INVESTIGATION ON MORPHOLOGY, CONDUCTIVITY AND THERMAL STABILITY STUDY OF THE ELECTROSPUN PAN NANOFIBER REINFORCED WITH MIXTURE CNT-CNF

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Abstract: Reinforced electrospun PAN nanofibers with mixture of carbon nanotubes and carbon nanofibers were produced via electrospinning techniques. The study was conducted to examine the effect of ratio CNT:CNF to the conductivity and thermal stability of the electrospun PAN nanofiber. The electro-spinning was performed using 10wt % of PAN slurry to a mixture of CNT: CNF with ratios 5:3, 5:5 and 3:5 respectively. The composition of the solution had a greater effect on the conductivity and thermal stability of the spun fibers. The morphological study revealed that the fiber diameters of the PAN/CNT-CNF electrospun had increased the ratio of CNT: CNF from 0.68 to 0.83 micrometer respectively. For the thermal stability study, it was observed that the thermal degradation of the PAN polymer had increased as the mixture of CNT:CNF ratios increased. The electro-conductivity study also revealed that the addition of 5:5 ratio CNT:CNF had greatly increased the conductivity of the PAN fiber from 1.6×10^{-7} Scm^{-1} to 4.8×10^{-4} Scm^{-1}.
Keywords: Electrospinning, Polyacrylonitrile, Electrospun fiber, Mixture CNT-CNF, Conductivity, Thermal properties.

INTRODUCTION

Electrospun PAN nanofibers are an exciting new class of material that can be utilized for several value-added applications such as in medical, filtration, barrier, wipes, personal care, composites, garments, insulation and energy storage. These electrospun PAN nanofibers are characterized by properties of high surface area per unit mass which are associated with high surface free energy [1-2]. Special properties of PAN nanofibers are suitable for a wide range of applications viz. from medical to consumer products and industrial to high-tech applications, such as in drug-delivery systems, information technology, transistors, battery separators, energy storage, fuel cells, and aerospace [3-4]. Reinforced conventional PAN using continuous fibers have an excellent in-plane strength, but conventionally impuissant against matrix-dominated failures. Nano carbon materials such as carbon nanotubes (CNTs) and carbon nanofibers (CNFs) are widely utilized as reinforced composite materials because

of their high elastic module, high mechanical strengths, and outstanding electrical conductivities. These electrospun nanofibers are great potential applications to automobiles, aircrafts, and fuel cells [3-4]. Carbon nanotubes (CNTs) have been intensively studied since their discovery in 1991 [5]. Moreover, CNT-filled composites have achieved paramount ameliorations in their properties such as in terms of conductivity and mechanical strengths [6-8]. However, CNTs are still too expensive to be utilized, especially in industrial-scale applications. Since CNTs can easily agglomerate, the fabrication of polymer matrix composites with uniformly distributed of CNTs is very difficult. In these cases, carbon nanofibres (CNFs) are perfect candidates to be utilized as fillers [7, 9-11]. CNFs present properties between carbon fibres and CNTs, and they have found amendments in the mechanical behavior of CNF-reinforced nanocomposites, especially in the polymer matrix composites [7, 9-11]. On the other hand, even though CNFs have fewer desirable mechanical properties than those of CNTs, their values (such as elastic modulus of 760 Gpa and tensile strength of 3.5 Gpa) are still higher than those of commonly reinforced materials. In addition, since CNFs are straight-shaped and less agglomerated than CNTs, they can therefore be handled more easily than CNTs. It is well-known that both CNTs and CNFs can make electrically conducting composites because of their intrinsic electrical conductivity [11]. Mixtures of CNTs and CNFs can thus be utilized as a reinforcement material in large-scale composites for the application of energy storages or fuel cells [12–17].

The electro-spinning technique is one of the general techniques to fabricate polymer matrix composites whereby electro-spinning is a process that spins fibers of diameters ranging from 10nm to several hundred nanometers. This method has been known since 1934 when the first patent on electro-spinning was filed. Yet, the electro-spinning technique is one of the cheapest and effective ways on synthesizing polymer nanofiber. The electro-conductivity properties of PAN fiber are highly dependable on the types and ratio of nanomaterials. The nanomaterials composition will have greater effects on the fiber diameters, electric conductivity, resistivity and thermal stability. The study of electrospinning carbon nanotube polymer composite nanofibers by Leslie et al. reported that the use of electro-spinning to synthesize polymer/CNT nanocomposite fibers could offer a possible way to simultaneously align CNTs along a single axis during processing without compromising the structural integrity of the individual CNTs [18]. The focusing of the meniscus into a sharp conical shape gave rise to a converging flow. Hence, concentration of the streamlines in the extremely narrow region occurred at the tip of the cone from which the jet and fiber emanated

[18]. According to Haoqin et al., MWNT and CNF were used to reinforce the polymer matrices for improved mechanical, thermal and electrical properties. Thus, the modification of the polymer had resulted in the production of nanocomposites with enhanced the polymer properties [19].

The major objective of this study is to evaluate the effects of the mixture of multi-walled CNTs and carbon nanofiber (CNFs) at different ratios into PAN polymer matrix on the conductivity and thermal stability, as well as the morphological characteristics of the electrospun PAN fibres. Besides, this study also wishes to investigate whether the conductivity and thermal stability, and morphology of electrospun PAN nanofiber composite with a reinforced mixture of CNT and CNF at different ratios would give the same or nearly optimum level achieved by using CNT alone into the PAN polymer.

EXPERIMENTAL

Three sets of solutions, including pure PAN as a control, PAN/CNT-CNF with three different ratios were electrospun. Mixture CNT-CNF was substituted with dimethylformamide (DMF) in concentrations (10wt%) where the viscosity of the solutions remained unchanged. Electrospinning parameters such as: applied voltage, needle target distance, and needle geometric dimensions were kept constant so as to prevent them from having a resultant effect on the fiber morphology.

MATERIALS

Polyacronitrile with MW 85,000 (PAN, 98%) was purchased from Sigma-Aldrich and *N, N* dimethylformamide solvent (DMF, 99%) was purchased from J.T Baker. The MWCNT (diameter 10-20 nm, 95%) and CNF (diameter 200 – 400 nm, 95%) were supplied by Global Science Resources. All the nanomaterials used were for further treatment.

PREPARATION OF PAN/CNT-CNF SLURRY

PAN polymer with molecular weight 85,000 g mol^{-1} (Sigma-Aldrich) was dissolved in the *N,N*-dimethylformamide solvent with a ratio of 10% w/w, and was stirred vigorously for 4 hours at 60 $^{\circ}$C. The ratio of 5:3, 5:5 and 3:5 of CNT:CNF were added respectively into the polymer slurry, and then continued stirring for another hour at 80 $^{\circ}$C. The solution was then cooled at room temperature and then fed into glass syringes so as to undergo the electrospinning process. Fixed electro spinning conditions were used. These conditions were: (i) working distance (H) : 15 cm, (ii) voltage applied (E) = 10.0 kV, (iii) metal screen cover

by clean aluminium foil, (iv) vertical spinning, (v) room temperature, (vi) clean glass pipette of 0.9 mm orifice diameter for each run and (vii) fix amount with two ml hr^{-1} of polymer solution for each run.

ELECTROSPINNING

The electro spinning setup consisted of a Terumo brand Terufusion syringe pump model TE-331 mounted vertically on a laboratory adjustable stand with 1½ inch aluminium length framing material. The electrospun fibers traveled downwards, and the distance was adjusted between the needle tip and the ground electrode (point to plate distance) by turning of the knob. The collector plate was made from aluminium. A second layer of aluminium plate collector was placed to provide a quick and remove method for obtaining multiple samples. Collector plates were insulated from the surrounding floor by a plastic separator. A high voltage of 21 gauges applied to 0.80 x 40 mm needle via an alligator clamp, and wire was attached to the high-voltage output of the PHYWE type HOCHSP, NETZGER 25 kV.

THERMAL TREATMENT

The electrospun PAN/CNT-CNF nanofiber was further treated under three stages of heat treatment in order to remove a non-carbon element, and to do pyrolysis of a long-chain carbon. In the stabilization stage, the heat treatment was done to remove a non-carbon element while the carbonization process would allow the carbon to self-arrange to become a ladder structure polymer [19]. The electrospun nanofiber was heated at the temperature of 280 ^{o}C under nitrogen condition and held for 1 hr. After the sample was cooled at room temperature, it was further carbonized at 850 ^{o}C, then followed by graphitization at a temperature 1300 ^{o}C for another hour under nitrogen conditions.

CHARACTERIZATION

The electrospun fiber had been characterized by using SEM Quanta FEI 200 so as to examine the morphologies of the electrospun fiber after the heat treatment. The thermal stabilities of the electrospun samples were well determined by using Thermal Gravimetric Analyzer (Perkin Elmer). This was done by heating the sample until 700 ^{o}C with a heating rate of 10 ^{o}C min^{-1} under nitrogen gas. For the measurement of electrical conductivity, SI 1260 Solartron impedance analyzer was used where all the samples were embedded together to form a flat piece of polymer nanocomposite with a tablet thickness of 0.5 cm and size area of 2.54 cm^{2}. The conductivity, σ, was calculated using the following equation:

$$\sigma = l/[R_b A] \tag{1}$$

Where R_b, bulk resistance, A is the area and l is the thickness of the sample [20].

RESULTS AND DISCUSSION

Figure 1 shows the SEM images of the pure electrospun PAN fibers fabricated at different ratios of CNT-CNF mixtures. The ratios of CNT-CNF mixtures are observed to have a significant effect on the PAN fiber's morphology. From the SEM images, it is revealed that the pure electrospun PAN fiber without mixture of CNT-CNF has a fine and smooth fiber with an average fiber diameter is 0.59 micrometer. It is also observed in both PAN/CNT-CNF nanocomposites samples (ATF, AFT and ATT) that there is a homogenous electrospun distribution with fewer amounts of beads. However, adding of CNT-CNF mixture into PAN matrix has markedly increased the fiber diameter.
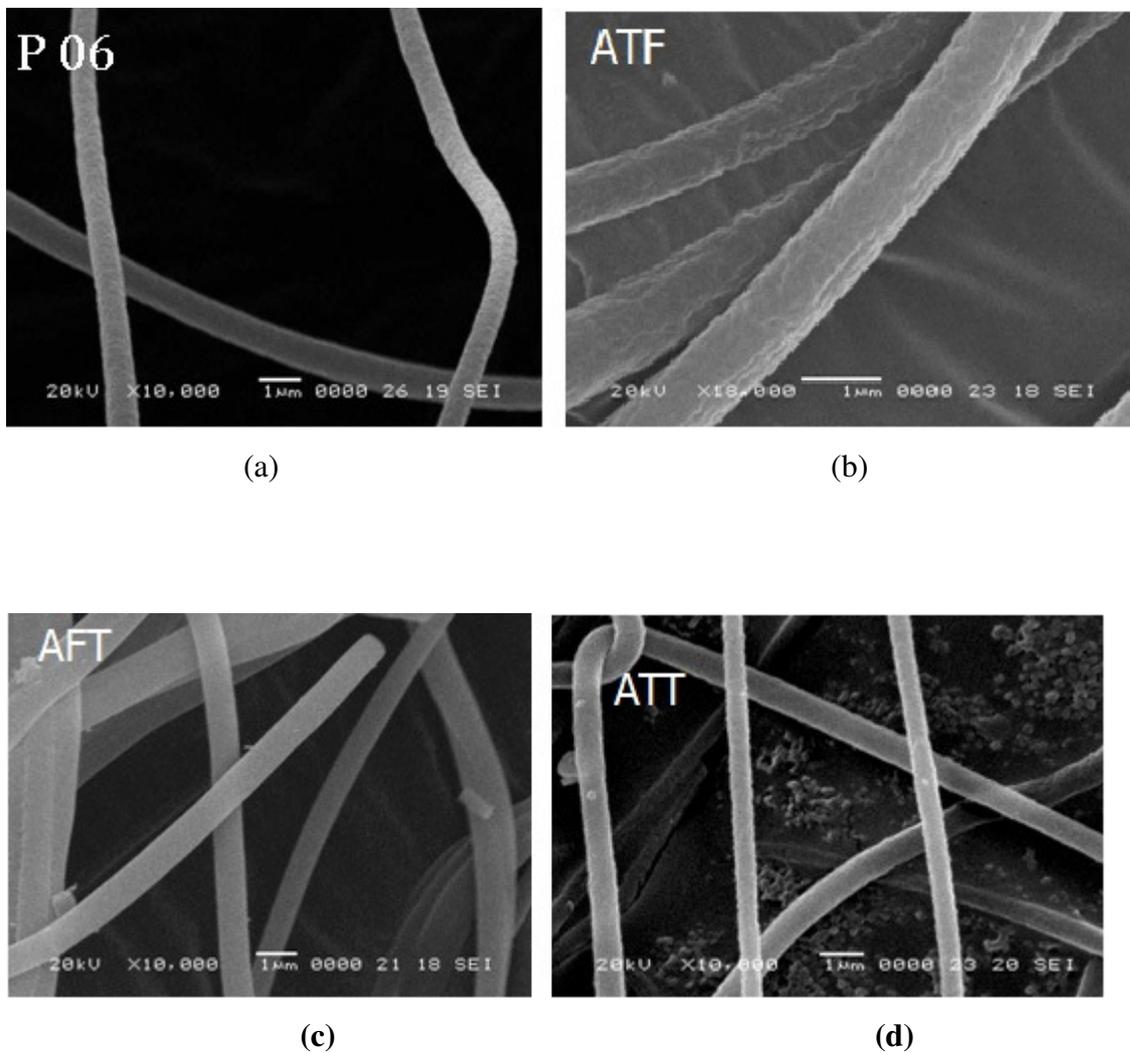

| (a) | (b) |

| **(c)** | **(d)** |

Figure 1 SEM images of a) PAN (control), b) PAN/CNT-CNF with ratio 5:3, c) PAN/CNT-CNF with ratio 3:5 and d) PAN/CNT-CNF with ratio 5:5

Comparing the fiber diameter as shown in Table 2, ATF sample of the ratio CNT-CNF 5:3 has the smallest fiber diameter with 0.68 micrometer, followed by the sample of AFT (ratio CNT-CNF is 3:5) is 0.76 micrometer, and then the ATT sample (ratio CNT-CNF is 3:5) with the fiber diameter 0.83 micrometer. ATF sample has the smallest diameter due to the lowest ratio of CNF to the PAN matrix. PAN matrix will lead to expanding more from the inside and the increase in density causes the specific density of the slurry to be high compared to ATF sample. This is explained by the size of CNF is 10 times bigger than the CNT, hence leading to un-homogeneous dispersion of CNF in the PAN matrix. This will thus produce the bigger fibre diameter. The smoothness of sample AFT can be contributed by the higher ratio of the CNF. It can be then suggested that the CNF nanoparticle cover the electrospun PAN and the CNT nanoparticle will fill the pores of the PAN electrospun.

Figure 2 and Table 1 describes the thermal degradation of the electrospun PAN/CNT-CNF nanocomposite. From the analysis, it can be concluded that all the samples have 3 stages of thermal degradation. The first stage occurs at a temperature range of 30 ^{o}C to 275 ^{o}C. This stage can be accounted for water crystal and impurities loss from the sample. The amount of weight percentage also has not reduced a lot, which confirms that the loss is only water and impurities in the sample. Since it is a mixture of CNT and CNF nanomaterials, it takes some time to eliminate all the water crystal and impurities in the polymer electrospun matrix. This can be accounted for the high temperature needed for the impurities loss.

Second stage of the thermal degradation occurs in the temperature range of between 300 ^{o}C to 370 ^{o}C. Compare to pure electrospun PAN, the second stage occurs in a slightly lower temperature between 300°C to 350 ^{o}C. This may be due to the interaction of mixtures of CNT-CNF to the PAN matrix. At this point, the polymer ladder chain break-off reaction at thermal degradation is more consistent and homogenous. The consistency of the range here can be well supported by the fact that the entire mix mode sample has a good polymer matrix arrangement.

The third stage of the thermal degradation starts at a temperature range of 330 ^{o}C to 700 ^{o}C. This stage is the stage where the PAN polymer electrospun chain has been burnt off, and only ash is left. So the burning of the ash is in the third stage process. The burning of the ash gives the end value at a temperature 700 ^{o}C which will show the amount of the PAN / mixture CNT and CNF mix electrospun nanocomposite left. From Table 1, it shows that sample ATT has the highest ash residue amount at 65 %, followed by ATF at 60 % and the least is sample AFT at 56 %. These show that sample ATT has the strongest thermal resistance ability.

Therefore, it can be concluded that the sample ATT with 5 % CNT and 5 % CNF is the sample with the highest thermal strength resistance ability.
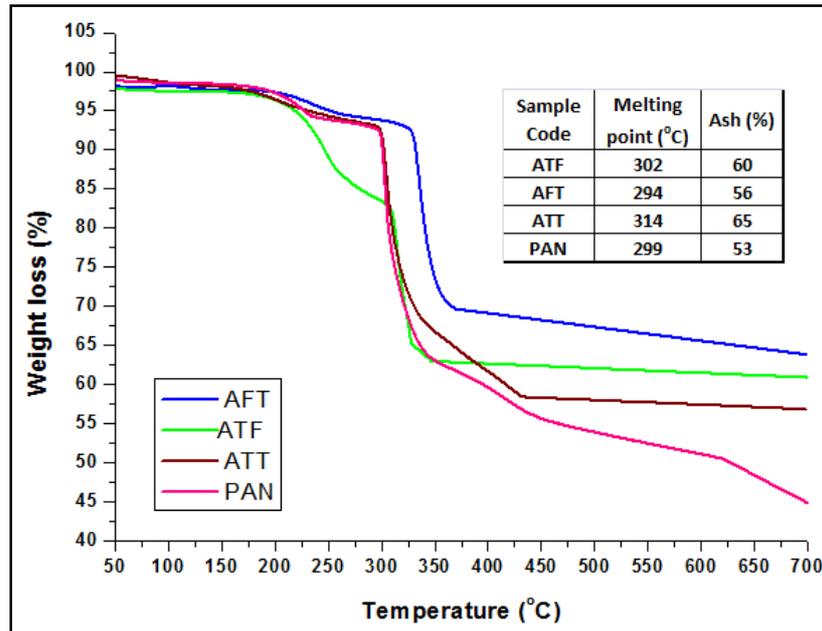

Figure 2 TGA profiles of PAN, PAN/CNT-CNF ratio 5:3 (AFT), PAN/CNT-CNF ratio 3:5 (ATF) and PAN/CNT-CNF ratio 5:5 (ATT)

Table 1 Summary of thermal properties of the PAN, PAN/CNT and PAN/CNF electrospun nanofibers

| Sample Code | Degradation stages | | | | | | Ash (%) |
| | First | | Second | | Third | | |
	Temp. (ºC)	E (%)	Temp. (ºC)	E (%)	Temp. (ºC)	E (%)	
P 06	35 – 256	9	299 – 353	38	353 - 653	54	46
ATF	34 – 274	15	302 – 327	35	343 -700	39	60
AFT	34 – 228	5	294 – 339	32	339 – 429	44	56
ATT	34 – 263	6	314 – 367	30	-	-	65

Figure 3 shows a typical high frequency semicircle and low frequency spike of a complex impedance plot for the highest conducting PAN/CNT-CNF (ATT) at room temperature (25 ºC). While, Table 2 shows the summaries electrospun PAN properties according to average fiber diameter, thermal stability, electric resistivity and conductivity. The high-frequency semicircle and a low-frequency spike correspond to charge transfer domination and interfacial impedance of the polymer respectively. In this study, however, the semicircle is significantly depressed and broadened indicating low capacitive properties of the fiber, while

the non-vertical spike at low frequency represents roughness and heterogeneity of the electrode/polymer surface [21-22].

The conductivities' membranes as function of CNT/CNF ratios are evaluated from their bulk resistance, R_b, in Figure 3 and the values are given in Table 2. While PAN exhibits lowest conductivity (1.6×10^{-7} Scm^{-1}) among other membranes, the highest conductivities obtained are those of membrane with equal amounts of CNT and CNF (ATT) i.e. 4.8×10^{-4} Scm^{-1}. The results also show a positive arrangement between conductivity of the membrane and amount of CNT added in which the conductivity has improved as CNT amount increased. The incorporation of CNT might be enhanced by the charge transfer, leading to an increase in the conductivity of final product [23]. However, varying the amount of CNF has not significantly improved the conductivity of polymer composite.
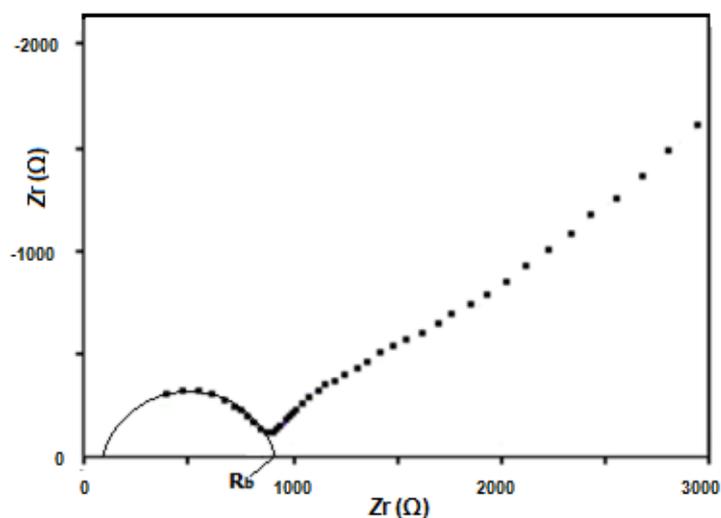

Figure 3 Complex impedance plot for the highest conducting of ATT sample at 25 °C.

Table 2: Summaries properties of electrospun PAN nanofibers

Sample	Average Fiber Diameter (micrometer)	Thermal Stability (%)	Electric Resistivity (Ω cm^{-1})	Conductivity (Scm^{-1})
PAN	0.59	45.9	2.49×10^{5}	1.6×10^{-7}
ATF	0.68	60.0	857.4	4.6×10^{-4}
AFT	0.76	56.0	1179.0	3.3×10^{-4}
ATT	0.83	65.0	817.2	4.8×10^{-4}

CONCLUSIONS

In this work, three ratios of mixture CNT-CNF filled PAN have been successfully fabricated by using electrospinning technique. The ratio of mixture of CNT into CNF was 3:5, 5:3 and 5:5 has been studies. The effects of CNT-CNF ratio into the morphological structure, thermal stability and conductive properties to the electrospun fibers were discussed. It was observed that increasing of CNT-CNF ratios tend to increase the fiber diameters of PAN. This was attributed to the stretching of fiber's diameter in the PAN polymer matrix then improved the thermal properties. Average fiber diameter was 0.68, 0.76 and 0.83 micrometer in ratio of CNT-CNF were 5:3, 3:5 and 5:5 wt% respectively. It was informed that all the fiber's samples had smooth, and fewer beads were observed. While, from the thermal study, it was found that electrospun with an equal ratio of CNT-CNF has a higher thermal stability with higher melting points. Also, from the conductivity study, it was revealed that the conductivity of electrospun was high at 4.8×10^{-4} Scm^{-1}. It could therefore be concluded that 5:5 ratio of mixture of CNT-CNF was giving a better thermal stability and higher conductivity.

ACKNOWLEDGEMENTS

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