New Strategy for Chemically Attachment of Imine Group on Multi-Walled Carbon Nanotubes Surfaces: Synthesis, Characterization and Study of DC Electrical Conductivity

Omar Al-Shuja'a[1*], Abeer Obeid[2], Yousuf El-Shekeil[3], Mohamed Hashim[4], Zinab Al-Washali[1]

[1]Department of Chemistry, Faculty of Applied Science, Thamar University, Thamar, Yemen
[2]Department of Chemistry, Faculty of Science, Sana'a University, Sana'a, Yemen
[3]Mechanical Engineering Department, College of Engineering, Taibah University, Madina, KSA
[4]Department of Environmental Pollution and Pesticides Analysis, Faculty of Agriculture, Sana'a University, Sana'a, Yemen
Email: *omrshugaa@yahoo.com

Abstract

This paper used a new approach of preparing poly-composites by covalent linkage between the MWCNT's by imine group. The Poly (Imine)/MWCNT Composite was synthesized by the solution blending method from reacted amino multi-walled carbon nanotubes (MWCNT-NH$_2$) with Terephthalaldehyde (TPAL). The obtained poly-composite was characterized by FT-IR, UV-Vis, XRD, TEM, SEM, TGA, DSC and DC electrical conductivity. The formation of Poly (Imine)/MWCNT composite was confirmed. The DC electrical conductivity of poly-composites was within the range 2.3×10^{-4} - 5.3×10^{-4} S/cm due to the interaction between the nanotubes.

Keywords

Amino Multi-Walled Carbon Nanotubes (MWCNT-NH$_2$), Polymer Nanocomposites, Functionalization, Solution Blending, Imine, Terephthalaldehyde, FTIR, SEM, TEM, XRD, UV, DSC, TGA and DC Electrical Conductivity

1. Introduction

Nanotechnology opens up a new perspective to shape new generations of composites structures. Nanoparticles possess unique mechanical and physical properties, which make them one of the most promising fillers to develop future compo-

sites materials [1]. Further, nanotechnology intends to reveal the size-related effects of nanoparticles to design innovative products with novel properties and functions [2] [3] [4].

The applications to which nanotechnologies can be applied cover materials manufacturing, nano-electronics and computer technology, medicine and health, aeronautics and space exploration, environment devices and information storage, biotechnology and polymer technology [5]-[11].

CNTs can be conductors like metals or semiconductors: they can transport electrons over long distances without significant interruption that makes them more effective than copper [12] [13]. This unique combination of mechanical and electrical properties makes CNTs an ideal reinforcing agent for many materials and products including polymers [14] [15]. There are many studies in the literature about composite polymers containing carbon nanotubes either with amine functional groups [16] [17] [18] [19]. However, there are no studies performed in detail with the aim of comparing the effect of carbon nanotubes with imine functional groups on poly-composites.

In this paper, a comparative analysis between the amino multi-walled carbon nanotubes (MWCNT-NH$_2$) and the Poly (Imine)/MWCNT composite was performed, using comprehensive characterization techniques such as Ultraviolet-visible spectroscopy (UV-Vis), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), Transmission Electron Microscopy (TEM), scanning electron microscopy (SEM) and DC electrical conductivity. Thus, a new approach of poly-composites by covalent linkage between the MWCNT's by imine group was synthesized.

2. Experimental

2.1. Materials

Amino Multi-walled carbon nanotubes (MWCNT-NH$_2$) were purchased from Timesnano (Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences) China. The diameter and length of MWCNT-NH$_2$ ranged between 8 - 15 nm and 50 μm respectively. Purity was over >95% and the amine group coverage was over the nanotube surface of (0.45 wt%). Terephthalaldehyde (TPAL), *N,N*-Dimethylformamide (DMF 99%), and Tetrahydrofuran (THF 99.9%) were purchased from Sigma Aldrich, and used as received without any further treatment.

2.2. Instrumentation

The FTIR spectra were recorded using the KBr disc technique on a JASCO 410 FTIR Spectrophotometer. The melting points were measured with an electro-thermal melting point apparatus. The thermal analyses (TGA and DSC) were carried out on a Mettler Toledo TGA/SDTA851e analyzer, and Mettler Toledo DSC823e analyzer, respectively, at 23°C to 1000°C, under 20 ml nitrogen per minute and a heating rate of 10°C per minute. UV-vis absorption spectra were

measured using a Specord 200, Analytik Jana, Germany in DMF (~10 - 4 mol/dm^3). The X-Ray diffraction was carried out on a BrukerAxs Da Advance, Germany. Electrical conductivity measurements were taken on a Keithley Picoammeter/Voltage Source Model 6487 using a double probe locally fabricated conductivity bridge cell. The Scanning Electron Microscope (SEM) was carried out on a (SEM HITACHI S-3400N) instrument. The Transmission Electron Microscope (TEM) was carried out on a Phillips CM-12, USA; and the samples were prepared by Leica ultracut UTC ultramicrotome (JEOL, Japan) with an accelerating voltage of 100 kV.

2.3. Preparation of Poly (Imine)/MWCNT Composites

0.3 g sample of MWCNT-NH$_2$ was dispersed in 15 ml THF and 0.1 g of TPAL was dissolved in 10 ml DMF and was added to the MWCNT-NH$_2$ dispersion in THF. The mixture was then stirred for 24 hours at 90°C under reflux. After cooling to room temperature, the mixture was vacuum-filtered through a 0.22 μm membrane and was thoroughly washed several times with THF. The filtered solid was then dried overnight in a vacuum oven at 90°C [20] [21].

## 3. Results and Discussion

3.1. Characterization

Poly (Imine)/MWCNT composite was prepared by the reaction of MWCNT-NH$_2$ with TPAL in refluxing solvent (DMF) to yield poly-composites products. The method employed to prepare the Poly (Imine)/MWCNT composite was solution blending. The scheme of synthesis of the Poly (Imine)/MWCNT composite is shown in Figure 1. The physical properties were studied of MWCNT-NH$_2$ and Poly (Imine)/MWCNT composite. The melting point >350°C and the color were black for both compounds, and the percentage yield was 87%. The solubility for MWCNT-NH$_2$ and Poly (Imine)/MWCNT composite was also studied, showing good solubility mainly in Dimethyl sulfoxide (DMSO) and partially soluble in Dimethyl formamide (DMF) and ethanol 99.99% (EtOH).

3.2. Fourier Transform Infrared Spectroscopy (FTIR)

In Figure 2, the IR spectra of MWCNT-NH$_2$ show the peak at 3448 cm^{-1}, which can be assigned to the NH$_2$ stretch of the amine group. While C-N bond stretch vibrations appear at 1050 cm^{-1}, the peaks at 1578 - 1654 cm^{-1} can be associated
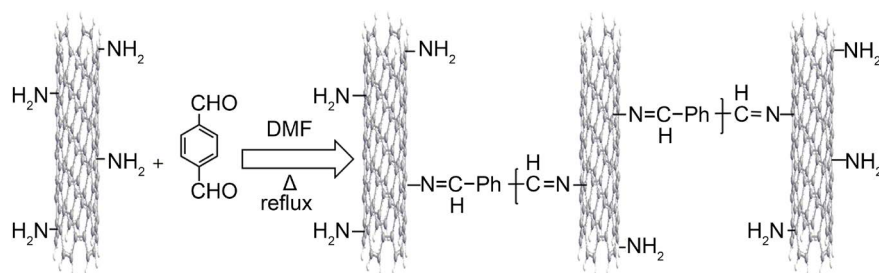
Figure 1. Synthesis of Poly (Imine)/MWCNT composite.
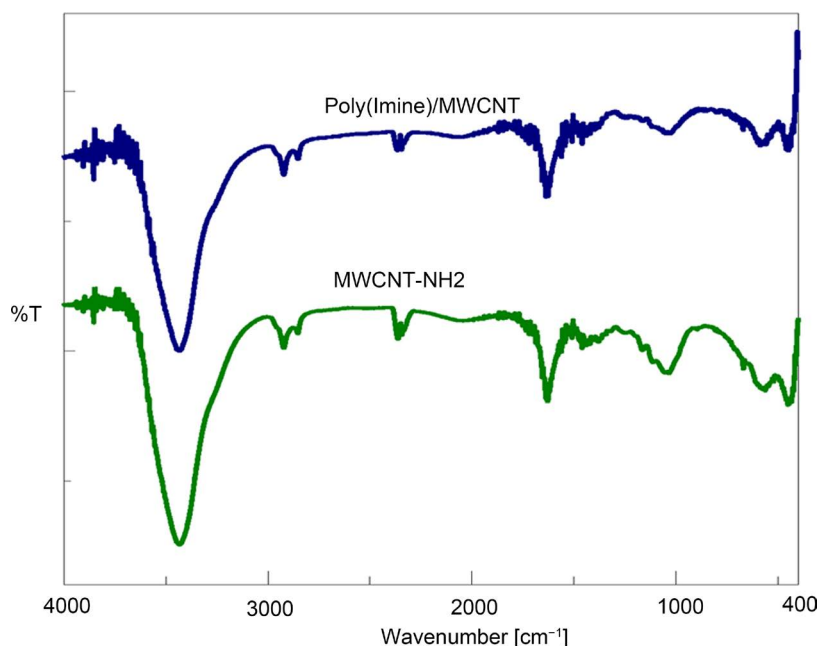
Figure 2. FTIR spectra of MWCNT-NH_2 and Poly (Imine)/MWCNT composite.

with the C=C stretching vibration of the MWCNT backbone [19].

Figure 2 shows the IR spectrum of the Poly (Imine)/MWCNT composite; and the bands around 1637 cm^{-1} correspond to the stretching vibration of the C=N group of the imine and C=C backbone [22]. The broad peak at 3433 cm^{-1}, which can be assigned to the N-H stretch from amine group, suggests that not all the amine group has been converted to imine. We can say that there is still a small amount of unreacted amine group. The peaks of aldehyde do not appear like C=O at 1725 cm^{-1} and C-H stretch at 2750 cm^{-1}.

3.3. UV/Vis Spectroscopy

UV-visible absorptions of MWCNT-NH_2 and Poly (Imine)/MWCNT are illustrated in Figure 3. MWCNT-NH_2 shows one π-π* transition λ_{max} at 280 nm and n-π* transition at λ_{max} at 324 nm. However, the spectra of the Poly (Imine)/MWCNT show absorption with a lower shift of π-π* transition λ_{max} at 278 nm. n-π* transition at λ_{max} shows the shift at 318 nm. This confirms the imine formation.

### 3.4. Microscopy Characterization (TEM, SEM)

3.4.1. Transmission Electron Microscopy (TEM)

Figures 4(a)-(d) display TEM microphotographs of the MWCNT-NH_2 and Poly (Imine)/MWCNT composite at different magnifications. Figure 4(a) & Figure 4(b) show TEM images of MWCNT-NH_2; it can be noticed that MWCNT-NH_2 compounds appear low-entangled with an average diameter of 8 - 15 nm and their average length is approximately equal to 50 μm as announced by the supplier (Timesnano). A spot shape is observed, which may be attributed to NH_2 groups.
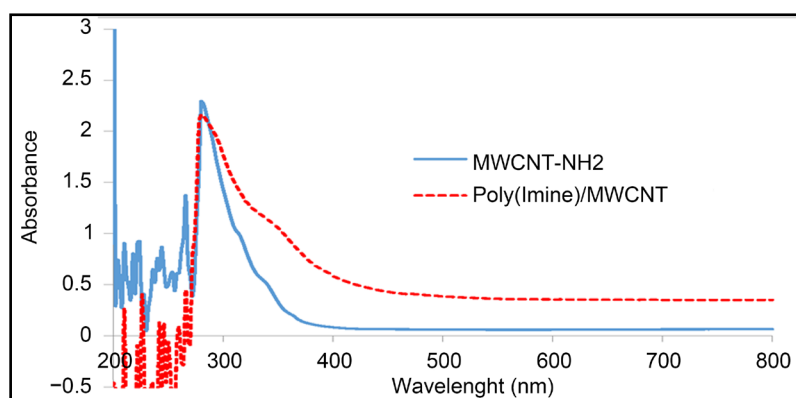
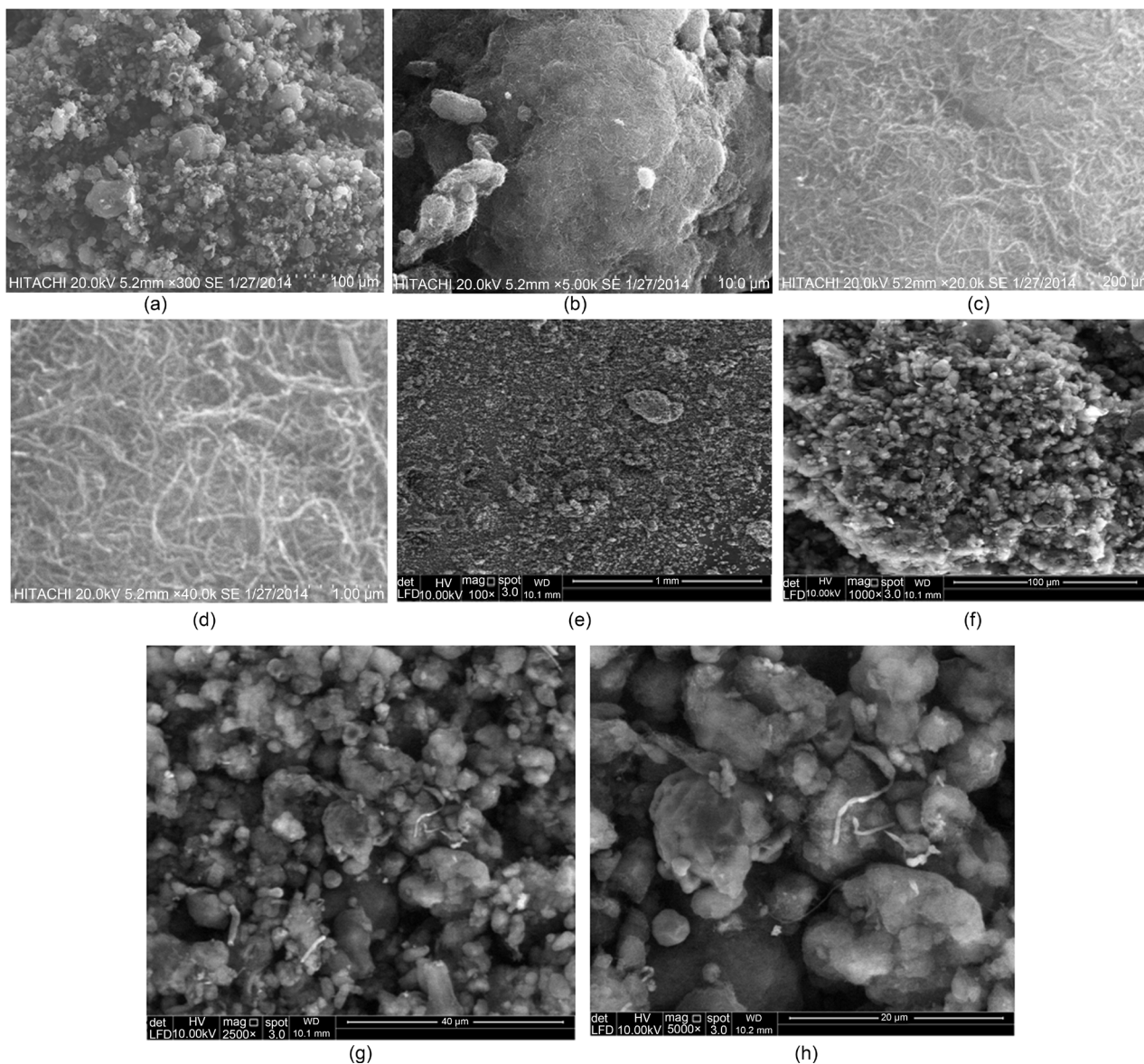**Figure 3.** UV-vis spectra of MWCNT-NH$_2$ and Poly (Imine)/MWCNT composite.
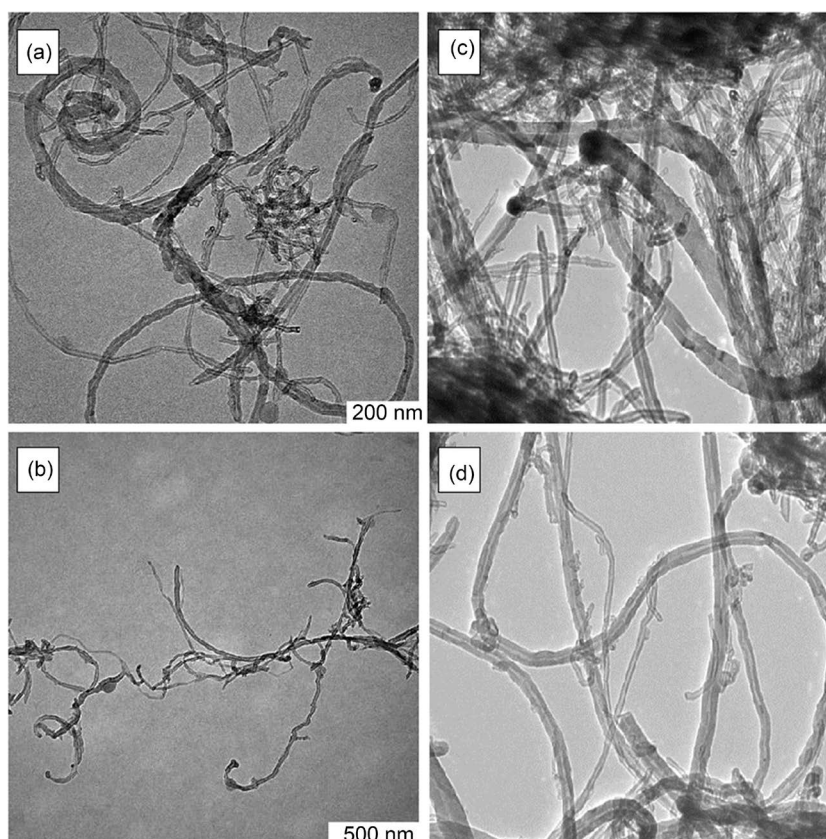
Figure 4. TEM microphotograph of MWCNT-NH$_2$ and Poly (Imine)/MWCNT composite: MWCNT-NH$_2$ (a) ×50,000; (b) ×100,000 and Poly (Imine)/MWCNT (c) low magnification; (d) high magnification.

As shown in **Figure 4(c)** & **Figure 4(d)**, the TEM of Poly (Imine)/MWCNT composite is the relatively good dispersion and more entangled than the pristine MWCNT-NH$_2$. In addition, the spot shape disappeared, which may be referred to the formed imine bonds, which make a tight crossed link between the nanotubes.

3.4.2. Scanning Electron Microscopy (SEM)
Figures 5(a)-(h) show SEM microphotographs of the surface morphology and

Figure 5. SEM microphotograph of MWCNT-NH$_2$ and Poly (Imine)/MWCNTcomposite: (a) MWCNT-NH$_2$ (×300), (b) MWCNT-NH$_2$ (×5000), (c) MWCNT-NH$_2$ (×20,000), (d) MWCNT-NH$_2$ (×40,000), (e) Poly (Imine)/MWCNT (×100), (f) Poly (Imine)/MWCNT (×1000), (g) Poly (Imine)/MWCNT (×2500), (h) Poly (Imine)/MWCNT (×5000).

dispersion of the MWCNT-NH$_2$ and Poly (Imine)/MWCNT composite at different magnifications. An agglomeration of MWCNT-NH$_2$ larger than Poly (Imine)/MWCNT was observed. The images clearly show that the surface morphology of Poly (Imine)/MWCNT composite is significantly different, compared to MWCNT-NH$_2$.
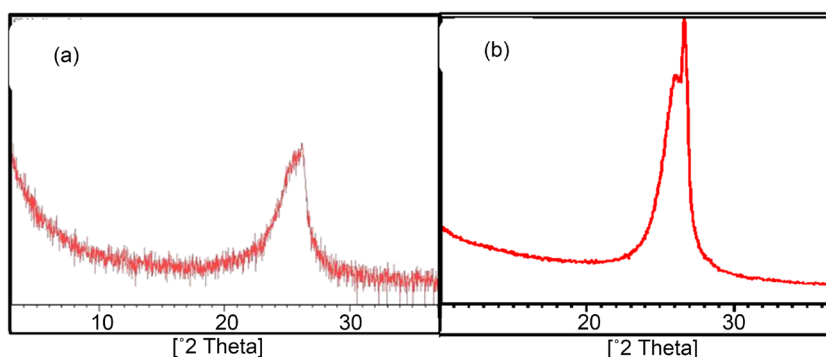
3.5. X-Ray Diffraction

Figure 6 exhibits the XRD pattern of MWNT-NH$_2$ and Poly (Imine)/MWCNT composite. XRD patterns show that the crystallinity of composite is higher than that of MWNT-NH$_2$. The diffraction patterns, having large diffraction peaks resulting from the nanoscale, suggest enhanced crystallinity. The sharp and strong

diffraction peak of MWCNT-NH$_2$ at $2\theta = 26.6°$ correspond to the hexagonal graphite structure support [23] in **Figure 6(a)**. In **Figure 6(b)**, it appears that the intensity of the diffraction peak of Poly (Imine)/MWCNT is sharper than that of the MWCNT-NH$_2$. This behavior may indicate that the crystallinity of Poly (Imine)/MWCNT is higher than MWCNT-NH$_2$ which may be due to co-valent linkage between the MWCNT's by organic compound (Imine group) with less angle strain. That constitutes the evidence for the fact that the treatment was safe and enhanced the graphene layer organization [18] [24].

3.6. Thermal Properties (Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry [DSC])

The TGA (TG and DTG) and DSC curves recorded for the MWCNT-NH$_2$ and Poly (Imine)/MWCNT composite are given in **Figure 7** and **Figure 8**, and summarized in **Table 1**. The high thermal stability of MWCNT-NH$_2$, which is related to the surface of nanotubes defects with very little amount of -NH$_2$ group (0.45%), has a similar behavior of MWCNT [25]. The degradation process of MWNT-NH$_2$ does not exhibit any step until 600˚C, which confirms the MWNT-NH$_2$ thermally stable [19].
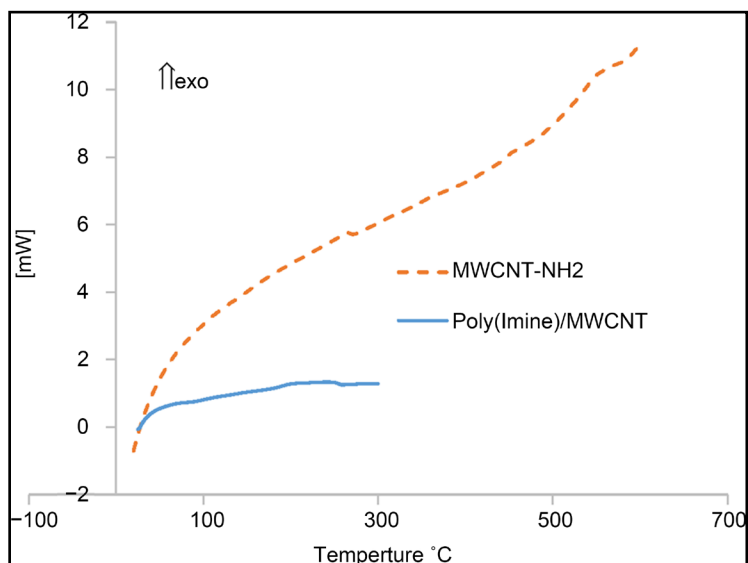
The degradation process of Poly (Imine)/MWCNT composite exhibits two

Figure 6. X-ray diffraction of (a) MWCNT-NH$_2$ and (b) Poly (Imine)/MWCNT composite.
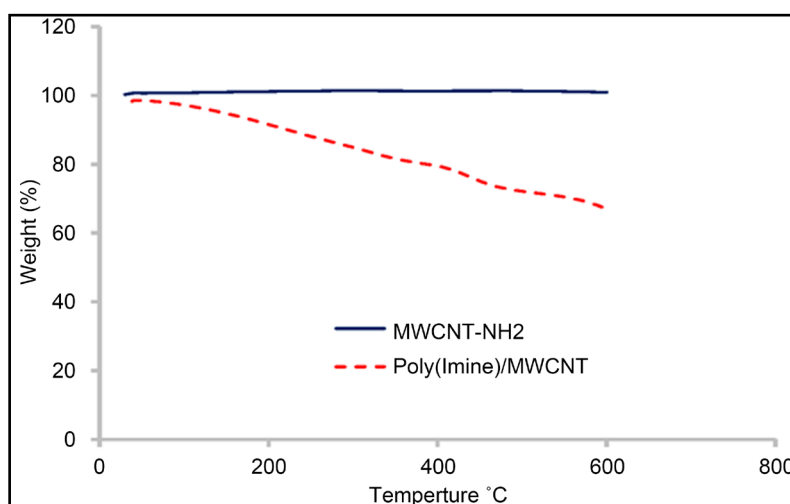
Figure 7. TGA curves of MWCNT-NH$_2$ and Poly (Imine)/MWCNT composite.

Figure 8. DSC curves of MWCNT-NH$_2$ and Poly (Imine)/MWCNT composite.

Table 1. TGA and DSC results of MWCNT-NH$_2$ and Poly (Imine)/MWCNT composite.

Compound	Step	TGA				DSC		Res. %
		Wt. Loss %	T_i/°C	T_f/°C	T_{DTG}	T_{DCS}	Peak	
MWCNT-NH$_2$	1st	0.0	-	-	-	-	-	100
	1st	16.9	74.6	359.6		90.86 258.23	endo	81.1
Poly (Imine)/MWCNT	2nd	9	359.9	500.8	-	-	-	72.1
	3rd	5.1	500.8	600	-	-	-	67.0

Endo: endothermic peak; T_i: Initial point temperature of decomposition; T_f: Final point temperature of decomposition; T_{DTG}: temperature of maximum rate of weight loss of the DTG curve; T_{DSC}: temperature of maximum rate of weight loss of the DSC curve.

steps: the first one at (75°C - 359°C) probably assigned to the broken imine groups and the 2nd and 3rd steps at (359 - 500) and (500°C - 600°C), respectively, are normally attributed to organic backbone structures degradation.

3.7. DC Electrical Conductivity

It is generally agreed that the mechanism of conductivity in the π-conjugated polymeric materials is based on the motion of charge defects within the conjugated framework. The charge carriers, either positive p-type or negative n-type, are the products of oxidizing or reducing the material, respectively. The following overview describes these processes in the context of p-type carriers although the concepts are equally applicable to n-type carriers [26] [27].

Figure 9 shows DC electrical conductivity of MWCNT-NH$_2$ and Poly (Imine)/MWCNT composite at room temperature. The order of DC electrical conductivity is Poly (Imine)/MWCNT > MWCNT-NH$_2$ (2.29E−04 and 5.37E−04 S/cm), respectively. There is a slight increase of the DC electrical conductivity of Poly (Imine)/MWCNT that may be attributed to less co-planarity according to
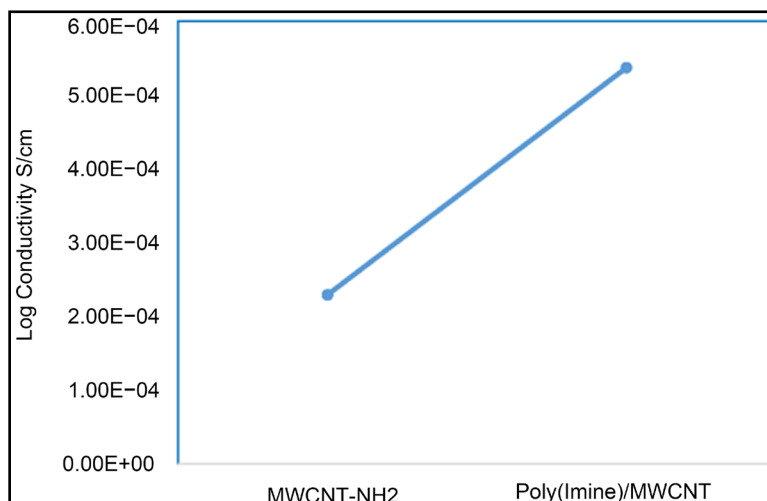
Figure 9. Shows DC electrical conductivity of MWCNT-NH$_2$ and Poly (Imine)/MWCNT composite at room temperature.

random distribution of the amino group in the surface of MWCNT [28] [29]. The results further show that the functionalization of carbon nanotubes with different functional groups has insignificant effect on conductivity [18] [30].

4. Conclusion

In conclusion, the method employed to prepare the Poly (Imine)/MWCNT composite was solution blending by the reaction of MWCNT-NH$_2$ with Terephthalaldehyde (TPAL). The obtained poly-composite was characterized by FT-IR, UV-Vis, XRD, TEM, SEM, TGA, DSC and DC electrical conductivity. X-ray diffraction shows that the crystallinity of composite is higher than of MWNT-NH$_2$; and the highest thermal stability of MWCNT-NH$_2$ is related to the hydrogen bond. Further, the thermal stability of Poly (Imine)/MWCNT connected to conjugation of aromatic ring. There is a slight increase of the DC electrical conductivity of Poly (Imine)/MWCNT, which may be attributed to less co-planarity according to random distribution of amino group in the surface of MWCNT. The results show that the functionalization of carbon nanotubes with imine functional groups has insignificant effects on conductivity.

Acknowledgements

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