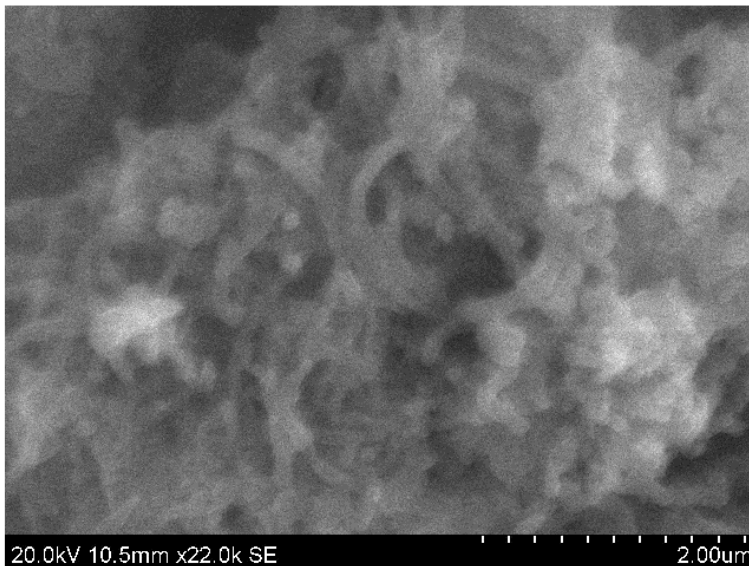
Fig 11 SEM image of PANI(HCl)-MWNT composite

Fig 12 SEM image of PANI (CSA)-MWNT composite

The SEM images give the surface morphology of the samples.From the figure,it is clear that aniline is polymerized between the wedges of MWNTs as well as on the tube surfaces.The rod like and coiled like structures of MWNTs are dispersed in the PANI matrix PANI macromolecules can also be absorbed at the surface of MWNTs forming a tubular shell of the composite [8].

4 DC CONDUCTIVITY STUDY

Measurement of conductivity of   PANI(HCl)-MWNT composite

Probe distance(S) =0.200±2% cm (fixed)

Current I(Ma)	Voltage V(Mv)	V/I Ω
25.1	2.44	0.0972
30.2	2.95	0.0972
34.8	3.42	0.0982
39.9	3.92	0.0982
45.0	4.43	0.0984
50	4.93	0.0984
55.1	5.44	0.0986
69.8	6.91	0.0989

Resistivity $\rho_0 = V/I \times 2\pi S$ =0.1232 Ω-cm

Correction factor $G_7(w/s)$ =2.78,

 Corrected ρ =0.04435Ω-cm

Conductivity $\sigma = 1/\rho$ =22.5479 S/cm

Measurement of conductivity of PANI (CSA)-MWNT composite

Current I(mA)	Voltage V(mV)	R=V/I

30	3.28	0.1093
39.8	4.38	0.11005
49.8	5.5	0.11044
60	6.56	0.109
70	7.9	0.1128
80.1	8.92	0.1113
90.2	10.05	0.1114
101.3	11.29	0.11145

Resistivity $\rho_0 = V/I \times 2\pi S = 0.13906$ Ω-cm

Correction factor $G_7(w/s) = 2,78$

Corrected $\rho = 0.05 \Omega cm$

Conductivity $\sigma = 1/\rho = 20$ S/cm

 HCl doped PANI showed a conductivity of 2S/cm.But PANI(HCl)-MWNT composite showed a conductivity of 22S/cm.It is almost 3times greater 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 charge delocalization[9].The improved crystallanity of PANI with the addition of MWNT as evident from the XRD investigations is another reason for the increase in conductivity.CSA doped PANI showed a conductivity of 0.09S/cm.But PANI(CSA)-MWNT composite showed a conductivity 20S/cm.In this case also, there is considerable increase in the conductivity of composite as compared to PANI.

IV.   CONCLUSION

 PANI-MWNT composite is successfully synthesized by chemical oxidative polymerization using HCl&CSA as dopantS. The XRD analysis revealed that PANI is only partially crystalline with conducting metallic islands separated by large amorphous regions. This peak is very much sharper in PANI-MWNT composite because of much enhanced – conjugation in MWNTs.The FTIR analysis confirmed the formation of PANI. SEM image shows that aniline is polymerized between the wedges of MWNTs as well as on the tube surfaces.The rod like and coiled like structures of MWNTs are dispersed in the PANI matrix.PANI macromoleules absorbed at the PANI-MWCNT composite showed good conductivity compared to PANI samples.The MWCNT may serve as conducting bridges connecting the isolated PANI.The sample prepared with HCL as dopant showed more conductivity than that of the sample prepared using CSA. Comparatively higher d.c. conductivity of HCL doped sample may be due to the presence of lighter dopant ions ie Cl^-ions in HCL.The light weight Cl^- ions have greater mobility than SO_3^{---} ions in CSA.

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