International Journal of Nanoelectronics and Materials
Volume 14 (Special Issue) August 2021 [191-200]

Preparation, Characterization, and Electrical Conductivity Investigation of Multi-Walled Carbon Nanotube-filled Composite Nanofibres

A. H. Nurfaizey [1,2,*], N. A. Munajat[1], S. R. Esa[3], M. A. Salim[1,2], A. M. Saad[1,2], M. A. M. Rosli [1,2], N. Tucker[4]

[1]Fakulti Kejuruteraan Mekanikal, Universiti Teknikal Malaysia Melaka,
Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia
[2]Centre for Advanced Research on Energy, Universiti Teknikal Malaysia Melaka,
Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia
3) Advance Analytical Services Laboratory, MIMOS Wafer Fab, MIMOS Berhad, Technology Park Malaysia,
57000 Kuala Lumpur, Malaysia
[4]University of Lincoln, Brayford Pool, Lincoln, LND 7TS, United Kingdom

ABSTRACT

There is a growing interest in carbon nanofibre materials especially for applications that require high surface area, excellent chemical inertness, and good electrical conductivity. However, in certain applications a much higher electric conductivity is required before one can take the full advantage of the nanofibre network. Therefore, incorporating superconductive materials such carbon nanotubes is thought to be a feasible approach to enhance the electrical properties of the carbon nanofibres. The objectives of this study were to prepare and characterize multi-walled carbon nanotube-filled composite nanofibres. Carbon nanofibres were produced via electrospinning technique using precursor solutions of polyacrylonitrile in dimethylformamide loaded with different amount of multi-walled carbon nanotubes (MWCNT). The electrospun fibre samples were then pyrolyzed in a nitrogen-filled laboratory tube furnace. Characterization process was performed using scanning electron microscope (SEM), transmission electron microscope (TEM), and four-point probe method. It was found that the incorporation of MWCNT into the carbon nanofibre structures could significantly increase the electric properties of the nanofibres. The composite nanofibres with 0.1 wt.% of MWCNT loading has the highest electrical conductivity of 155.90 S/cm compared to just 10.71 S/cm of the pure carbon nanofibres. However, the electrical conductivity of the composite fibres reduced drastically when higher weight percentages of MWCNT were used. This was caused by agglomeration of MWCNT causing premature percolation, and broken fibre network as evidenced by SEM and TEM examinations. The results obtained from this study may facilitate improvements in the development of superconductive high surface area materials for electronic applications.

Keywords: electrospinning, electrospun fibre, composite, carbon nanotube, conductivity

1. INTRODUCTION

Carbon nanofibres have received a significant amount of attention by researchers due to their promising properties such as large surface area, high mechanical strength, and good electrical properties [1]. These superior properties of carbon nanofibres are made possible owing to their nanoscale size as compared to conventional microscale fibres. Carbon nanofibres have been proposed for various applications such as sensors, supercapacitors, filtrations, smart materials, tissue engineering, and textile technologies [2]–[6]. Several nanofibre synthesis techniques have been introduced such as electrospinning, chemical vapour deposition, self-assembly, template-based synthesis, blow spinning, and plasma-induced synthesis [7], [8]. Amongst these

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*nurfaizey@utem.edu.my

techniques, electrospinning is regarded as the most user-friendly technique for synthesising nanofibres.

Electrospinning is a simple and inexpensive method to produce nanoscale fibres using electric charge [9]. A typical electrospinning setup consists of a high voltage power supply, a polymer solution supply that is channelled through an orifice (also known as spinneret), and an electrically grounded collector (Figure 1). The high voltage power supply is used to charge the polymer inside the spinneret. The high amount of electrostatic charges causes a jet of polymer to be ejected from the tip of the spinneret towards the grounded collector. Initially, the jet travels in a fairly straight path before the whipping instability takes place [10]. From this point onwards, the jet continues its journey in a spirally looping motion until it reaches the collector electrode. During the flight, fibre thinning process takes place mainly due to mechanical stretching and solvent evaporation. Electrospinning produces fibres with a typical fibre diameter between 100 to 1000 nm, depending on materials and processing parameters [11].

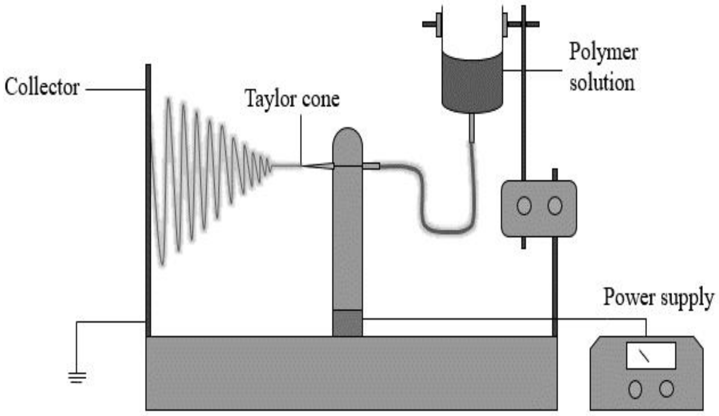

Figure 1. A schematic diagram of electrospinning setup.

Previously, the authors have described a method of preparing carbon nanofibres from electrospun polyacrylonitrile (PAN) precursor fibres using a two-step pyrolysis process; stabilization and carbonization [9]. Stabilization process converted the C≡N bonds in PAN polymer chains to C=N bonds, transforming the PAN polymer from thermoplastic to non-plastic cyclic also known as the ladder-type structure [12]. The process was then followed by carbonization process to eliminate other chemical elements except carbon atoms at an elevated temperature between 800 °C to 1200 °C [13]. Previous studies have reported that electrical conductivity of the carbon nanofibres increases with carbonization temperature. It was reported that depending on carbonization temperature, the electrical conductivity of carbonized PAN nanofibers were in the range of a 0.2 to 0.7 S/cm, which were much higher compared to uncarbonized fibres of a few µS/cm [9], [14].

In applications such as for producing supercapacitors and fuel cells electrodes, a much higher electrical conductivity is required [15], [16]. Therefore, addition of superconductive fillers into carbonized PAN nanofibres was thought as a feasible option to enhance the electrical conductivity of carbon nanofibres. In this study, multiwalled carbon nanotubes (MWCNT) were used due to their good properties such as high electrical conductivity, high mechanical strength, lightweight, and high energy storage [17]. In addition, MWCNT has also been adapted into electrospinning process with encouraging success, in particular studies on PAN/CNT and PAN/MWCNT composites [12]–[14].

Therefore, the aims of this study were to prepare, characterize, and investigate the electrical conductivity of MWCNT-filled composite carbon nanofibres. Carbon nanofibres were synthesized by thermal treatment of PAN electrospun precursor fibres. MWCNTs were added into the solution prior to electrospinning process. The effects of different filler loadings on morphology, fibre diameter, and electrical conductivity were investigated. The results presented in this study would facilitate improvement in miniaturization of highly conductive electronic components.

2. MATERIALS AND METHODS

Polyacrylonitrile (PAN) polymer powder with an average molecular weight of 124,000-130,000 g/mol was purchased from Sigma Aldrich (Aldrich 181315). The solvent was N,N-Dimethylformamide (DMF) with an average molecular weight of 73.09 and linear formula of $HCON(CH_3)_2$ (Merck 1030532500). The MWCNT used in the experiment was an industrial-grade -OH functionalized multi-walled carbon nanotube from Nanostructured & Amorphous Materials, Inc. (USA). The MWCNT has an average outside diameter of 10-30 nm, inside diameter of 5-10 nm, and length of 10-30 µm.

A 10 wt.% of PAN-DMF base solution was prepared by dissolving 5 g of PAN powder in 45 g of DMF. The mixture was stirred at room temperature using a magnetic stirrer (Model C-MAG HS7, Ika Works) for approximately 6-7 hours or until a clear and homogeneous solution was obtained. Then, a known amount of MWCNT was added and sonicated for 1-2 hours until all of the MWCNT were completely dispersed. The step was repeated to prepare solutions at different concentration of CNT, which are 0.1 wt.%, 0.3 wt.%, 0.5 wt.%, 0.7 wt.% and 1.0 wt.%. The colour of the solutions became darker after the addition of MWCNT as compared to yellowish appearance of the pure PAN-DMF solution.

The polymer solution was filled into a 10 mL syringe which was mounted on a syringe pump (Model NLS20, Progene Link). The syringe pump was used to provide a consistent feeding of the solution through the spinneret. The high voltage power supply (Model PS35-PCL, Progene Link) was set at 20 kV. The distance between the spinneret and the collector electrode was set at 15 cm. Triplicate samples were collected for each solution. The electrospinning process was conducted in a closed electrospinning chamber that was equipped with an exhaust ventilation system for safety precaution. After electrospinning process, the samples were dried overnight to make sure all remaining solvent has evaporated.

Thermal treatment process was performed using a laboratory tube furnace Model TF70-1600 (Company, Origin). The furnace was equipped with a nitrogen gas supply. The collected electrospun nanofibre samples were folded (about 70 mm × 70 mm) and placed onto a ceramic crucible boat. In the fabrication process of carbon nanofibre, the samples underwent thermal treatment that consists of two stages: stabilization and carbonization process. The stabilization process was carried out at 240^oC with ramping time $1^oC/min$ while carbonization process was performed at 1000 ^oC with a ramping time of 5 $^oC/min$.

The morphology of electrospun carbon nanofibre was observed using a scanning electron microscope (SEM) Model JSM-6010PLUS/LV (JEOL Ltd., Japan) and transmission electron microscope (TEM) Model FEI Helios Nanolab^{TM} (Thermo Fisher Scientific, USA). The average fibre diameter of the samples was measured from SEM micrographs using ImageJ software version 1.50 (National Institutes of Health, USA). The conductivity of the nanofibres was measured using a four-point probe machine from Jandel Engineering Limited (UK) in accordance with ASTM F390.

3. RESULTS AND DISCUSSION

The as-deposited pure PAN electrospun fibres (0 wt.% of MWCNT) were white in appearance as can be seen in Figure 2(a). However, the MWCNT-filled PAN fibres became darker as the weight percentage of MWCNT increased as shown in Figure 2(b) to Figure 2(f). After thermal treatment process, all of the samples became brownish after stabilization process and finally, the samples turned completely black after carbonization process.

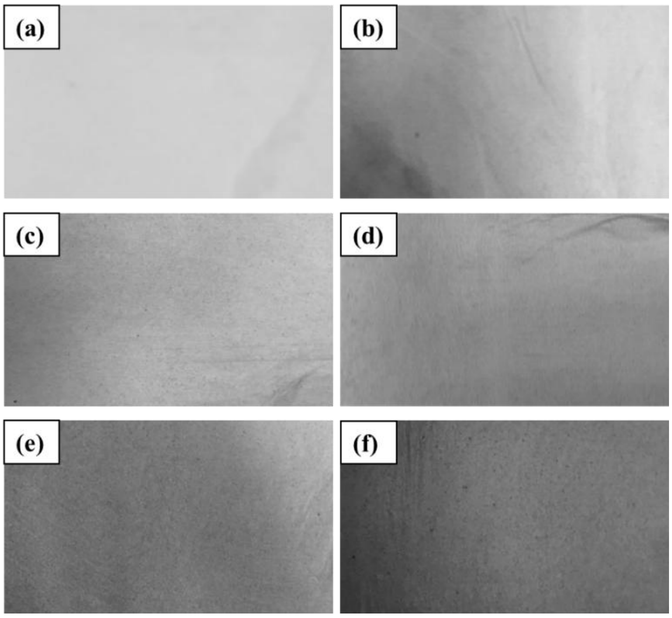

Figure 2. The colour change of as-deposited PAN electrospun nanofibres with different percentages of MWCNT (a) 0 wt.% (b) 0.1 wt.% (c) 0.3 wt.% (d) 0.5 wt.% (e) 0.7 wt.% and (f) 1.0 wt.%.

The scanning electron microscope (SEM) images of the electrospun fibres are shown in Figure 3. The pure PAN fibres (0 wt.% of MWCNT) were the smallest among the samples with an average fibre diameter of 496 nm (Figure 3(a)). After the addition of 0.1 wt.%, 0.3 wt.%, 0.5 wt.%, 0.7 wt.%, and 1.0 wt.% of MWCNT, the average fibre diameters were increased to 572 nm (15.4%), 595 nm (20.0%), 820 nm (65.4%), 843 nm (70.1%), and 1194 nm (140%), respectively (Figure 3(b) to Figure 3(f)). The increase in weight percentage of MWCNT influenced the consistency of fibre formation process and therefore producing fibres with larger fibre diameters. Irregularities in the form of rough and curled fibres were also found on the surface of MWCNT-filled fibres. The occurrence of irregularities such as beaded, agglomerated, curled and uneven diameter fibres have been previously reported when incorporating CNT in electrospun fibre production [18], [19].

The SEM images of carbonized fibres (after thermal treatment) are shown in Figure 4. In general, the fibres became smaller in size after carbonization process due to reduction of chemical compounds in PAN polymer molecules. The average fibre diameter for 0 wt.%, 0.1 wt.%, 0.3 wt.%, 0.5 wt.%, 0.7 wt.%, and 1.0 wt.% CNT samples were 475 nm, 446 nm, 748 nm, 752 nm, 782 nm, and 1044 nm, respectively. The pure PAN fibres maintained its smooth appearance even after thermal treatment process (Figure 4(a)). However, although the surface of 0.1 wt.% and 0.3 wt.% MWCNT carbon fibres were fairly smooth (Figure 4(b) and Figure 4(c)), some irregularities on the surface of the fibres can be observed. As the percentage of MWCNT was further increased, even more irregularities appeared in the SEM images. As can be seen clearly in Figure 4(d) and Figure 4(e), the MWCNT-filled fibres with rough surfaces were produced. The worst case was observed for 1.0 wt.% MWCNT sample where some of the fibre networks were broken (Figure 4(f)).

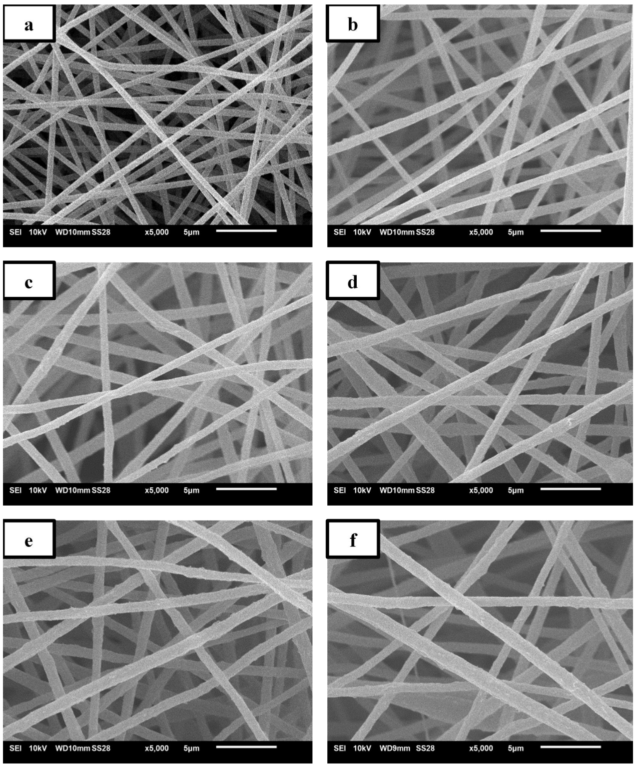

Figure 3. SEM images (×5000 magnification) of PAN electrospun fibres with different percentages of MWCNT (a) 0 wt.% (b) 0.1 wt.% (c) 0.3 wt.% (d) 0.5 wt.% (e) 0.7 wt.% and (f) 1.0 wt.%.

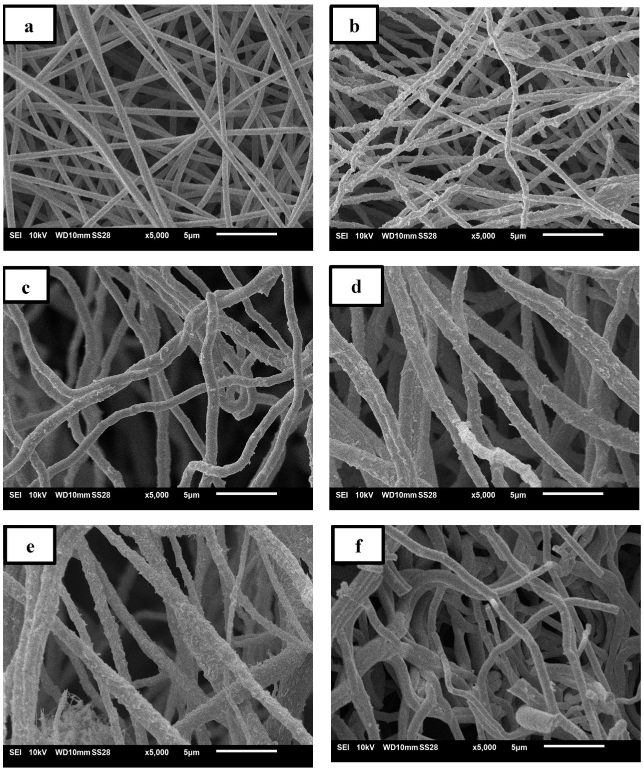

Figure 4. SEM images (×5000 magnification) of carbonized fibres with different percentages of MWCNT (a) 0 wt.% (b) 0.1 wt.% (c) 0.3 wt.% (d) 0.5 wt.% (e) 0.7 wt.% and (f) 1.0 wt.%.

The microstructure of MWCNT-carbon nanofibres was investigated using transmission electron microscopy (TEM). Figure 5(a) to 5(d) show the TEM images of the MWCNT-carbon nanofibres with different loadings of 0.1 wt.%, 0.3 wt.%, 0.5 wt.% and 1.0 wt.% of MWCNT, respectively. In the TEM images, MWCNTs appear darker in contrast with concentric tubular structures due to their higher electron densities as compared to the electrospun fibres [20]. TEM images showed that the distribution and orientation of the MWCNTs were random throughout the samples. The arrows in Figure 5 show the locations of the MWCNTs. Figure 5(a) shows the microstructure of a broken 0.1 wt.% MWCNT carbon fibre. Based on Figure 5(a), the 0.1 wt.% addition of MWCNT produced fibres with fairly aligned MWCNTs along the fibre's thread. There was no evidence of agglomerated MWCNT structures accumulated outside the fibre surface. This result explains the smooth surface of 0.1 wt.% MWCNT fibres as observed in the SEM image (Figure 4(b)).

At higher loading of 0.3 wt.% and 0.5 wt.% MWCNT, agglomerated MWCNTs were observed outside the fibre threads as shown in Figure 5(b) and Figure 5(c). These agglomerated MWCNTs were created during electrospinning solution preparation. Initially, the agglomerated MWCNTs were not visible before the thermal treatment process as can be seen earlier in Figure 3. However, after thermal treatment, the fibres shrank exposing the agglomerated MWCNTs on the surface of the fibres. The worst-case condition was observed for 1.0 wt.% MWCNT fibres. Figure 5(d) shows that some of the MWCNTs were aggregated outside the fibre's thread.

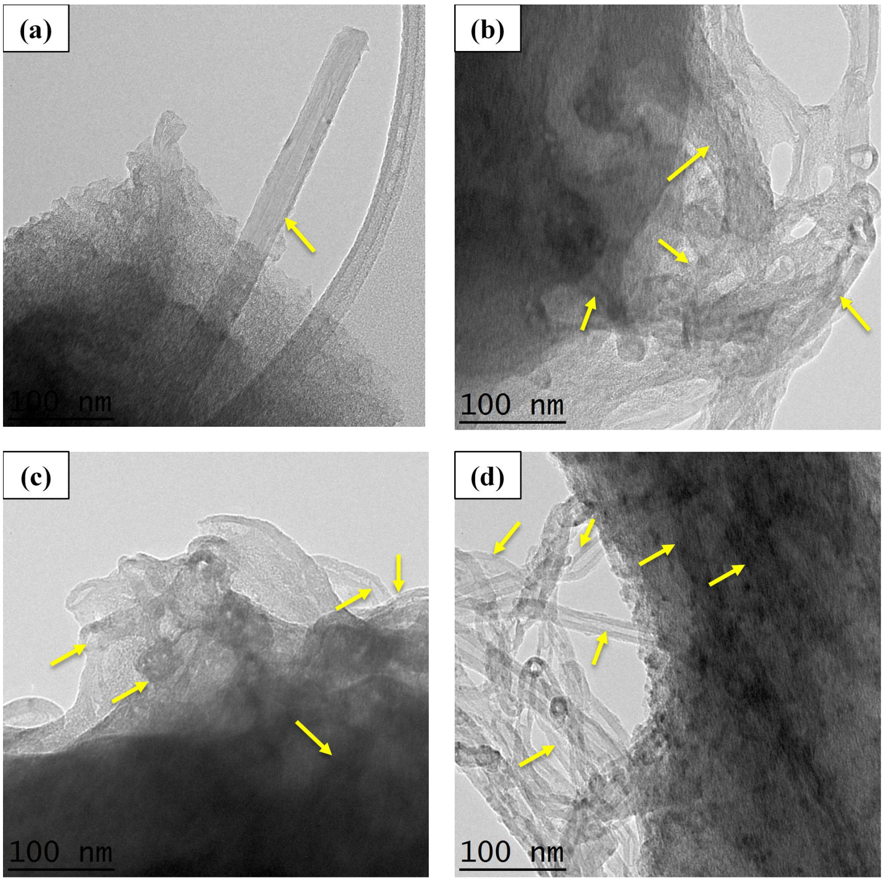

Figure 5. Transmission electron microscope (TEM) images of electrospun carbon nanofibres with different MWCNT loading of (a) 0.1 wt.% (b) 0.3 wt.% (c) 0.5 wt.% and (d) 1.0 wt.%. The arrows show the locations of the MWCNTs. Scale markers of 100 nm.

As expected, the addition of MWCNT in the fabrication of electrospun carbon nanofibre composites would increase electrical conductivity of the fibres. This is mainly due to superior electrical conductivity properties of carbon nanotubes of about 10^4 S/cm [21]. Table 1 tabulates the sheet resistance and electrical conductivity values of the samples. The electrical conductivity of 0 wt.%, 0.1 wt. %, 0.3 wt.%, 0.5 wt.%, 0.7 wt.%, and 1.0 wt.% of MWCNT-filled fibres were 10.71 S/cm, 155.90 S/cm, 41.33 S/cm, 33.01 S/cm, 30.76 S/cm, and 21.56 S/cm, respectively.

Table 1 Sheet resistance and electrical conductivity of MWCN-filled composite carbon nanofibre samples.

Sample	Sheet resistance, Rs (Ω/sq.)	Conductivity (S/cm)
PAN/CNT	20.5905	10.71
PAN/CNT/0.1	1.4153	155.90
PAN/CNT/0.3	5.3385	41.33
PAN/CNT/0.5	6.6835	33.01
PAN/CNT/0.7	7.1725	30.76
PAN/CNT/1.0	10.232	21.56

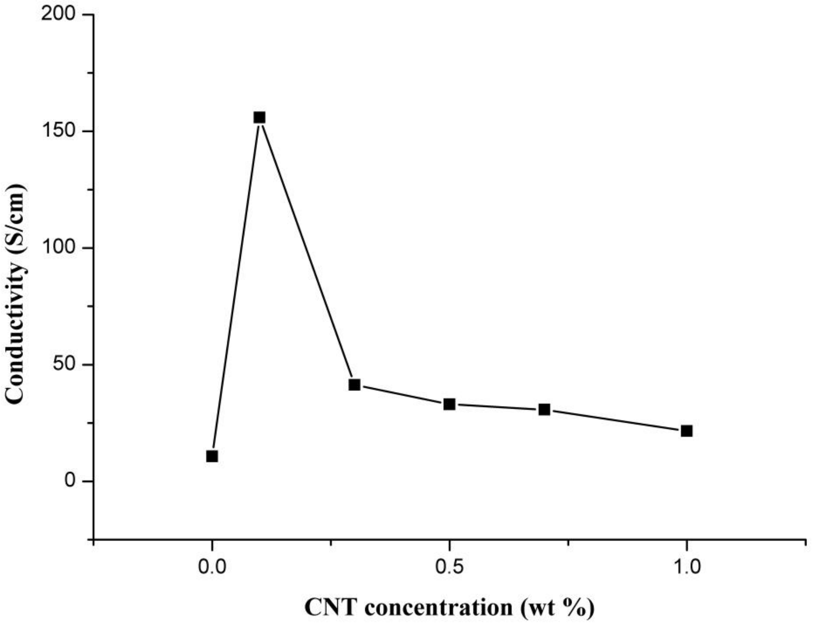

Figure 6. Electrical conductivity as a function of MWCNT loading percentage.

The results showed that the electrical conductivity of the MWCNT-filled fibres was at an increase trend from 0.0 wt.% to 0.1 wt.% of MWCNT (10.71 S/cm to 155.90 S/cm). Later at 0.3 wt.% of MWCNT and above, the electrical conductivity was drastically dropped as illustrated in Figure 6. Although the results seem to suggest that percolation threshold happened at 0.1 wt.% of MWCNT loading, the loading percentage was lower compared to previous studies [22]. However, it is known that agglomeration of such carbon-based fillers could promote percolation at an earlier loading percentage [23]. Therefore, this situation could be caused by inhomogeneous of MWCNTs in PAN-DMF electrospinning solution. Furthermore, the presence of MWCNT agglomerations and broken fibre networks (as evidenced in Figure 4) impeded the flow of electrons resulting in poor electrical conductivity [24], [25].

4. CONCLUSION

In this study, MWCNT-filled composite carbon nanofibres were successfully synthesized via thermal treatment of PAN electrospun precursor fibres. The average fibre diameter of the as-spun PAN nanofibres increased as the percentage of MWCNT loading increased. After thermal treatment process, the fibres shrank in size due to reduction of chemical compounds in PAN polymer molecules. Based on SEM examination, the carbonized fibres appeared to have rough surfaces. The worst-case condition was showed by samples with the highest percentage of 1.0 wt.% MWCNT loading. It was also observed that some of the fibre networks were broken. TEM examination confirmed that the irregularities of the fibre surfaces were caused by agglomeration of MWCNTs. The electrical conductivity of the carbonized carbon was significantly improved by the addition of MWCNT. The highest electrical conductivity was demonstrated by samples with 0.1 wt.% MWCNT loading. However, at higher MWCNT loadings, the electrical conductivity of the fibres reduced. This can be explained by the existence of agglomerated MWCNTs and broken fibre networks that would impede the flow of electrons.

ACKNOWLEDGEMENTS

The authors would like to thank the Ministry of Higher Education Malaysia and Universiti Teknikal Malaysia Melaka through the funding of Collaborative Research Grant PJP/2019/FKM-CARE/CRG/S01706. Special thanks to the members of Advanced Materials Characterization Laboratory (UTeM), Academia-Industry Collaboration Laboratory, Advance Analytical Services Laboratory (MIMOS), and the members of the Faculty of Mechanical Engineering, UTeM.

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