

Synthesis and Characterization of PANI and Polyaniline/Multi Walled Carbon Nanotube Composite

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ABSTRACT

The study reports the synthesis of doped polyaniline (PANI) with multi-walled carbon nanotube (MWCNT) composites. These composites have been characterized by atomic force microscopic (AFM) and Fourier Transformer- Infra Red (FT-IR) to study the contribution of MWCNT on the morphology and the structure of polyaniline. The AFM studies distributed morphology of MWCNT in these composite films, the surface roughness seems to increase with increasing the amount of MWCNT. FT-IR investigations show the formation of MWCNT doped composite at the molecular level and their interaction with PANI can be attributed to charge transfer. The nanocomposites showed increased conductivity by increasing the frequency and MWCNT amount. The exponential factor was more than unity. Real and imaginary parts of dielectric constant were decreased with increasing frequency which can be attributed to the power-law behavior known as low frequency dispersion.

Keywords:- multi-wall-carbon nanotubes; polyaniline; composite; Electrical properties.

1. INTRODUCTION

Since Iijima's report on CNTs in 1991 [1], there was enormous interest in exploring and exploiting their unique properties for various applications [2,3]. Conductive polymers got a great interest over the last decade due to its excellent electrical conductivity. They have a conjugated structure with alternate σ and π bonds. The π bonds are delocalized throughout the entire polymer network [4,5]. Among various conductive polymer polyaniline (PANI) is one of the most intensively investigated conducting polymers due to its easy synthesis, well-behaved electrochemistry, good environmental stability, high conductivity [6].

Due to their ability to combine the remarkable properties of CNTs, polymeric composites based on carbon nanotubes (CNTs) are of great interest in both academic and technological areas, properties such as extremely high electrical and thermal conductivity, low density, high tensile strength, and Young's modulus, with the versatility, processability, and mechanical properties of polymers [7].

Significant progress has been made in fabricating PANI/MWCNT composites that demonstrate site selective interaction between the quinoid ring of the polymer and MWCNT [8]. It is well known that the strong interaction between the aromatic rings of PANI and the graphitic structures of CNT would be a great benefit to the charge-transfer interaction between the two components [9]. Fourier Transform Infrared (FTIR) analysis was done to study the nature of the material individually and in composite. In this work we reported the preparation, characterization and electrical properties of PANI/MWCNT composite.

2. EXPERIMENTAL

2.1 Materials

MWCNT (purity =95%) was supplied by neutrino factory, India. The diameter of the MWCNT was in the range of 10-20 nm and the length 30 μ m. The monomer of aniline (purity 99.99%) was purchased by Hopkin and William Germany.

2.2 Synthesis of Polyaniline

The preparation of PANI is based on the oxidation of 0.2M aniline hydrochloride with 0.25M ammonium peroxydisulfate in an acidic medium. The aniline is dissolved in some of 1M HCl aqueous solution, ammonium peroxydisulfate is also dissolved in some of HCl, both solution are mixed in a rounder and gentle stirring to polymerize the mixture. After polymerization, the mixture is left at rest to the next day PANI precipitate is collected by a filter and washed with 300ml of 0.2M HCl. PANI hydrochloride emeraldine powder is dried in air for 15 minutes then in a vacuum oven at 80°C for 4 hours. The polymerization of aniline and formation of the emeraldine salt is illustrated in Figure 1.

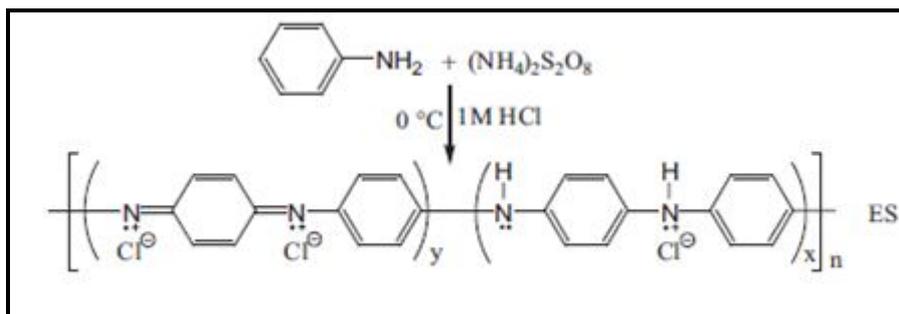


Figure1 The polymerization of aniline and formation of the emeraldine salt (ES).

2.3 Synthesis of PANI/MWCNT Composite

In a typical synthesis experiment, various weight ratios of MWCNT (table 1) were sonicated at room temperature for 30 min. To remove the aggregation, then it was added to 0.3gm weight of PANI at room temperature. Then they were mixed by magnetic stirrer at 500rpm for 30min, to have good distribution and less agglomeration.

Table 1

| Sample | Symbol |
|--------------|--------|
| 0.0001 MWCNT | A1 |
| 0.0005 MWCNT | A2 |
| 0.001 MWCNT | A3 |
| 0.05 CNT | A4 |

2.4Structural Analysis

FTIR spectra were recorded by using solid KBr discs using Shimadzu FT-IR 8000 series Fourier Transform infrared spectrophotometer.

2.5Electrical Properties

The samples of PANI, and PANI/MWCNT composite were pressed into pellet form under 200 bar. The conductivity at room temperature was measured using the LRC meter (model Agilent 4294A) of holder of 0.5cm diameter was used for the measurements.

3.RESULTS AND DISCUSSIONS

3.1 AFM Measurements

To investigate the surface properties, AFM studies have been carried out for MWCNT/PANI composite film. Figure 2 shows a 2D micrograph of the composite films with a uniform distribution of MWCNT in PANI with no aggregation. The roughness values (estimated as root mean square, rms) of the composite film (table2) obtained using height distribution analysis. It may be noted that this value of the roughness is increasing with increasing the MWCNT amount which indicates increased available surface. The high value of roughness observed indicates porous morphology of the film.

Table 2: The surface roughness and surface bearing index of the composite films.

| Sample | Surface roughness(nm) | Surface bearing index |
|--------|-----------------------|-----------------------|
| A1 | 2.3 | 5.38 |
| A2 | 2.59 | 4.08 |
| A3 | 10.3 | 5.58 |
| A4 | 6.74 | 4.53 |

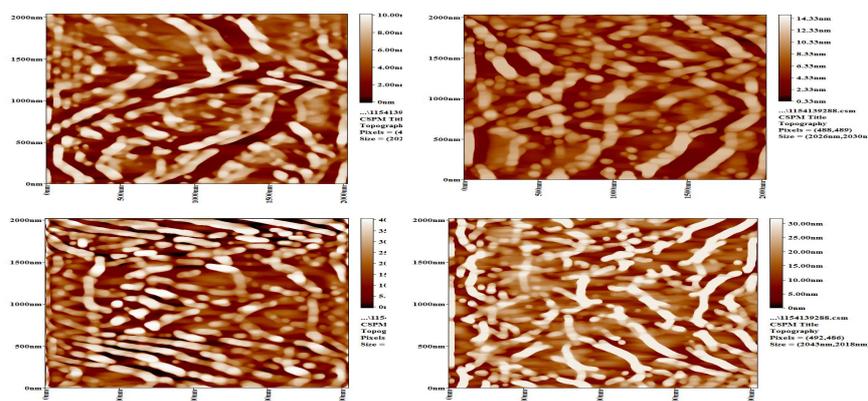


Figure (2) AFM analysis of PANI/MWCNT composite films (a) A1 (b) A2 (c) A3 (d) A4.

3.2 FTIR Measurements

Fig. 3 shows the FTIR spectra of PANI, MWCNT, and nanocomposites in the region of 4000–500 cm^{-1} . The PANI (Fig.3a) a clear presence of benzoid at 1494 cm^{-1} and quinoid ring vibration at 1560 cm^{-1} which indicating the oxidation state of PANI [10]. The strong band at 1150 cm^{-1} is the characteristic peak of PANI conductivity which was described by Macdiarmid et al as the "electronic-like band" and was considered to be a measure of the degree of the delocalization of electrons[11]. 3440 cm^{-1} is assigned to the N-H stretching mode and its very weak and broad band.

MWCNT (Fig.3b) shows the band around 3433 cm^{-1} is correspond to OH stretching vibration in –COOH group. The weak peak at 2877 cm^{-1} is corresponding to –CH stretching mode. The band at 1083 cm^{-1} is assigned to O-H deformation vibration, peaks at 1130 cm^{-1} and 1180 cm^{-1} assigned to C-O stretching vibrations. Peak around 1400 cm^{-1} is corresponding to C=C stretching.

For the nanocomposites the spectrum illustrates several clear differences from the spectrum of PANI. The spectrum shows an inverse intensity ratio of all composites which indicates that PANI in the composites is richer in quinoid units than pure PANI and that is due to the interaction promote and /or stabilize the quinoid ring structure in the composite film[10]. Around 3400 cm^{-1} shows strong and broad peak which correspond to the N-H stretching vibration of aromatic ring in PANI and MWCNT, its due the interaction between PANI and MWCNT which may result in charge transfer where the MWCNT sp^2 carbons compete with chloride ions and perturb the H-band and increase the N-H stretch intensity[10]. The intensity of 1150 cm^{-1} increased and shifted to 1130 cm^{-1} for all samples and this increase of the electronic-like absorption peak (-N=quinoid=N-) [12].

The emeraldine salt form of PANI and the composite was indicated at 1580 cm^{-1} can be assigned to C=C bond in MWCNTs. The peak around 1560 cm^{-1} corresponds to the IR active phonon mode of the CNT [13].

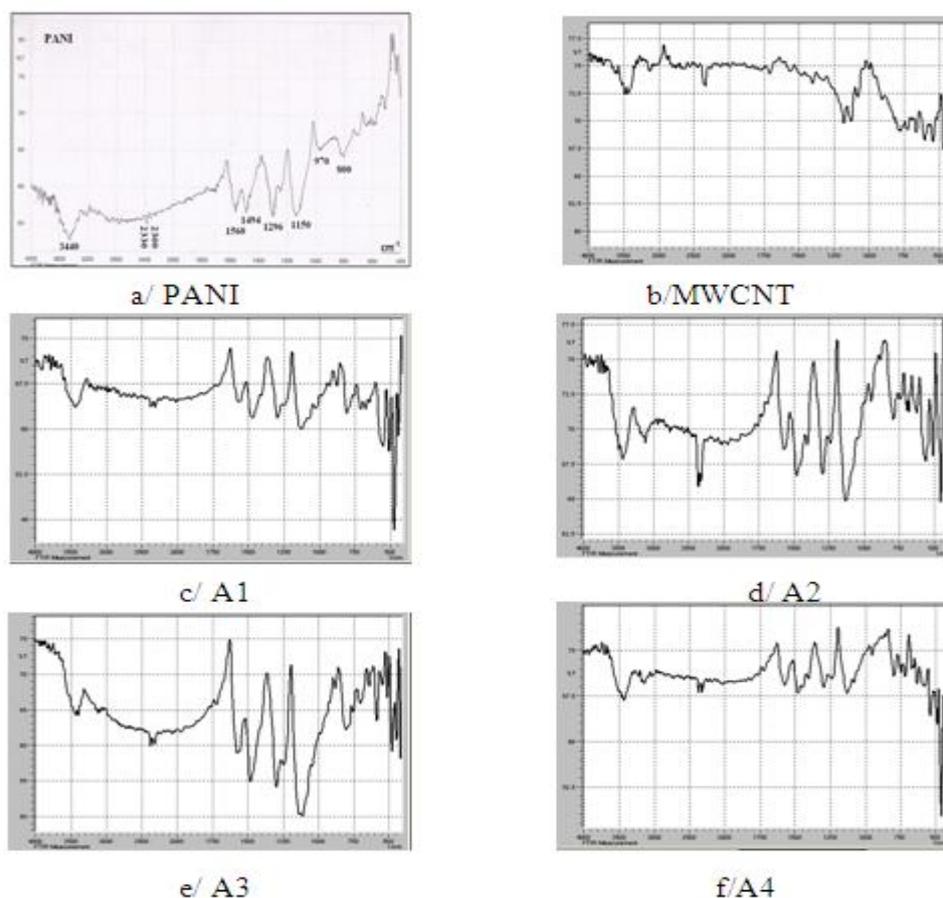


Figure 3 FTIR spectra of MWCNT and different PANI-MWCNT composites.

3.3 Electrical Properties

Generally, the AC conductivity can be expressed as follows:[13]

$$\sigma_{\text{total}} = \sigma_{\text{dc}} + \sigma_{\text{ac}} \quad (1)$$

Where σ_{dc} is the dc conductivity $\omega \rightarrow 0$, and $\sigma_{\text{ac}} = A\omega^S$ where A and S are parameters dependent on temperature and the concentration of fillers.

In fig. 4 the $\ln\sigma$ versus $\ln\omega$ is in a good exponential relationship. The conductivity increased with frequency, the interfacial polarization of the MWCNT/PANI composites is induced [14].

The values of the exponent s (which illustrated in table 3) are estimated from the slope of the curves plotted between \ln_{AC} versus $\ln\omega$, which declared in Figure 4.

Table (3): S-factor for PANI-MWCNT composite.

| Sample | S-factor |
|-----------|----------|
| Pure PANI | 0.638 |
| A1 | 0.676 |
| A2 | 0.714 |
| A3 | 0.722 |
| A4 | 0.799 |

Fig.4 shows the composite films increase with increment of nano content. In general, charge transport in PANI illustrated by various hopping mechanism [15]. So the addition of CNT to the PANI matrix lead to an increase in highly ordered sites distributed in the polymer known as metallic islands which eventually increase the probability of charge hopping between conjugated polymer chain [16].

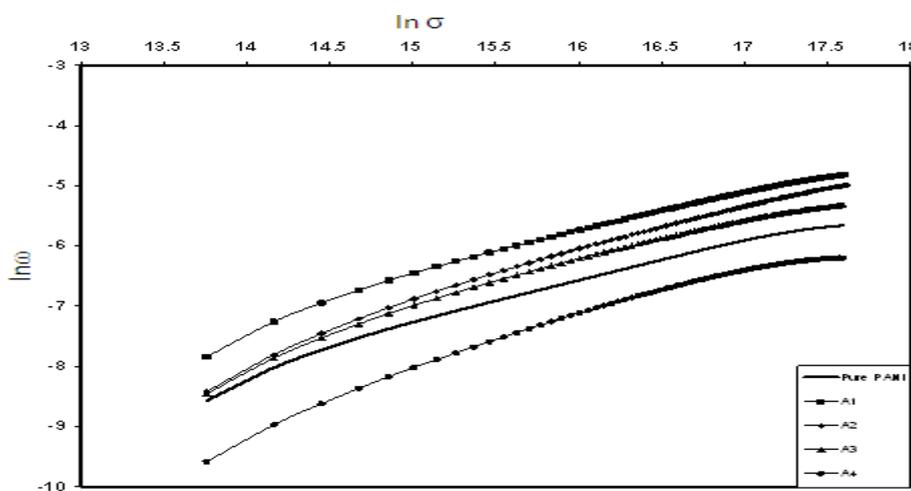


Figure 4 $\ln\sigma$ as a function of $\ln\omega$ for composite films

The dielectric results shown in Figure 5a shows a sharp decreases in permittivity at low frequencies, which can be attributed to the power-law behavior known at low frequency dispersion (LFD)[14]. In higher frequency regions the dielectric permittivity is mainly dependent on polarization of CNTs due to the function of space charge and the weakness of interfacial polarization [14]. Dielectric loss at low frequencies is due to the composite resistance, and is independent of frequency. At higher frequencies, the dielectric permittivity is mainly dependent on the space charge polarization character (response of charge carrier polarization).

Figure 5b shows the imaginary permittivity for PANI and MWCNT-PAN composites for different MWCNT concentrations. The higher conductivity resulted in greater energy dissipation in the system, which resulted in higher imaginary permittivity. At low frequencies dielectric loss, which is the ratio of imaginary to real permittivity, was mainly controlled by the resistance of polymer. At higher frequencies, as charge polarization occurred, the composites exhibited decreasing dielectric losses [15].

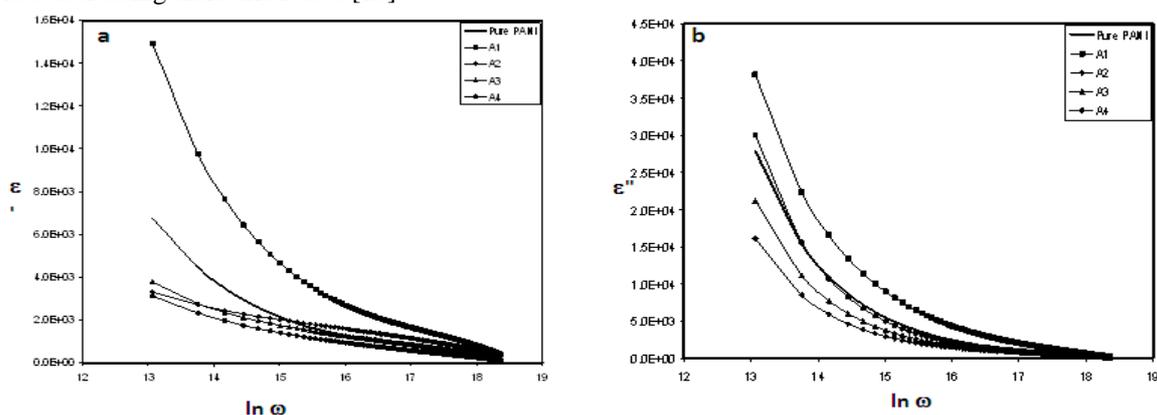


Figure 5 a) real, and b) imaginary permittivity for PANI and PANI / MWCNT nanocomposite

4. CONCLUSIONS

PANI and PANI-MWCNT composite was synthesized. FTIR shows the effective structural modification of PANI – MWCNT. The FT-IR shows the MWCNTs interaction site with doped polyaniline. AFM shows uniform distribution of MWCNT in PANI with no aggregation and an increasing with surface roughness. Electrical parameters of PANI-MWCNT composite show the composite is better electronic material than pure polyaniline. A.C. conductivity was increased for composite films by increasing frequency while the composites exhibited decreasing dielectric losses.

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