

Chemically Synthesized Polyacrylic Acid / Polyaniline/MWCNT Nanocomposite

Muktikanta Panigrahi *

Materials Science, Maharaja Sriram Chandra Bhanja Deo University, 2nd Campus, Keonjhar-758002, Odisha, India

DOI: <https://doi.org/10.5281/zenodo.7023012>

Published Date: 25-August-2022

Abstract: PAA/polyaniline/MWCNT nanocomposite is successfully synthesised using aniline as monomer and MWCNT as additive by chemical oxidation method. The composite is characterized by XRD, FTIR, and UV-Visible, FESEM with EDS, HRTEM, DC conductivity and magnetoresistance. DC conductivity of aforementioned nanocomposites is determined by linear four-probe technique and the Highest DC conductivity of PAA/PANI/MWCNT (0.3 wt%) nanocomposites is found to be 0.0325 S/cm. Temperature dependent DC conductivity signifies semiconducting nature. Magnetoresistance of PAA/PANI/MWCNT (0.3 wt%) nanocomposite with different temperatures is studied and is non-linearly related to magnetic field.

Keywords: Acrylic Acid, Polyaniline, MWCNT, Composite, FESEM, HRTEM, Electrical Conductivity, and Magnetoresistance.

I. INTRODUCTION

In the present time, researchers have focused more on light weight conducting polymers because of their technological applications (such as rechargeable batteries, electrochromic windows, biosensor and antistatic coating materials) [1-6]. Among the conducting polymer family, polyaniline is one of the most important conducting polymers. It is because of simple synthetic routes, good environmental stability, unique oxidation reduction chemistry and cost-effective synthesis process, etc [7-9]. Still to date, polyaniline salt is insoluble in common organic solvents like water, ethanol, carbonate tetrachloride, N-methyl-2-pyrrolidone (NMP), and dimethyl sulphoxide (DMSO). Due to their limitation(s), it has not been used in technological applications [10]. To achieve our goal, researchers are dedicated and try to modify the process. Hence, solubility and electronic properties of polyaniline salt are changed. Generally, dopants (i.e., organic and inorganic acid) are used and affect the conductivity of polyaniline. Different ways such as bigger size dopants, polymeric acid dopants, and substituted form in conducting PANI polymeric backbone, researchers are put their intention to overcome the limitations of conducting polyaniline polymer. Purpose of using polymeric acid dopants is to enhance the flexibility as well as conductivity of the polyaniline. Some related reports on polymeric acids dopants are available and are poly (ethanesulfonic acid) [11], poly (acrylic acid) [12, 13], poly (styrene sulfonic acid) [14-18], poly (2-(acrylamido)-2-methyl-propanesulfonic acid) [19], and poly (amic acid) [20]. Polymeric acid dopants are used during in-situ conducting polymer synthesis by chemical or electrochemical polymerization via oxidative polymerization method [21, 22]. Properties of polymeric acid doped polyaniline are different from pristine polyaniline [11-20]. Because of the occurrence of protonic acid groups on polymer chains in the polymeric dopant, conformational hindrance is created by the flexible chain. It is believed that not all of the acidic dopants are capable of doping. Hence, non-uniform distribution may occur.

Presence at the nitrogen atom in the polyaniline chain is another type to assist the improvement of processability. Number of articles are available and are alkyl group-, alkyl ring- are attached to the N-atom of polyaniline. Usually, polymers are synthesised directly from monomers and are soluble in common organic solvents [23, 24]. Incorporation of the side groups into polyaniline backbone has changed its properties. Other than the Incorporation of the side groups, suitable substituted

monomer is used to prepare substituted conducting polymers, which is supported to improve its solubility in organic solvents [25, 26]. Another kind is to utilize functionalized acid, (*e.g.*, dodecyl benzenesulphonic acid or 10-camphorsulphonic acid) of polyaniline and to improve the processability [27].

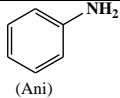
The work is undertaken to study XRD, FTIR (spectroscopic analysis), microstructural analysis, measurement of resistivity (room temperature and temperature dependent), and magnetoresistance at different temperature of PAA/PANI/MWCNT nanocomposite.

II. EXPERIMENTAL SECTIONS

CHEMICALS AND MATERIALS

In PAA/PANI/MWCNT nanocomposite synthesis, desired chemicals are used and indicated in **Table I**. Distilled water and Ice bath is used during the composite synthesis. Acrylic acid is procured from Merck India. Multi-wall carbon nanotube (MWCNT) is collected from Prof Basudam Adhikari.

Table I. Desired Chemicals are specified, which are used for synthesis of PAA/PANI/MWCNT nanocomposite

Chemicals	Chemical structure	MW (g/mol)	Density (g/mL)	Assay	Supplier
Ani	 (Ani)	3.13	1.02	99%	Merck India
APS	$(\text{NH}_4)_2\text{S}_2\text{O}_8$	228.20	---	98%	Merck India

SYNTHESIS OF PAA/PANI/MWCNT NANOCOMPOSITES

PAA/PANI/MWCNT nanocomposite is synthesised by chemical oxidation process [28]. It follows three steps;

Step -1

Acrylic acid is added to an appropriate amount of water with constant stirring at room temperature to form a colourless solution. Further, a requisite amount of aniline monomer is added to it to form aniline solution. 0.5 wt% multi-walled carbon nanotube (MWCNT) is put on the reaction mixture. Reaction mixture is cooled to 5 °C and continuously stirred for 1 h.

Step-2

In this step, APS solution (0.01 mol APS in 50 mL water) is prepared freshly. It is added slowly to the above aniline reaction mixture through a funnel with continuous stirring.

After 2 h, the solution product is brought to room temperature. It is stirred continuously (6 h) to complete the polymerization reaction. Color of the solution product changed from colourless to deep green. Product is kept overnight to complete the polymerization.

Step-3

The product mass is filtered with the help of Buckner funnel followed by washed with distilled water several times (pH ~7) till the filtrate is colourless. It is dried under vacuum at 60 °C for 6 h to get desired materials *i.e.*, PAA/PANI/MWCNT nanocomposite.

The Schematic synthesis process of PAA/PANI/MWCNT nanocomposite is shown in **Fig. 1**.

In comparison purpose, pure polyaniline is prepared in similar way

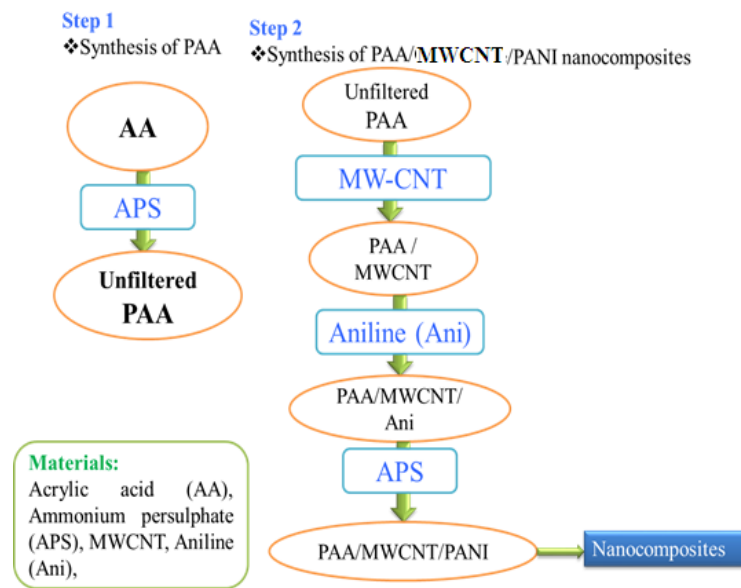


Fig. 1. Schematic diagram for preparation of PAA/PANI/MWCNT nanocomposite

PELLETS PREPARATION

Pellets are obtained from prepared pure PANI and PAA/PANI/MWCNT nanocomposite materials. It is prepared by compression molding using a pelletizer. Before using the palletiser, assembled items are cleaned first. 10 MPa pressure is applied and left for five minutes. After the pressure, the pallet is removed from the palletiser. Thicknesses and diameter of prepared pellets are estimated to be 1.10 mm and 15.76 mm (pure PANI-ES), 1.09 mm and 15.76 mm (PAA/PANI/MWCNT nanocomposite), respectively using slide callipers. Samples are ready for different tests.

TEST METHODS

Phillips PW-1710 advanced wide angle X-ray diffractometer and Phillips PW-1729 X-ray generator (Cu K α radiation, $\lambda = 0.154$ nm) are employed to perform **XRD** experiments. Generator is operated at 40 kV and 20 mA.

Thermo Nicolet Nexus 870 spectrophotometer is used to do the **FTIR** test. Spectra are recorded between 400-4000 cm^{-1} . Instrument settings are 50 scans at 4 cm^{-1} resolution and absorbance mode.

Carl Zeiss Supra 40 field emission scanning electron microscope machine is employed to study surface topography of prepared materials. For this test, operating voltage is to be maintained i.e. at 30 kV.

JEM-2100 HRTEM, JEOL, Japan is a **HRTEM** instrument. It is used to identify the internal structure and dispersion status of the prepared. For the HRTEM experiment, specimens of prepared materials are prepared by microtome technique (LEICA Microsystem, GmbH, A-1170). Then, It is transferred onto Cu TEM grids.

DC conductivity of the prepared pure PANI-ES and PAA/PANI/MWCNT nanocomposite is measured using linear four-probe technique. Contact is prepared using silver paste. A constant current from a current source (Keithley 2400 programmable current source) is allowed to pass through two terminal leads of the four probe. Also, voltage (V) across the other two leads is measured using a multimeter (Keithley 2000 digital multimeter). According to four point-probe method, first the resistivity (ρ) is calculated using the relation [29]

$$\rho = 2\pi S \left(\frac{V}{I} \right) \dots\dots\dots (1)$$

where S is the probe spacing in centimetres (cm), which is kept constant, (I) is the supplied current in milliamperes (mA) and the corresponding voltage (V) is measured in millivolts (mV). Conductivity (σ) is calculated by the relation mentioned below

$$\sigma = \frac{1}{\rho} \dots\dots\dots (2)$$

Also, temperature dependent resistivity is measured without magnetic field using a linear four-probe technique of prepared pure PANI-ES and PANI-ES/PAA/MWCNT nanocomposite. Lake shore 331 temperature controller is used. Such measurement is performed at various temperatures using a computer controlling measuring system. A constant current (I) from a current source (Keithley 220 programmable current source) is allowed to pass through two terminals leads of four probe and the voltage (V) across the other two leads is measured using a multimeter (2182 NANOVOLTMETER Keithley).

III. RESULTS AND DISCUSSION

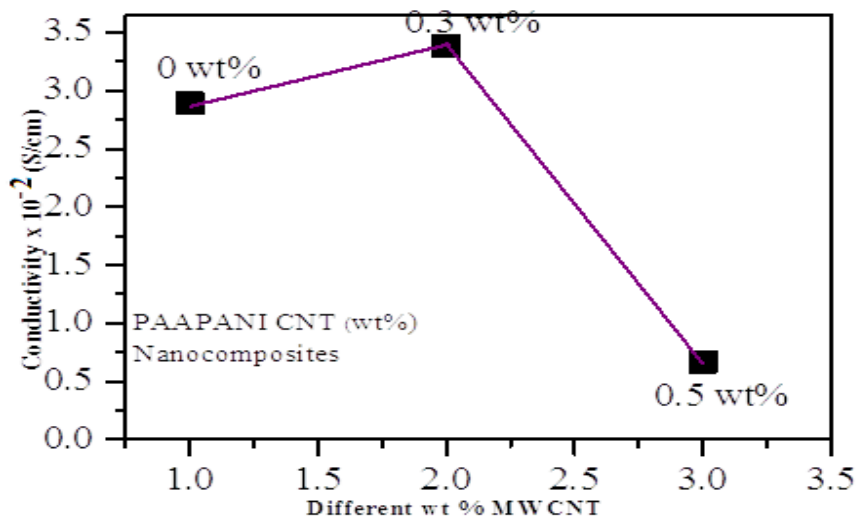


Fig. 2. DC-Conductivity indicated materials

Fig. 2 shows the DC conductivity value of PANI-ES and PAA/PANI-ES/MWCNT nanocomposites. DC conductivity is estimated using linear four-probe technique at room temperature. In this measurement, a pellet is used, which is prepared from PANI-ES and PAA/PANI-ES/MWCNT nanocomposites samples. It is obtained from applied current(s) and obtained voltage(s) and relation between them is reported. [29] DC conductivity value of PANI-ES is found to be 0.0275 S/cm. DC conductivity value of PAA/PANI-ES/MWCNT nanocomposites is found to be 0.0325 S/cm (for 0.3 wt%) and 0.005 S/cm (for 0.5 wt %), respectively. With the addition of different weight percentage multi-wall carbon nanotubes, the DC conductivity value of prepared PANI-ES is increased. Highest DC conductivity value is 0.0325 S/cm for PAA/PANI-ES/MWCNT nanocomposite (0.3 wt%). In PAA/PANI-ES/MWCNT nanocomposites (0.3 wt% and 0.5 wt% MWCNT), there is a difference in DC conductivity. This is due to the percolation effect of MWCNT [30].

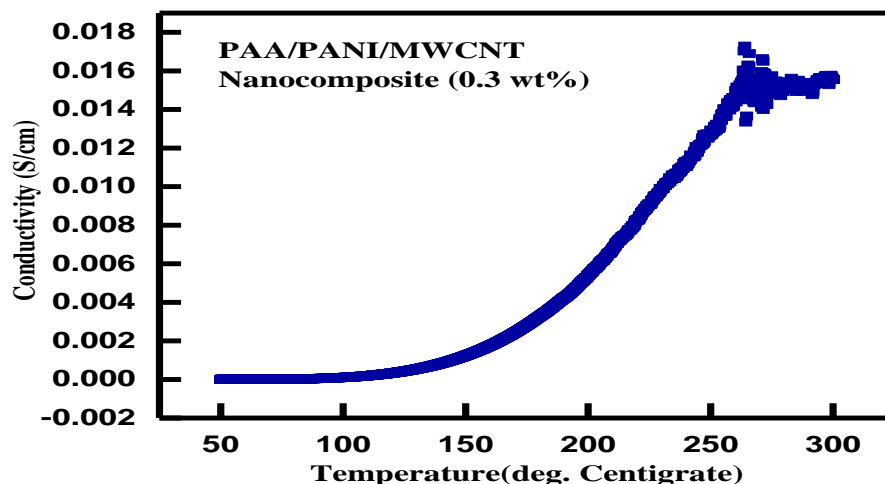


Fig. 3. Temperature Dependent conductivity of indicated materials

Temperature variation DC conductivity of PAA/PANI-ES/MWCNT nanocomposite (0.3 wt%) is shown in **Fig. 3**. **Fig. 3** displayed increase of conductivity with increase in temperature. Temperature ranges from 50 to 300 K. This type of activity is similar fashion to inorganic semiconducting material [31]. Hence, PAA/PANI-ES/MWCNT nanocomposite is called organic semiconductor.

Fig. 4A, 4B, and 4C show FESEM images (with magnification 20 kX) of polyacrylic acid (PAA), PANI-ES, and PAA/PANI-ES/MWCNT (0.3 wt%) nanocomposite. **Fig. 4A** shows irregular crystal like morphology. FESEM image of PANI-ES possess tangled fiber like morphology [28, 29]. **Fig. 4B** indicates FESEM image of PAA/PANI-ES/MWCNT (0.3 wt%) nanocomposite with lower magnification. From **Fig. 4B and 4C**, it is clear that surface morphology of compacted crystal and crystals are connected to each other. This is possible that dopant (Acrylic acid), MWCNT, and PAA are contributed in closing polyaniline Chains. Henceforth, the nanocomposite(s) become more ordered state. Mostly, ordered state materials displayed higher electrical conductivity. Diameters of these compacted tangled fibers are indicated in nano regimes and it is providing higher surface area. Predominantly, gas sensing application, it may be helpful to diffuse more gas molecules and show better response.

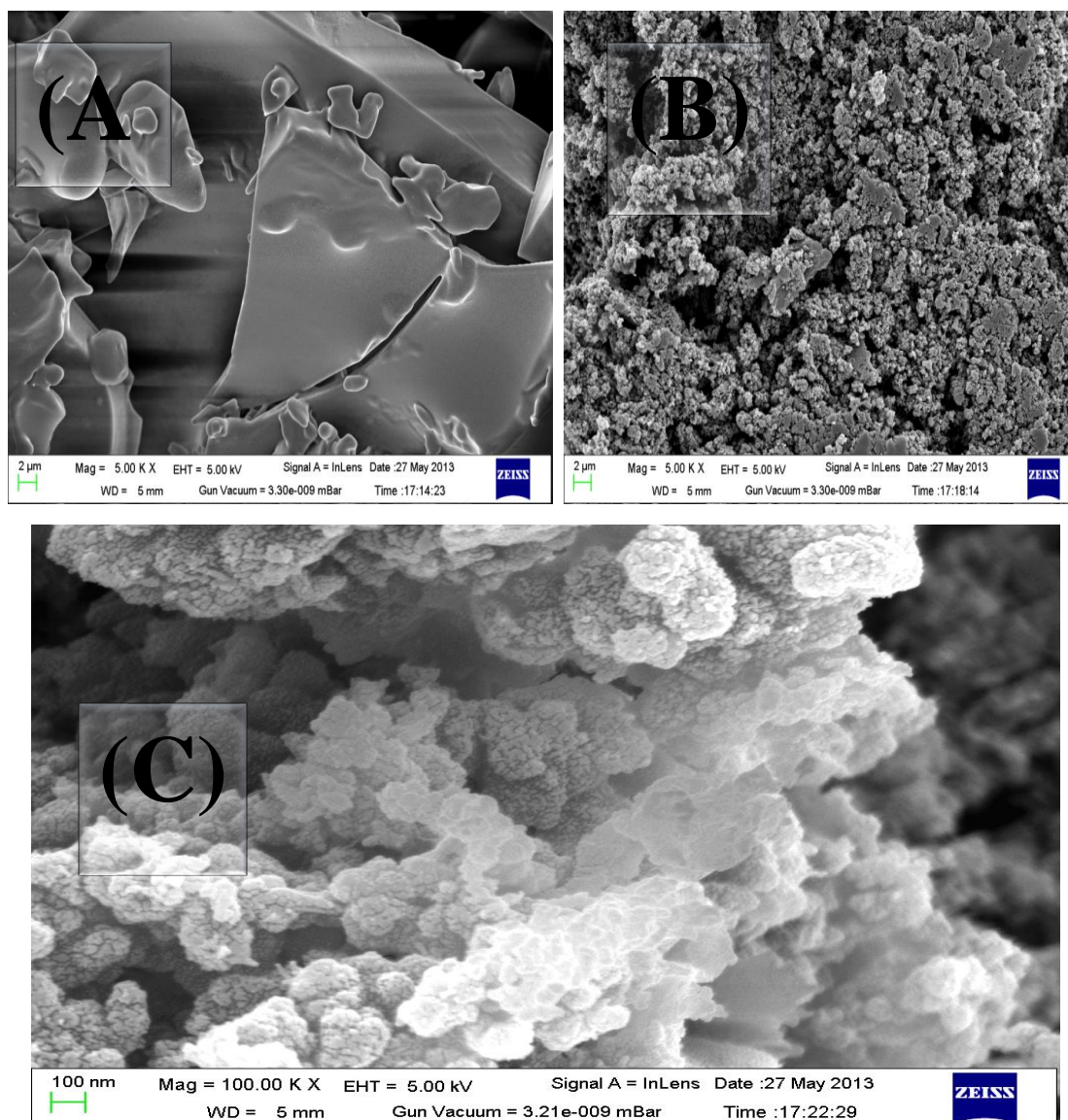


Fig. 4. FESEM image of PAA (A), low magnification PAA/PANI –ES (B) and High magnification PAA/PANI-ES (C)

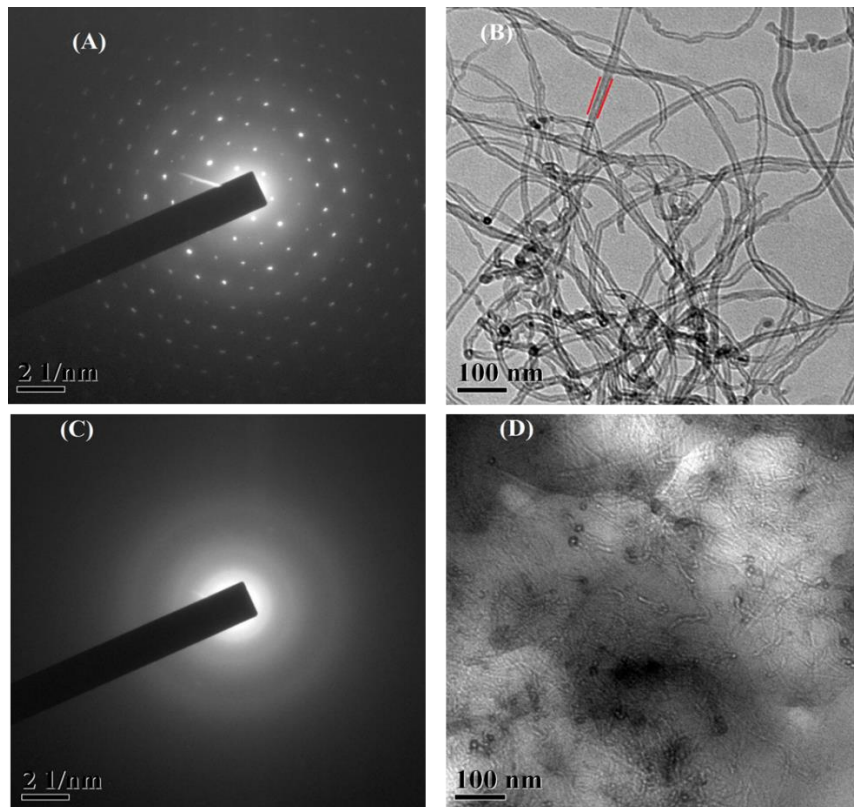


Fig. 5 SAD pattern of MWCNT (A), HRTEM image of MWCNT (B), SAD pattern of PAA/PANI/ MWCNT nanocomposite (C), and HRTEM image of PAA/PANI/ MWCNT nanocomposite (D)

SAD pattern and HRTEM image of MWCNT and PAA/PANI/MWCNT nanocomposite is indicated in Fig. 5. Fig. 5A shows SAD pattern of multi-wall carbon nanotube. Light spots are ring structured. It signifies crystalline in nature. Fig. 5B displays image of Multi-wall carbon nanotube. It looks-like tangled fibers having diameter 20-40 nm. Fig. 5C shows SAD pattern of PAA/PANI/MWCNT nanocomposite. There are no light-spots in ring structured. It signifies amorphous in nature. Fig. 5D show high resolution transmission electron microscopy (HRTEM) image of PAA/PANI/MWCNT nanocomposite. In the nanocomposite, there is disorder tangled MWCNT are found in PANI-ES matrix. This result showed a well dispersion in PANI-ES matrix.

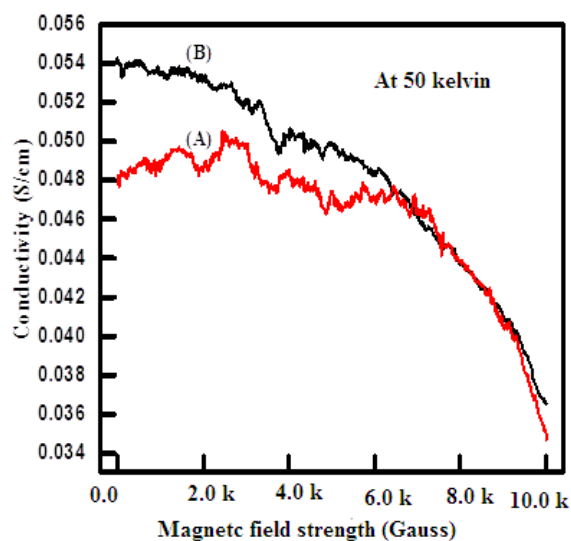


Fig. 6. Temperature dependent DC conductivity at of PAA/PANI/ MWCNT nanocomposite at 50 Kelvin with magnetic field (A) and without magnetic field (B)

In PAA/PANI-ES/MWCNT nanocomposite (0.3 wt%), Magnetic field strength variation of DC conductivity (at 50 kelvins) is shown in **Fig. 6**. **Fig. 6** indicates DC conductivity decreases with increase in magnetic field strength, particularly at 50 kelvins. Nature of dependency is parabolic.

IV. CONCLUSIONS

PAA/PANI/ MWCNT nanocomposite is prepared by chemical-oxidation method. PAA/PANI-ES/MWCNT nanocomposite (0.3 wt%) exhibited higher DC electrical conductivity than other wt% of PAA/PANI-ES/MWCNT nanocomposite and PANI-ES polymer. Also, DC electrical conductivity describes that DC conductivity is a function of temperature. FESEM image of PAA/PANI-ES/MWCNT nanocomposite indicates interconnected crystals. The SAD pattern of MWCNT shows crystalline, whereas PAA/PANI-ES/MWCNT nanocomposite displays amorphous nature. PAA/PANI-ES/MWCNT nanocomposite HRTEM image indicates well dispersion of MWCNT nanomaterials in polymer matrix. Magnetic field dependent DC conductivity (at 50 kelvins) shows parabolic nature.

ACKNOWLEDGMENTS

I acknowledge Prof Basudam Adhikari, Materials Science Centre for supporting the lab facility. I acknowledge CRF, Indian Institute of Technology, Kharagpur for supporting experimental works.

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