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Research Article

Electrical Properties of Polyaniline/Functionalized Multi Walled Carbon Nanotubes Nanocomposite

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Abstract

Conducting polyaniline (PANI) nanocomposites containing various concentrations of carboxylic acid functionalized multi-walled carbon nanotubes (f-MWCNT) were synthesized by in situ polymerization of aniline monomer. The morphological, structural and electrical properties of pure PANI and MWCNT–PANI nanocomposites were studied by using Fourier transform- infrared spectroscopy (FT–IR), X-ray Diffraction(XRD)and an ac computerized sensitive impedance analyzer type, respectively. FTIR spectra indicates that the carboxylic acid groups formed at the both ends of the sidewalls of the MWCNTs. The aniline monomers were polymerized on the surface of MWCNTs, depending on the π-π^* electron interaction between aniline monomers and MWCNTs and hydrogen bonding into interaction between the amino groups of aniline monomers and carboxylic acid group of f-MWCNT. XRD result shows that CNTs were well dispersed in polymer matrix. The electrical conductivity of the PANI-MWCNT nanocomposites was higher than pure-PANI increased by increasing the amount of MWCNT to the nanocomposite.

Keywords: *PANI, MWCNTs, electrical properties.*

1. Introduction

Conductive polymers have a great attention due to their electrical, electrochemical and good chemical stability [Kondawar *et al* 2009]. It characterized by its partial oxidation or reduction. It behaves as a semiconductor because it has a π-conjugation along its backbone. Among the conducting polymers polyaniline (PANI) is the most desirable polymer because of its properties; ease of preparation in aqueous medium, simplicity in doping, good stability in air, excellent environmental stability, and high conductivity in the doped state and potential applications in electronic devices [Kerileng M.]. For chemical synthesis, an appropriate oxidant is required. There are three forms of PANI, namely fully oxidized pernigraniline, half-oxidized emeraldine base (EB) and fully reduced leucoemeraldine base (LB). Emeraldine is said to be the most stable form of PANI and also the most conductive form when doped (emeraldine salt) [Ran Y. S. *et al* 2011, Prasanna *et al* 2014].

Since the discovery of CNT by Iijima et. al. [Iijima et. al. 1993] it takes a lot interest for several applications due to their unique mechanical, structural and electrical properties [Ginic -Markovic *et al*. 2006, Zelikman *et al*. 2010]. There are two types of CNTs, single -walled (SWCNTs) and multi- walled (MWCNTs). SWCNTs are hollow single cylinders of a graphene sheet, while the MWCNTs are a group of concentric SWCNTs often capped at both ends, with diameters reaching tens of nanometers depending on the number of concentric walls [Estabrak *et. al.* 2011]. By the combine of CNT and PANI as nanocomposite this leads to improve the electrical conductivity by facilitating charge-transfer processes between the two components [Bhadra *et. al.*2009, Johny et. al. 2013 Rupesh *et al* 2005]. There are many methods to prepare CNT/PANI nanocomposite, solution processing, melt blending, in situ-polymerization and grafting macromolecules to the CNTs [Valentin 2004, Ran *et al* 2011]. This work describes the synthesis and characterization of PANI and PANI/functionalized MWNT nanocomposites fabricated by in situ polymerization, where PANI was synthesized by chemical polymerization of HCl. Chemical functionalization of MWNT is used in order to increase the interfacing binding between the MWNT and PANI.

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 30μm. The monomer of aniline salt (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 aqueous medium. The aniline was dissolved in 1M HCl aqueous solution, also the ammonium peroxydisulfate, both solution were mixed in a rounder and gentle stirring to polymerize the mixture. After polymerization, the mixture is left to rest for 24 hour. PANI precipitate was collected by a filter and washed with 300ml of distilled water and 50ml of acetone. PANI hydrochloride emeraldine powder was dried in air for about 15 min. then put in a vacuum oven at 80C° for 4 hours (Fig. 1).

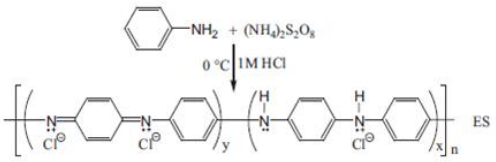


Fig.1 The oxidation of aniline yielding the emeraldine salt (ES) [Estabraq *et. al.* 2015].

2.3 Functionalization of MWCNT

A solution of Sulfuric acid (6M H_2SO_4) and Nitric acid (6M HNO_3) in 3:1 ratio was stirred for 10 minute. MWCNT was added to the solution and stirrer for 4 hours at 50°C. After centrifuge the MWCNT, it was collected by filter papers and washed with 300ml of distilled water, then it entered electrical oven at 50°C for 4 hours to avoid any effect of moisture absorption [Kondawar *et. al.* 2012].The results of this process shows Fig. 2.

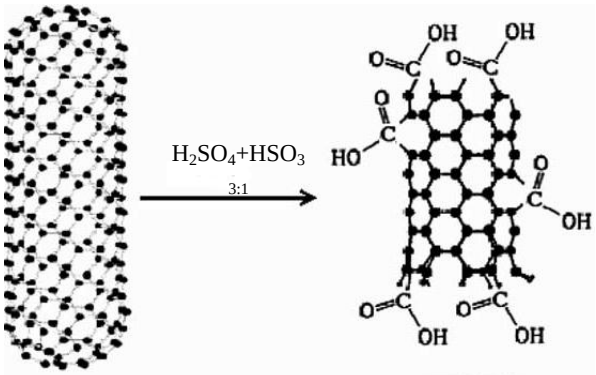


Fig. 2: Carboxylation of MWNTs [Tzong-Ming W 2006]

2.4 Preparation of PANI-MWCNT nanocomposites

The synthesis of PANI-MWCNT nanocomposites was performed using in-situ oxidative polymerization by measuring different quantities of MWCNT (0.2, 0.5 and 1% wt) which were added to the aniline solution, and then it was polymerized at room temperature employing the same procedure as that of PANI preparation.

The prepared PANI-MWCNT nancomposites were collected on filter papers and washed with 300ml of distilled water and 50ml of acetone. The mixture was dried under the hood for about 20 minute and then in vacuum oven at (80°C) for 4 h, to obtain green-black powder of PANI-MWCNT nanocomposites.

2.5 Structural Analysis

The FT-IR spectroscopy and X-ray diffraction were used to characterize the structure of PANI and PANI-MWCNT nanocomposites in the form of powder. FT-IR was recorded at Shimadzu 8000 series. Samples in KBr were analyzed at room temperature. The degree of interaction for PANI and PANI-MWCNT nanocomposites powder have been examined by X-ray diffraction by (XRD-6000) model, Shimadzu Co.

2.6 Morphology Analysis

Atomic Force Microscopy (AFM) was used to analyze the surface of all samples, its type SPM AA3000 Angstrom Advanced Inc., 2008, USA contact mode.

2.7 Electrical Properties

The samples of MWCNT, f-MWCNT and PANI/MWCNT nanocomposites were pressed into pellets form under 200bar. The conductivity at room measurement was measured using a computerized sensitive impedance analyzer type. Capacitance C, dielectric loss (ε'') and loss tangent (tanδ) of the investigated samples were measured directly. The AC conductivity σ_{AC}., dielectric constant(ε') were calculated from the following relations [Estabrak *et al* 2011]

$$\sigma = \frac{t}{RC} \quad (1)$$

$$\varepsilon' = \frac{Ct}{\varepsilon_\circ A} \quad (2)$$

$$\varepsilon'' = \varepsilon' \tan\delta \quad (3)$$

Where ε_o is the permittivity of free space = 8.85×10^{-12} F/m, t and A thickness (m) and surface area (m^2) of the sample respectively and R: is the resistance Ω. AC electrical conductivity $\sigma_{AC}(\omega)$ is measured by the following equation [Elliott, (1987)]:

$$\sigma_{AC}(\omega) = \sigma_{total}(\omega) - \sigma_{DC}(\omega) \quad (4)$$

Where ω is the angular frequency (=2πf), $\sigma_{total}(\omega)$ is the measured total electrical conductivity, $\sigma_{DC}(\omega)$is the DC conductivity which depends strongly on temperature, it dominates at low frequencies and high temperatures. Whereas the σ_{AC}, which has a weaker temperature dependence than σ_{DC}, and dominates at high frequency and low temperature. The relation for the frequency dependence AC conductivity is given by:

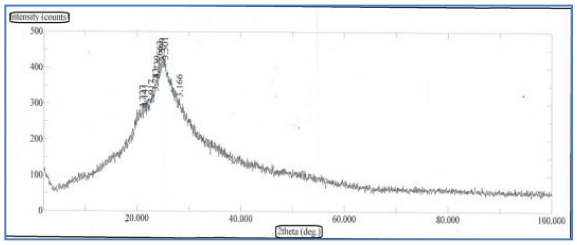
$$\sigma_{AC}(\omega) = A_1\omega^s \quad (5)$$

A_1 is a constant, and (S) is a function of frequency which is determined from the slope of a plot ln $\sigma_{AC}(\omega)$ versus ln(ω) (Elliott, 1987), then the value of S can be calculated from ;

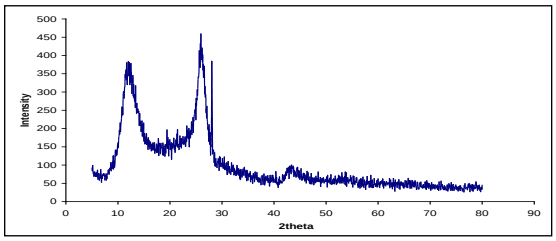
$$s = \frac{d[\ln \sigma_{ac}(\omega)]}{d[ln(\omega)]} \quad (6)$$

Results and Discussion

The XRD pattern of pure PANI and PANI-MWCNT nanocomposite are shown in Fig. 3. For pure PANI, the characteristic peaks appeared at 25.4, corresponding to (100) crystal planes of PANI [Liang *et. al.* 2012]. When carbon nanotubes were incorporated into the PANI matrix, the sharp and strong diffraction peak of CNT at (26.28) was observed as overlap with the peak of PANI which results in the broad and intense peak in the nanocomposites. The data indicates that no additional crystalline order has been introduced into the nanocomposites. Compared with functionalized CNT, the obvious characteristic peaks in PANI/CNT can be described to the formation of crystal appearing on the outer layers of nanotubes. This result shows that CNTs were well dispersed in polymer matrix [Kondawar *et. al.* 2012, Mishra *et al* 2015].



(a)



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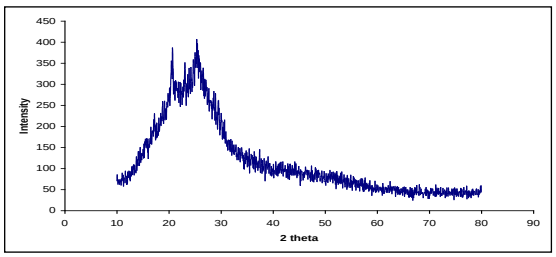

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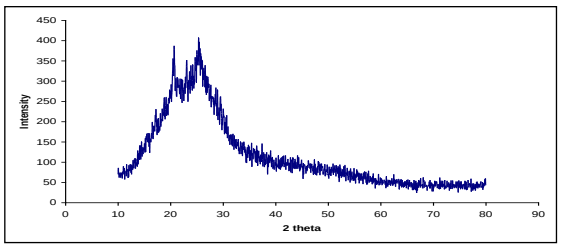
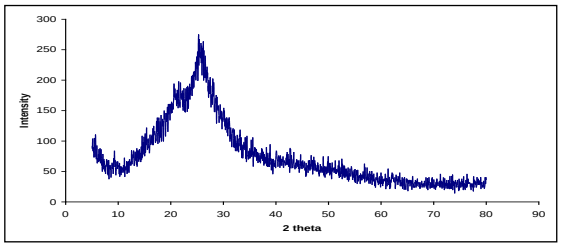


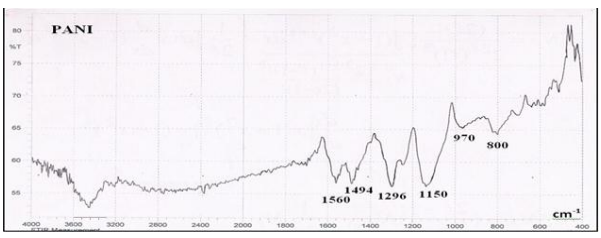
(d)



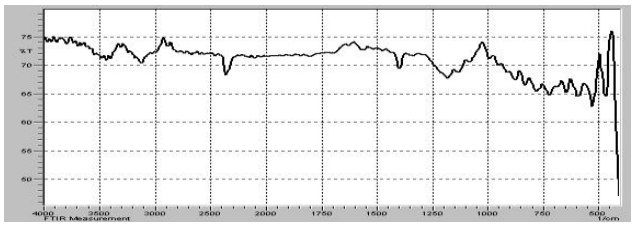
(e)

Fig.3 X-ray diffraction of (a)pure-PANI (b)f-MWNT, (c)0.2wt% (d)0.5wt% (e)1wt% MWNT doped PANI nanocomposites

The FTIR spectra of pure PANI, f-MWCNT and PANI-CNT nanocomposites and are shown in Fig.4. The characteristic peaks of pure PANI were observed at 1566.2 and 1485.19 cm^{-1} are assigned to the C=C stretching of quinoid rings and benzenoid rings, respectively[Trchová *et al* 2011, Bachhav *et al* 2015]. The characteristics peaks at 1296 and 1150 cm^{-1} are attributed to the C-N stretching vibration of the secondary aromatic amine group and aromatic C-H in plane bending vibration, respectively. 870 cm^{-1} peak represents the para-distributed aromatic rings indicating polymer formation[Kulkarni *et al* 2013]. The conducting emeraldine salt form is indicating at the peak 1225 cm^{-1} [Sharma 2012]. For f-MWCNT the broad peak at 3429 cm^{-1} is related to the O-H stretch which attributed to alcoholic or phenolic carboxylic groups[Liu *et al* 2013]. The small peak at 1570 cm^{-1} is attributed to the vibration bending of carbonyl. For the PANI/MWCNT nanocomposite no new absorption peaks found, the intensity of the nanocomposites decreased by increasing the amount of MWCNT such behavior ensure the formation of PANI on the wall of MWCNTs by in situ chemical polymerization process [Abdul Almohsin *et al* 2012].



(a)



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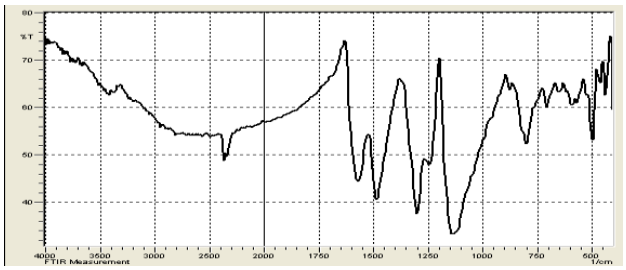
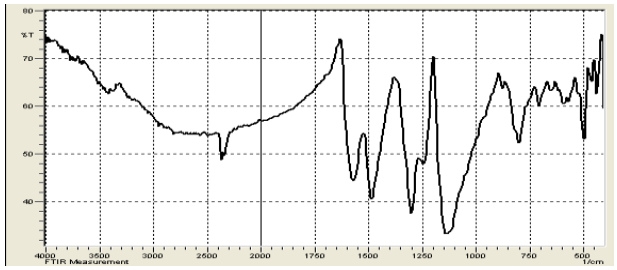
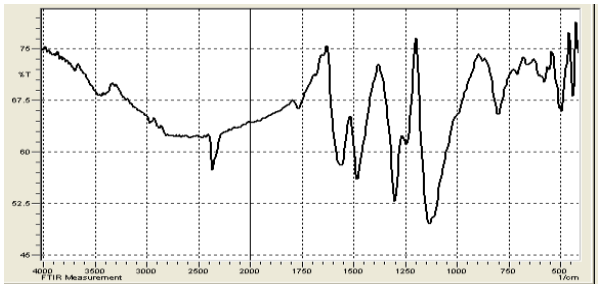


(c)



(d)



(e)

Fig. 4 FTIR of a) pure PANI, b) f-MWCNT c)0.2%wt d)0.5%wt e)1%wt of MWCNT doped PANI nanocomposites

The AC electrical conductivity of pure PANI, and PANI/MWCNT nanocomposites was shown in Fig. 6. The conductivity of the nanocomposites were increased by one order of magnitude. Such enhancement in conductivity can be attributed to the dopant effect or charge transfer from the quinoid unit of PANI to MWCNT. Also MWCNTs have a large aspect ratio and surface area, , they may serve as conducting bridges connecting PANI conducting domains [Valentin *et al* 2004, Estabraq *et al* 2015].

Conductivity which is attributed to the contribution of MWCNT and distributes on the PANI chains that causes an increasing in the concentration of the charge carrier and increasing the charge transfer along the polymer chain. The adding of MWCNT during the polymerization process in nanocomposites, causing a homogenous distribution of MWCNT on PANI chain, then the possibility of bond formation between – NH of PANI on the surface of MWCNT is increased. This will make the conductivity of prepared nanocomposites by polymerization to be more than it of prepared nanocomposites by additive.

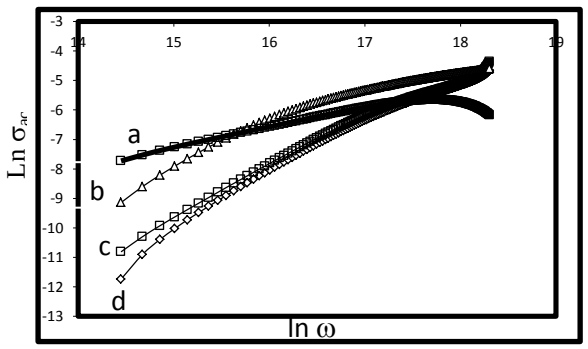


Fig. 6 Electrical conductivity (σ) of a) purePANI b)0.2%wt, c)0.5%wt and d)1%wt MWCNT/PANI nanocomposites

Conclusion

PANI/MWCNT nanocomposites were prepared successfully in situ polymerization. The FTIR, X-ray described the strong interaction between PANI and CNT. The nanocomposites showed an increase in the electrical conductivity over pure PANI. That is because the functionalized MWNT serves as a 'conducting bridge' between PANI conducting domains, and that leads to increase in the effective path.

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