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Research Article

Polyaniline Composites with Nanodiamond, Carbon nanotube and Silver Nanoparticle: Preparation and Properties

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Abstract

Nanodiamond (ND), functionalized multi-walled carbon nanotube (MWCNT), and silver nanoparticle were reinforced in polyaniline (PANI) matrix using simple emulsion polymerization method. In this way, different nanocomposites were obtained including polyaniline/nanodiamond/non-functional nanotube (PANI/ND/MWCNT), polyaniline/ nanodiamond/functional nanotube (PANI/ND/MWCNT-COOH), and polyaniline/nanodiamond/functional nanotube/silver nanoparticle (PANI/ND/MWCNT-COOH/Ag 1 & 2). Fourier transform infrared spectroscopey (FTIR) and X-ray diffraction (XRD) were used to study the composite structure and presence of silver nanoparticle. Morphology study (scanning electron microscopy) of the PANI/ND/MWCNT-COOH/Ag exhibited uniform polymerization of aniline monomer over the surface of well-dispersed MWCNT-COOH/ND and silver nanoparticles. The recompenses of Ag nanoparticle comprise the improvement in electrical and thermal properties without deteriorating polyaniline structure. The electrical conductivity of PANI/ND/MWCNT-COOH/Ag 2 nanocomposite with greater Ag nanoparticle content was 39 % higher than the same weight percent nanocomposite without Ag. The PANI/ND/MWCNT-COOH/Ag 1 nanocomposite also showed continuous increase in electrical conductivity over a range of temperature. Thermal stability was also noticeably increased in PANI/ND/MWCNT-COOH/Ag 2

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1. Introduction

Nanodiamond (ND) particles have been widely investigated due to their surface chemistry that allows a variety of functionalization and biocompatibility [1, 2]. In spite of striking features of ND particles, they have tendency to contaminate and aggregate that might limit their convenient applications [3]. Successful employment of ND requires ample dispersion and besieged specificity for technical applications. The loading of ND in a conducting polymeric matrix boost the properties for various relevancies. Conductive polymers have been employed as sensors and actuators, antistatic coatings, electrically conducting adhesives, and electromagnetic interference shielding materials for electronic devices [4, 5]. The common conducting polymer is polyaniline (PANI). It has been widely studied due to unique electrochemical, chemical, and physical properties in addition to electrical conductivity and environmental stability [6, 7]. Moreover, PANI has significant tunable chemical structure [8, 9]. However, PANI has disadvantage of poor lasting thermal stability [10]. Among various conducting polymers, PANI has been successfully used to synthesize polymer/carbon nanotube composites because of good processability, environmental stability, and conductivity through protonation and charge-transfer doping [11]. Carbon nanotube was discovered by Iijima [12]. They have applications in several new classes of advanced materials due to inimitable structural features, thermal properties, electrical conductivity, and mechanical properties (Young’s modulus, stiffness, flexibility). These properties are due to high aspect ratio and high degree of association of carbon nanotubes. However, pure CNT are difficult to dissolve or disperse in organic solvents or polymers so cannot be processed. The most probable reason is their chemical inert nature and strong π–π interaction. Consequently, the side-walls of CNT are chemically modified to develop better dispersion or solubility in various solvents and polymer matrices [13, 14]. Several studies have been reported to fabricate multi-walled carbon nanotube (MWCNT)-based composites having fine thermal stability, mechanical strength, and electric conductivity [15]. The combination of PANI and MWCNT might generate outstanding composite material for electronic devices with morphological modification or electronic interaction between these two components [16]. In recent times, metal nanoparticles have been included in polymer/CNT composites to improve their properties [17]. In this regard, Ag nanoparticles (Ag-NPs) have gained significant attention due to potential applications in advanced materials [18, 19]. In this study, silver nanoparticles were incorporated into the *in-situ* polymerized PANI composite with nanodiamond and functional nanotubes. A straightforward approach was utilized to form the hybrids of functionalized MWCNT and ND with polyaniline through emulsion polymerization. In addition, the silver nitrate solution was used to form Ag nanoparticle through precipitation route to avoid any agglomeration and obtain uniform particle dispersion. The composite was reinforced with silver nanoparticle through the same emulsion polymerization procedure. The structure, morphology, thermal and electrical properties of composites was characterized using suitable techniques.

2. Experimental

2.1. Materials

The MWCNT (purity of 95% and a diameter of 10-15 nm, supplied by Hanwha Nanotech, Korea. Diamond nanopowder (<10 nm particle size, ≥97%), aniline (99.5%), ammonium persulfate (98%), silver nitrate (≥99.0%), cetrimonium bromide (CTAB, 90 %), and hydrochloric acid (37%) were purchased from Aldrich (USA).

2.2. Instrumentation

The structure of nanocomposites was analyzed using Fourier transform infrared (FTIR) Spectrometer, Model No. FTSW 300 MX, manufactured by BIO-RAD, California, USA (4 cm^{-1} resolution). The FTIR spectra were recorded in the wavenumber range of 4000-400 cm^{-1}. The SEM images were obtained by Scanning Electron Microscope S-4700 (Japan Hitachi Co. Ltd.). Electrical conductivity of the nancomposites was measured using Zetasizer Nano (Malvern Instruments Ltd., Malvern, UK). Thermal stability was determined by NETZSCH thermo gravimetric analyzer (TGA), model no. TG 209 F3 (California, USA), using 1-5 mg of the sample in Al_2O_3 crucible from 25 to 800 °C at a heating rate of 10 ℃/min under nitrogen atmosphere with a gas flow rate of 30 mL/min. X-ray diffraction patterns were obtained at room temperature on X-ray diffractometer (3040/60 X'pert PRO) using Ni-filtered Cu Kα radiation (40 kV, 30 mA).

2.3. Preparation of silver nanoparticle

0.01 M $AgNO_3$ solution was used as a metal salt precursor and 0.01 M CTAB was used as a stabilizing agent. The CTAB solution was added dropwise to the salt solution. The appearance of color was the indication silver nanoparticles. The nanoparticles were filtered and dried at 60 for 12 h [20].

2.4. Acid treatment of MWCNT (MWCNT-COOH)

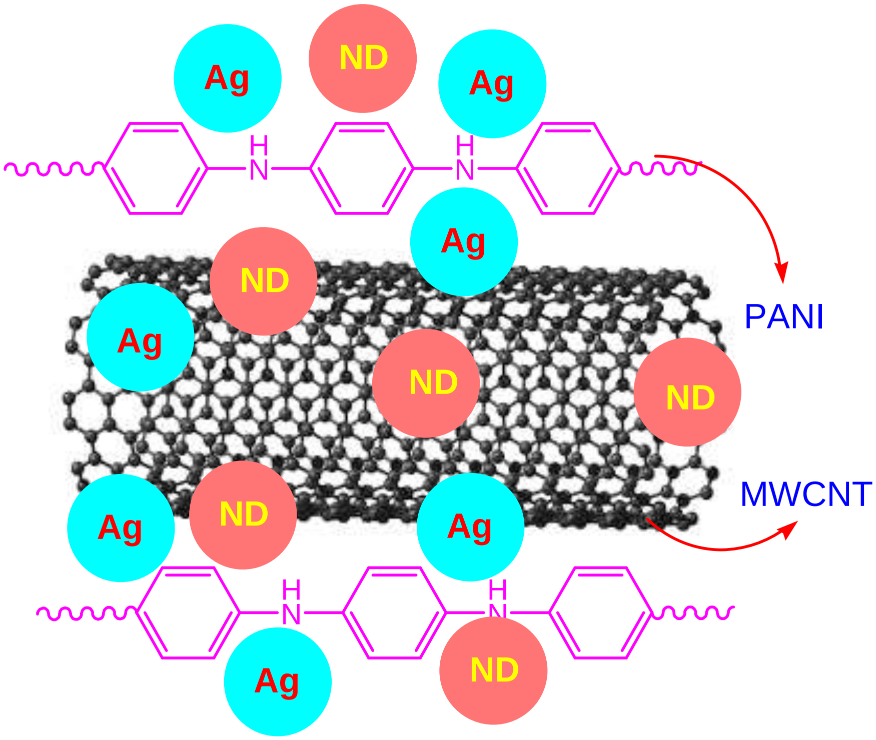
Typically, 1.0 g of raw MWCNTs was added to 100 mL of H_2SO_4/HNO_3 (3:1, v/v) and ultra-sonicated for 0.5 h. Then the solution was refluxed with stirring at 70 ℃ for 6 h. After cooling to room temperature, the mixture was filtered and washed several times with distilled water until a pH ~7.0. The filtered solid was dried under vacuum for 12 h at 60 ℃ [16]. FTIR (KBr, cm^{-1}): 3402-3324 (O–H stretching), 1719-1630 (C=O carboxylic acid), 1460-1380 (O–H bending), and 1156-1020 (C–O stretching).

2.5. Synthesis of PANI/ND/MWCNT-COOH composite

The monomer aniline to ND and MWCNT-COOH ratio was kept at 3:1:1. The mixture was added in 1 M HCl (100 mL) solution and cooled to 4 ℃ in an ice bath. The oxidant ammonium peroxydisulfate [$(NH_4)_2S_2O_8$)] (0.025 M) was dissolved in 200 mL of 1 M HCl solution. The ammonium peroxydisulfate solution was added slowly into the aniline/nanodiamond/nanotube mixture, and the reaction was continued for 12 h. The dark green precipitate of PANI/ND/MWCNT-COOH composite was filtered, and washed using deionized water/methanol to remove low molecular weight PANI oligomers. The precipitate was dried at 80 ℃. The obtained emeraldine salt form of composite was treated with aqueous ammonia for 24 h. The undoped composite was washed by using distilled water and acetone and dried at 80 ℃ for 12 h. PANI/ND/MWCNT-COOH was obtained as dark blue powder i.e. emeraldine base form of the conducting polymer-based composite [21]. FTIR (KBr, cm^{-1}): 3440 (N–H stretch), 3020 (aromatic C−H stretch), 1650, 1591 (C=C quinoid and benzenoid rings), 1456 (C−N stretch).

2.6. Synthesis of PANI/ND/MWCNT-COOH/Ag composite

The procedure mentioned in Section 2.3 was also adopted for the preparation of PANI/ND/MWCNT-COOH/Ag composite. The difference was that the monomer aniline to ND**,** MWCNT-COOH, and silver nanoparticle ratio was kept at 3:1:1:1 and 3:1:1:2. The product was filtered and rinsed several times with distilled water. The black powder was dried under vacuum at 60 ℃ for 12 h (Scheme 1). FTIR (KBr, cm^{-1}) (Fig. 1): 3444 (N–H stretch), 3070 (aromatic C−H stretch), 1666, 1598 (C=C quinoid and benzenoid rings), 1036 (C−N……Ag electronic-like band).



Scheme 1. Representation of PANI/ND/MWCNT-COOH/Ag nanocomposite.

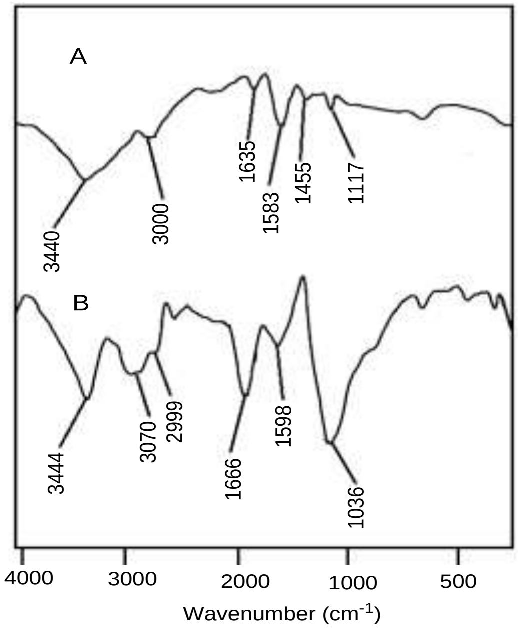


Fig. 1 FTIR spectra of (A) PANI; and (B) PANI/ND/MWCNT-COOH/Ag 1.

3. Results and discussion

3.1. FTIR analysis

The FTIR spectra were used to corroborate the presence of the polymer and nanofillers in composite before and after the addition of the Ag nanoparticle. Fig. 1A shows the FTIR spectrum of PANI. For the pure PANI, peak at 3440 cm^{-1} was characteristic of N–H stretching vibration while C–H appeared at 3000 cm^{-1}. The peaks at 1635 and 1583 cm^{-1} were characteristic of the C=C stretching of the quinoid and benzenoid ring vibrations. This indicated the oxidation state of polyaniline (emeraldine salt). The peaks at 1455 and 1117 cm^{-1} were assigned to the stretching of C–N bonds of aromatic amine and electronic-like band respectively [22]. This is often considered as a measure of delocalization of electrons and so the characteristic peak of PANI conductivity. For the acid treated MWCNT, the absorption peaks at 1719-1630 cm^{-1}, 1460-1380 cm^{-1}, and 1156-1020 cm^{-1} correspond to carboxylic acid group C=O stretching, O–H bending and C–O stretching, respectively. The spectrum of PANI/ND/MWCNT-COOH/Ag 1 is displayed in Fig. 1B. The spectrum was somewhat identical to pure PANI, indicating the successful polymerization on the surface of the ND/MWCNT [23]. For the composite, interaction between polyaniline and silver nanoparticle was confirmed by an absorption peak at 1036 cm^{-1}. The other bands were nearly identical to pure polyaniline. The results indicated that the presence of the silver nanoparticle on the polyaniline surface did not spoil the composite structure.

3.2. Morphology study

Scanning electron microscopy (SEM) images of the composites (PANI/ND/MWCNT, PANI/ND/MWCNT-COOH/Ag 1 and PANI/ND/MWCNT-COOH/Ag 2) prior to and after integration of Ag nanoparticles are given in Fig. 2A-C. The PANI/ND/MWCNT composite exhibited a typical core-shell structure, where the MWCNT acted as core and were dispersed into the PANI matrix (Fig. 2A). The aniline monomer was not uniformly polymerized on the surface of non-functional MWCNT and formed bulk phase. The PANI/ND/MWCNT-COOH/Ag 1 composite showed relatively dispersed morphology. The ND and PANI formed tubular shell of MWCNT-COOH and Ag nanoparticle composite (Fig. 2B). Furthermore, the tubes were almost uniform in diameter. Compared to the average diameter in the composite (PANI/ND/MWCNT-COOH/Ag 1), the diameters in tubular composite after adding greater Ag nanoparticle content was increased (Fig. 2C). These results corroborated better dispersion of Ag nanoparticles in the composite (PANI/ND/MWCNT-COOH/Ag 2). Furthermore, the tubes were more uniform after adding greater Ag nanoparticle content. This confirmed the uniform polymerization of aniline monomer on the surface of well-dispersed MWCNT-COOH/ND and the silver nanoparticles. The occurrence of Ag nanoparticle in the PANI/ND/MWCNT-COOH/Ag 1 composite was analyzed using XRD (Fig. 3). The Fig. 3B shows the crystalline structure of composite due to the presence of Ag nanoparticle.

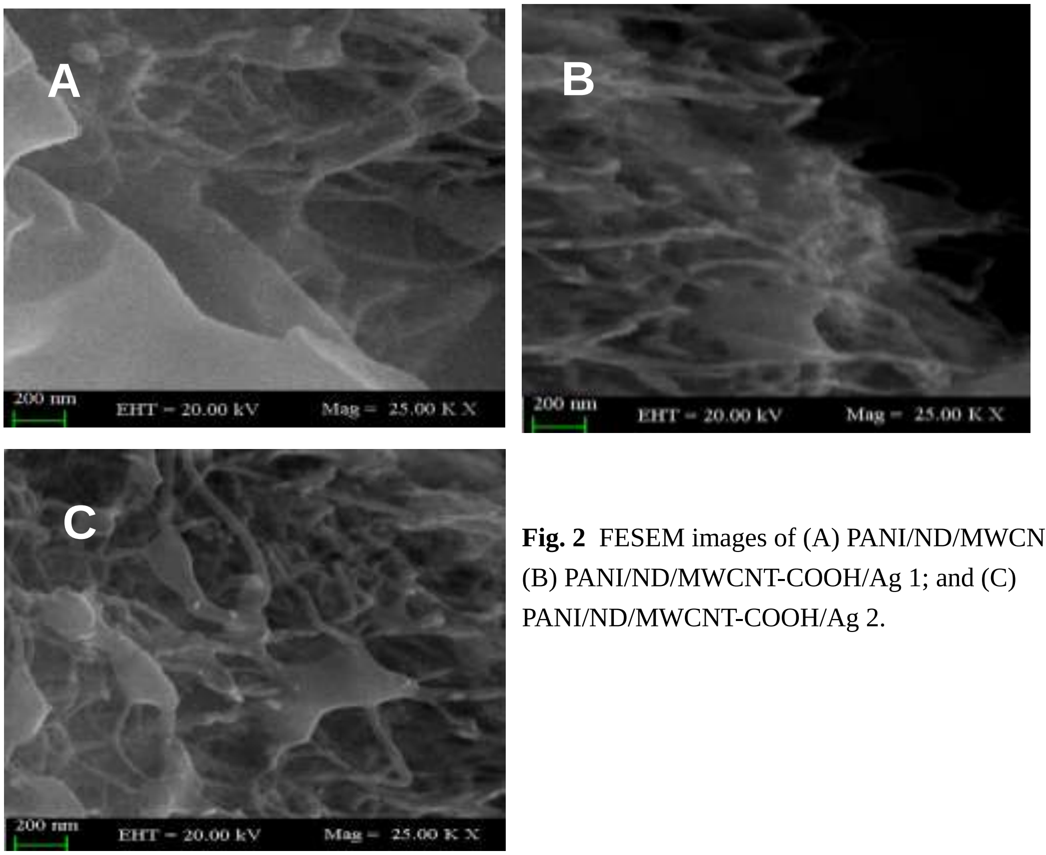


Fig. 2 FESEM images of (A) PANI/ND/MWCNT; (B) PANI/ND/MWCNT-COOH/Ag 1; and (C) PANI/ND/MWCNT-COOH/Ag 2.

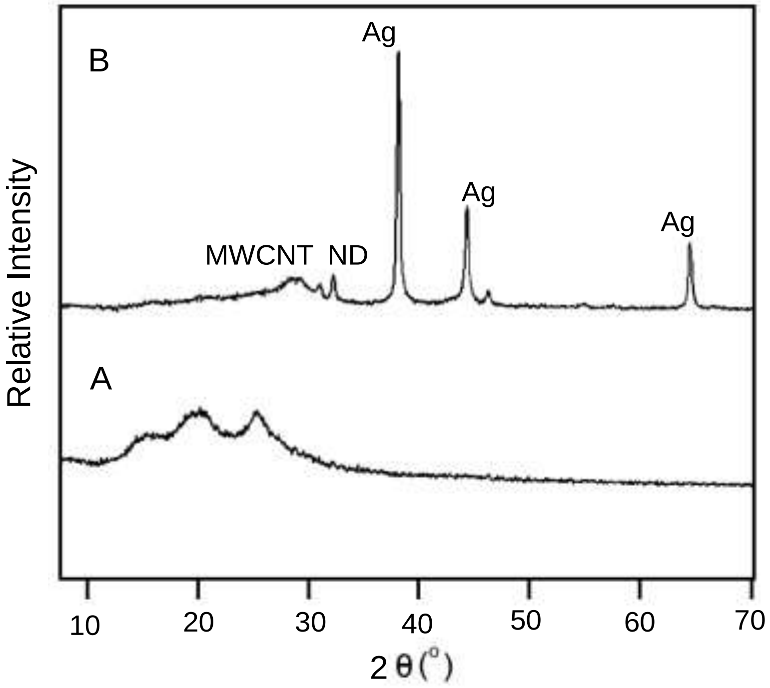


Fig. 3 XRD patterns of (A) pure PANI; and (B) PANI/ND/MWCNT-COOH/Ag 1.

3.3. Thermal analysis

The thermal behavior of hybrid material was studied using thermogravimetric analysis. The thermograms in Fig. 4A-C show an unambiguous comparison between the thermal stability of PANI/ND/MWCNT-COOH, PANI/ND/MWCNT-COOH/Ag 1, and PANI/ND/MWCNT-COOH/Ag 2 (Table 1). The typical three-step weight-loss was observed for PANI/ND/MWCNT-COOH. The water molecules were lost from the composite structure in the first step between 10-200 ℃ (5 %). The second weight loss occurred in the range of 200-450 ℃ (15 %) due to the loss of dopant and short chain molecules. The third weight loss occurred above 450 ℃ (31 %) because of the degradation of main composite backbone. The TGA measurement of PANI/ND/MWCNT-COOH/Ag 1 showed improved heat constancy. The thermal stability of the nanocomposite was enhanced through the incorporation of silver nanoparticle in the polyaniline matrix. The thermal stability increased because of the reduced mobility of PANI chains in the nanocomposite. In PANI/ND/MWCNT-COOH/Ag 2, the thermal stability was further increased and thermogram was shifted towards right. Accordingly, the degradation process was slowed down due to the presence of greater nanoparticle content. Hence the decomposition occurred at higher temperature [24]. The superior thermal stability of the PANI/ND/MWCNT-COOH/Ag 2 nanocomposite was also attributed to the physical interaction between the Ag nanoparticle and the PANI chains.

Table 1. % Weight-loss data of PANI and nanocomposite at various temperatures.

Sample	First weight loss (10-200 ℃)	Second weight loss (200-450 ℃)	Third weight loss (above 450-550 ℃)
PANI	7	48	65
PANI/ND/MWCNT	6	25	42
PANI/ND/MWCNT-COOH	5	15	31
PANI/ND/MWCNT-COOH/Ag 1	3	12	30
PANI/ND/MWCNT-COOH/Ag 2	2	10	28

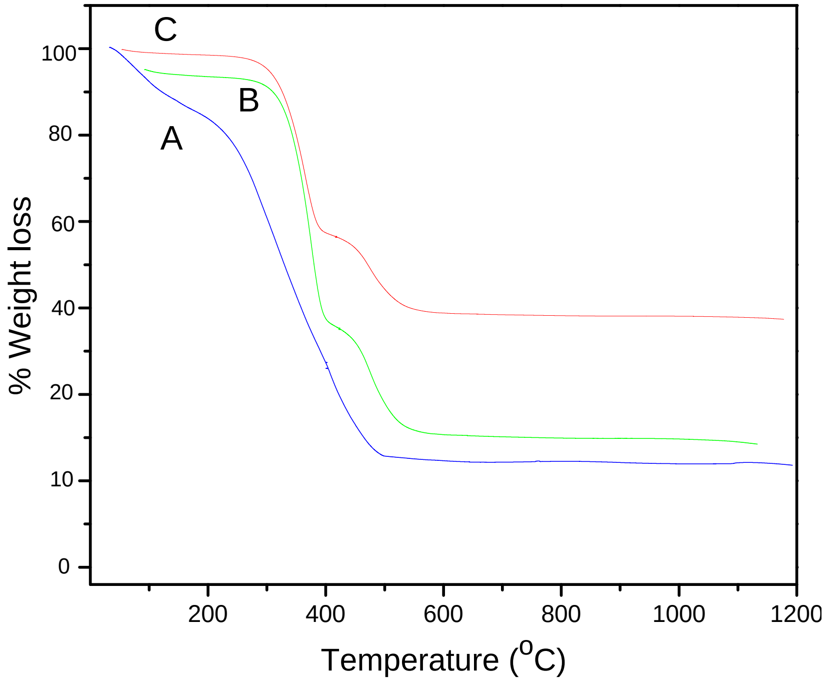


Fig. 4 TGA thermograms of (A) PANI/ND/MWCNT-COOH; (B) PANI/ND/MWCNT-COOH/Ag 1; and (C) PANI/ND/MWCNT-COOH/Ag 2.

3.4. Electrical conductivity measurement

The electrical conductivity values of the nanocomposite are summarized in Table 2. The incorporation of Ag nanoparticles into PANI/ND/MWCNT-COOH composite increased the conductivity value of the composites. The electrical conductivity of the PANI/ND/MWCNT composite with non-functional nanotube was 0.54 Scm^{-1}. Addition of functional nanotube raised the conductivity to 0.81 in PANI/ND/MWCNT-COOH. After the incorporation of Ag nanoparticle at the same weight percent of the composite (PANI/ND/MWCNT-COOH/Ag1), the electrical conductivity was increased to 1.98 Scm^{-1}. By increasing the silver nanoparticle content, conductivity was further enhanced to 2.09 Scm^{-1}. The incorporation of silver nanoparticles on the surface of the nanodiamond/carbon nanotube coated polyaniline greatly affected the electrical conductivity. The reason was the high electrical conductivity of the silver nanoparticles [25]. Moreover, the crystalline structure of the composite, due to increased interaction between the Ag nanoparticles and PANI, also played important role in increasing the electrical conductivity. Besides the effect of temperature on the conductivity of PANI/ND/MWCNT-COOH and PANI/ND/MWCNT-COOH/Ag 1 nanocomposite were studied. The PANI/ND/MWCNT-COOH/Ag 1 showed continuous increase in electrical conductivity over a range of temperature (Fig. 5).

Table 2 Electrical conductivity of PANI and nanocomposites.

Sample	**Conductivity (Scm^{-1})**
PANI	0.07
PANI/ND/MWCNT	0.54
PANI/ND/MWCNT-COOH	0.81
PANI/ND/MWCNT-COOH/Ag 1	1.98
PANI/ND/MWCNT-COOH/Ag 2	2.09

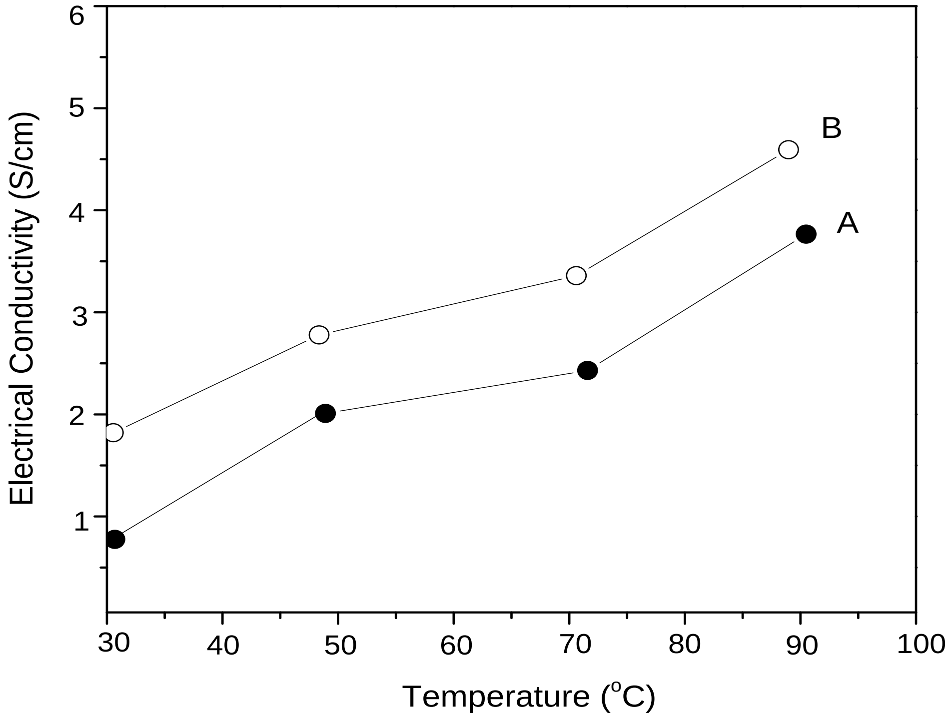


Fig. 5 Electrical conductivity of nanocomposites (A) PANI/ND/MWCNT-COOH; and (B) PANI/ND/MWCNT-COOH/Ag 1.

4. Conclusions

The polyaniline incorporated nanodiamond, functionalized carbon nanotube and silver nanoparticles were successfully synthesized through emulsion polymerization. The covalent functionalization of MWCNT developed better compatibility with polyaniline and ND. The FTIR studies established the carbon nanotube functionalization, PANI polymerization and incorporation of silver nanoparticle in polyaniline structure. Additionally, the spectral characterization corroborated the interaction between polyaniline and Ag nanoparticle. The presence of Ag nanoparticle was confirmed using XRD analysis. The incorporation of Ag-nanoparticle significantly changed the thermal and electrical properties of the composites. The four-point probe investigation exposed that the electrical conductivity of the composite with Ag nanoparticle (PANI/ND/MWCNT-COOH/Ag 1 and PANI/ND/MWCNT-COOH/Ag 1) was increased considerably relative to pure PANI and non-functional composite.

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