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Invited Paper

Morphology and Mechanical Properties of Polyacrylonitrile/Multi-Walled Carbon Nanotube (PAN/MWNTs) Nanocomposite Electrospun Nanofibers

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Abstract. *In this research the morphology and mechanical properties of PAN/MWNTs nanofibers are studied. The electrospinning process is used to produce fiber at micro and nano scale. The dispersion of MWNTs in polymer solution is the key factor to obtain desirable properties in the final product. Thus, the dispersion condition is investigated using SEM images. The morphological study of fiber mats show that by increasing the amount of MWNTs in the polymer from 0 to 1 wt%, the surface roughness of fibers is increased. Increasing the percentage of MWNTs in fiber improves the tensile stress at maximum load for about 114% and modulus for about 40%.*

Keywords: *Nanofiber; Electrospinning; Mechanical property; Carbon nanotube; Nanocomposite.*

INTRODUCTION

The special properties of carbon nanotubes (CNTs) have caused considerable interest in investigating their physical and mechanical potential toward the development of a variety of technological applications. It has been theoretically and experimentally confirmed that nanotubes possess remarkably high stiffness and strength [1]. Carbon nanotubes also have high electrical and thermal conductivities [2]. The unique mechanical and physical properties of carbon nanotubes combined with their high aspect ratio and low density have brought about extensive research in preparing and synthesizing the various nanocomposites of carbon nanotube to improve mechanical, electrical, thermal and other properties of materials at macro and nano scale [1,3,4]. The effective superior properties of carbon nanotubes transformed to nanocomposites are crucial. It is necessary to create strong interfacial bonding between carbon nanotubes and polymers.

In recent years, researchers have become interested in the composition of polymeric fibers with carbon nanotubes for a variety of applications. Different types of polymers were used to produce nanocomposites through different processes. Electrospinning is a unique method in which CNTs can be embedded in nanofibers formed as a non-woven web. The performance of this method relies on how well the CNTs are dispersed within fibers. It was found that in the electrospinning process, carbon nanotubes could be well-aligned along the fiber axis.

In a common electrospinning process, a high voltage is applied to create an electric field between the droplet of polymer solution at the tip of a needle and a collector plate. A voltage source is used to charge the solution while the collector is electrically earthed. This creates an electrostatic force between the needle and the collector. As the voltage is increased, the electric field is intensified causing a force to be built up on the pendant drop of polymer solution at the tip of the needle. This force acts in the direction opposing the surface tension of the drop. The increase of electrostatic force causes the drop to be elongated and forms a conical shape known as Taylor cone. When the electrostatic force overcomes the surface tension

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of the drop, the charged continuous jet of solution is ejected from the cone. The jet of solution accelerates towards the collector, whipping and bending wildly. As the solution moves away from the needle toward the collector, the jet is rapidly thinned and dried as the solvent evaporates. On the surface of the grounded collector, nanofibers are deposited as a web with random orientation [5-7].

The incorporation of carbon nanotubes into nanofibers has demonstrated the enhancement of electrical conductivity of polyurethane/polyaniline/ MWNT and poly(vinylidene fluoride)/SWNT nanofibers [8,9].

The improved thermal stability and Young's modulus in PAN/SWNT nanofibers have also been observed [10].

Since the macroscopic orientation of MWNTs in the polymer matrix of nanofibers during electrospinning is necessary toward many meaningful technological applications, in the present work, the dispersion and distribution of the multi-walled carbon nanotubes embedded in electrospun polyacrylonitrile (PAN) nanofibers and the morphology and mechanical properties of nanofibers formed as a web are investigated.

EXPERIMENTAL

Material

Industrial Polyacrylonitrile (PAN) from Iran Polyacryle Co. with M_w 100,000 g/mol, and N,N-dimethyl formamide (DMF) from Sigma-Aldrich as the solvent for PAN were used. Multi-walled carbon nanotube (MWNT) was purchased from Shenzhen Nanotechnologies Port Co. The purity of carbon nanotubes was more than 95% with 5-15 μm lengths and 10-20 nm diameters. Figure 1 is the SEM image of the nanotubes.

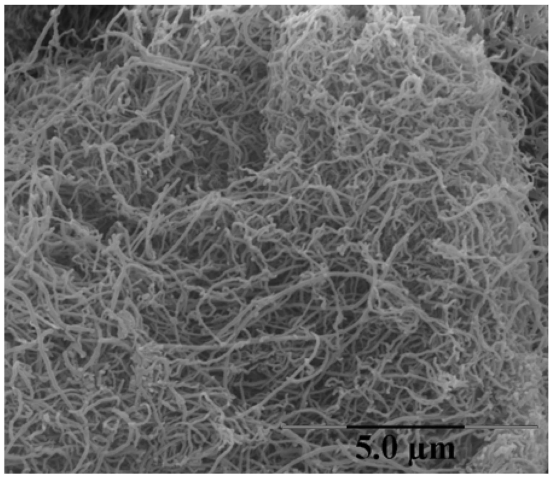


Figure 1. SEM image of multi-walled carbon nanotubes.

Polymer Solution Preparation

Different percentages of multi-walled carbon nanotubes (0.01, 0.05, 0.1, 0.3, 0.5, 1 and 2 wt.%) were added to 5 cc of N,N-dimethylformamide (DMF) that was used for preparing 15% (w/v) PAN solution, in order to disentangle the nanotubes that typically tend to cling together and form lumps which are very difficult to be processed [11]. Multi-walled carbon nanotubes were dispersed in DMF at different concentrations using probe sonicatore (SONICS) at room temperature for about 1 hour. Magnet stirrer (Heidolph) was used to mix the polymer with carbon nanotubes solution until the polymer was uniformly dissolved in the solvent.

Electrospinning

Figure 2 shows the experimental set-up used to produce nanofiber. The electrospinning process was carried out by connecting a high voltage power supply from Gamma High Voltage Research (± 30 kV, 1.5 mA). The voltage of 14-20 kV was applied to the nozzle whose tip was at 14 cm distance from the surface of the grounded collector. The nozzle was a B-D 22.5G needle with a flat tip. A KD scientific syringe pump was used to provide a constant feed rate of solution during electrospinning.

Methods

The nanofiber morphology was analyzed by scanning electron microscope (SEM: Quanta 200F) and transmission electron microscopy (TEM: JEM 3010, JEOL). The sample holders for SEM were coated with gold by

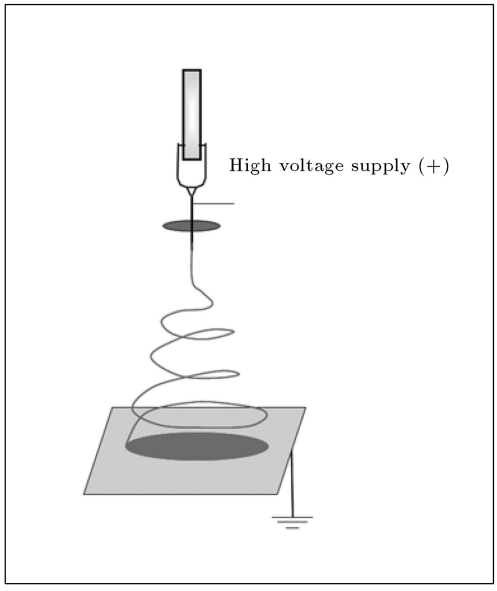


Figure 2. Schematic experimental set-up of electrospinning.

ion sputtering for 90 seconds using an auto fine coater (JEOL JFC-1600).

The diameter of the nanofibers was measured by ImageJ software using the SEM images. The mechanical properties of electrospun webs were analyzed using a universal testing machine (INSTRON 2519) under a crosshead speed of 10 mm/min and gauge length of 2 cm at room temperature with 10 N and 10 kN load cell. The nanofibers thicknesses were measured by the digital micrometer (Mitutoyo).

RESULTS AND DISCUSSION

Polymer Solution Characterization

PAN/MWNTs solution was prepared using ultrasonic energy to disperse the nanotubes in the solvent and incorporate them into nanocomposites. Polyacrylonitrile solutions containing MWNTs were then electrospun to yield nanofiber MWNTs composite. MWNTs were homogeneously dispersed and stabled having a dark black ink-like appearance without precipitation for several days (Figure 3).

For improving mechanical properties of polymer and preparing nanofibers with homogeneous surface morphology, the condition of dispersion is very critical and plays a significant role in achieving effective properties in nanofibers. It is important that nanotubes can be dispersed without any breakage and aggregation. To have the optimum dispersion, the time and intensity of ultrasonic wave were studied in this effort. By considering the SEM images of dispersed nanotubes, it was found that mixing for about 1 hour with 30% magnification was sufficient to achieve a well-dispersed solution. In Figures 4 and 5, two different weight percentages of nanotubes at two magnifications are shown. They reveal that by incrassating of carbon nanotubes in the solution, the dispersion action is not properly performed.

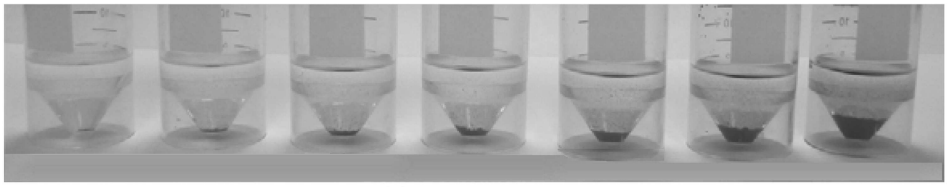
To improve the dispersion of nanotubes at high concentration, the multi-walled carbon nanotubes were refluxed in nitric acid 65% and stirred at 150°C for 8 hours to attach functional groups of carboxyl and hydroxyl groups. MWNTs were then cool dried after rinsing 3 times by distilled water.

Morphology of Electrospun Nanofibers

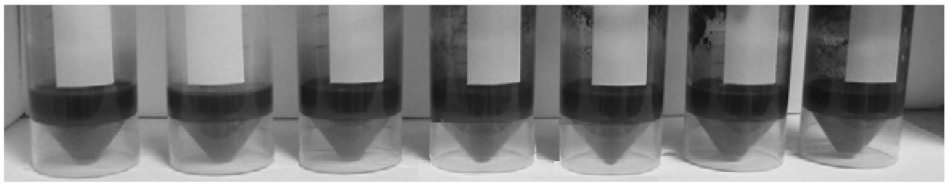
The morphology of the nanofibers was considered by SEM. Figure 6 shows the SEM image of PAN nanofibers webs at different concentrations of MWNTs. It was observed that fibers without any beads could be produced at 15% (w/v) concentration of polymer. Bead areas act as stress concentration points and affect the mechanical properties of mat.

It was necessary to minimize any aggregated MWNTs on the surface of fibers to have beadless and uniform nanofibers webs. By increasing the amount of MWNTs in fiber, the surface roughness of fibers was changed.

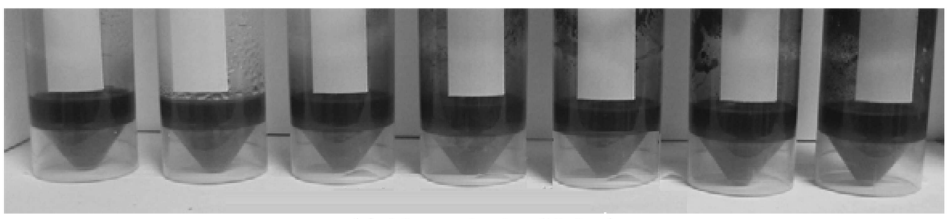
MWNTs aligned along the nanofiber axis were expected to enhance the mechanical properties of



(a) Before sonication



(b) After sonication (1 day)



(c) After sonication (15 days)

Figure 3. Different percentage of MWNTs (0.01, 0.05, 0.1, 0.3, 0.5, 1 and 2 wt%) in DMF that was sonicated for 1 hour. (a) Before sonication; (b) after 1 day; and (c) after 15 days.

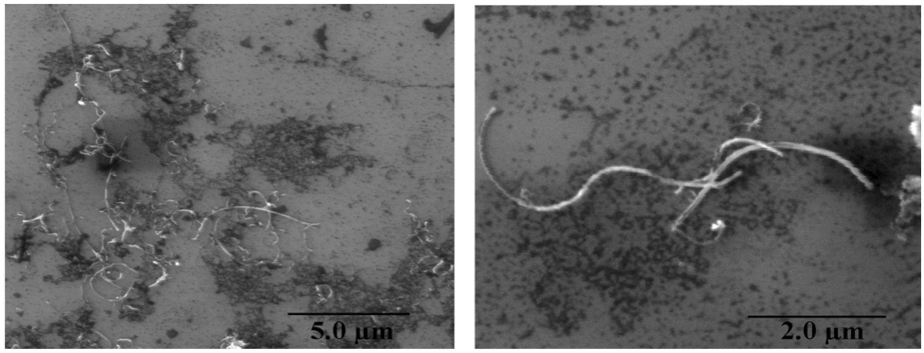


Figure 4. SEM of thin film that was prepared with dispersed 0.01 wt% MWNTs in DMF.

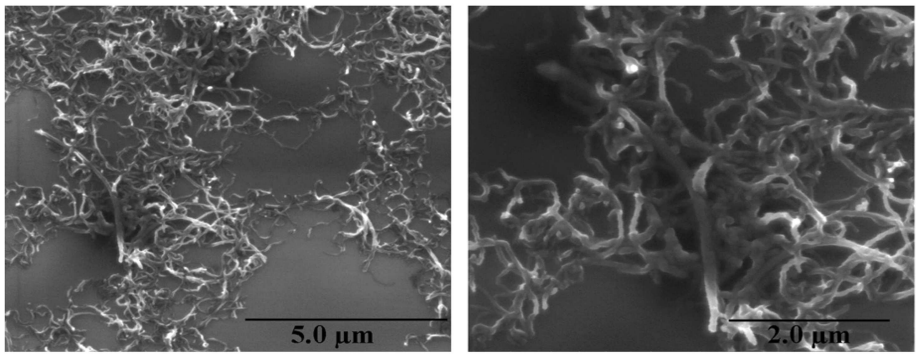


Figure 5. SEM of thin film that was prepared with dispersed 1 wt% MWNTs in DMF.

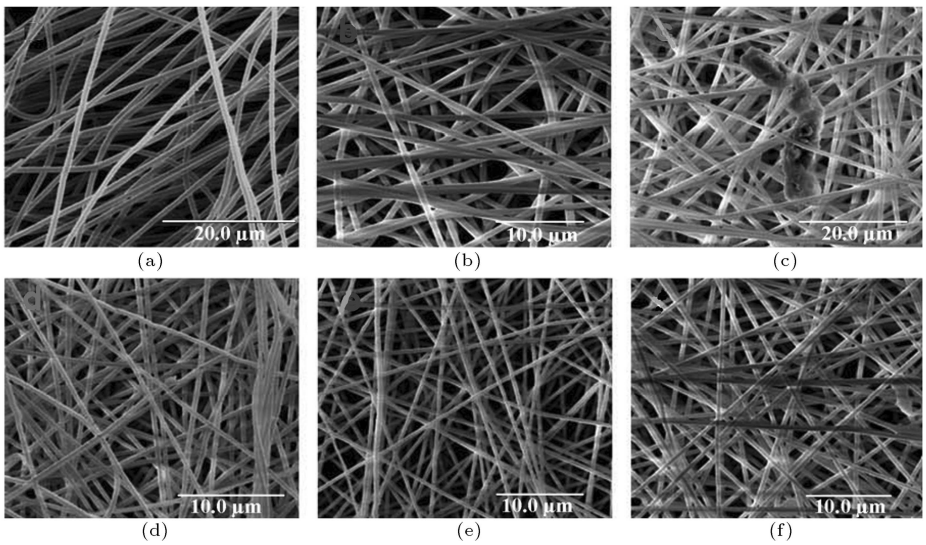


Figure 6. SEM image of nanofibers with different weight percentage of MWNTs. (a) PAN 15%; (b) PAN/MWNT 0.01 wt%; (c) PAN/MWNT 0.05 wt%; (d) PAN/MWNT 0.1 wt%; (e) PAN/MWNT 0.5 wt%; and (f) PAN/MWNT 1 wt%.

fibers. In Figure 7, the high-magnified SEM images of nanocomposite fibers and also the TEM image are shown. In SEM images, nanotubes can be mostly observed on the surface of fibers. They show how the high modulus nanotubes can bend the nanofibers.

Since the carbon nanotubes possess a high electron density compared with the PAN polymer matrix, the nanotubes are displayed as darker structures embedded in the PAN nanofibers. The MWNTs were aligned along the fiber axis of the nanofibers.

Mechanical Characterization

The traditional stress-strain method using stretching test was employed to evaluate the mechanical properties of the electrospun nanofiber mats. 10 pieces of the

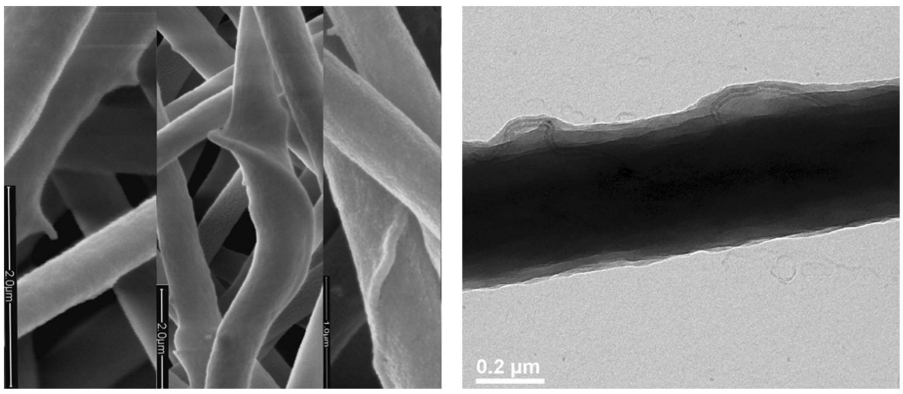


Figure 7. SEM images of PAN/MWNT 1 wt% (left); TEM images of PAN/MWNT 0.5 wt% (right).

Table 1. Mechanical properties of nanofibers mat and their average diameter (with their confidence level value ±).

	Modulus (MPa)	**Tensile Stress at Maximum Load (MPa)**	**Tensile Strain at Maximum Load (%)**	**Nanofiber Diameter (nm)**
PAN//MWNT 0.0%	0.24 ± 0.06	1.9 ± 0.3	33 ± 5	210 ± 21
PAN/MWNT 0.01%	0.26 ± 0.04	1.5 ± 0.2	14 ± 2	691 ± 43
PAN/MWNT 0.05%	0.25 ± 0.02	1.7 ± 0.2	21 ± 4	511 ± 29
PAN/MWNT 0.1%	0.25 ± 0.04	2.2 ± 0.4	53 ± 7	438 ± 29
PAN/MWNT 0.5%	0.28 ± 0.02	2.3 ± 0.3	48 ± 4	386 ± 21
PAN/MWNT 1.0%	0.33 ± 0.02	3.1 ± 0.4	68 ± 5	520 ± 4

nanofiber mats from each group (PAN15%, PAN15% with 0.01, 0.05, 0.1, 0.5 and 1 wt% of MWNTs) were stretched. The average of tested features was reported as the properties of composite nanofibers.

The results are presented in Table 1. The results confirm the enhancement of mechanical properties by increasing the MWNTs contents in the nanofibers. More improvement can be achieved above the percolation threshold value of MWNTs in fibers.

For a simple composite system without micromechanical interlocking and chemical bonding between the filler and the matrix, load transfer from the matrix to the filler is realized through a weak van der Waals bonding between the filler and the matrix [12]. Thus, it can be similarly stated that the load can be transferred from the PAN matrix to the MWNTs fillers by van der Waals bonding.

To achieve the significant mechanical enhancements, the main challenges lie in obtaining a good dispersion, optimizing the interface between polymer and nanotubes, and having high quality structures in sufficient quantities.

The mechanical data in Table 1 show that the tensile modulus of PAN/MWNTs composites is improved, specially for 0.5 and 1 wt% of MWNTs. For tensile stress and strain at maximum load, the improvement takes place above 0.1 wt% of MWNTs in nanofibers. Considering the higher value of nanofiber average diameters in 0.01 and 0.05 wt% concentrations, it can be concluded that the homogenous dispersion of MWNTs seems to be poor for these concentrations. In non-homogenous dispersion of nanotubes in polymer matrix, the nanotube can be considered as a stress concentration point in nonofiber's structure and it can result in the weakness of mechanical properties of nanofibers.

The volume density of fibers in the mat, the mixing level of nanofibers, the fusion frequency of the nanofibers, the existence of imperfections and branching in fibers are expected to affect the tensile properties of a mat electrospun under different process conditions even from the same polymer/solvent system.

CONCLUSION

The morphological and mechanical properties of homogeneous PAN/MWNTs nanocomposite mats of nanofibers containing different concentrations of MWNTs were investigated. TEM images showed that MWNTs were almost aligned along the electrospun nanofibers. By increasing the amount of MWNTs in polymer, the surface roughness of fibers was increased.

The tensile modulus in PAN with 1 wt% MWNTs was increased about 40% in comparison with PAN without MWNTs. The tensile stress at maximum load was also improved about 114%.

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BIOGRAPHIES

Maryam Yousefzadeh received her B.S. in Textile Technology Engineering from Amirkabir University of Technology in 2002. She also received her M.S. and Ph.D. degrees (with the highest honor) in the same field and from the same university in 2004 and 2010, respectively. She is a member of Iranian National Elite Foundation and Iranian Inventors Association. Her active fields of research are Electrospinning and Nanofibers, Polymeric Nanocomposite and Image Analysis.

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Masoud Latifi is Professor in the Department of Textile Engineering, Amirkabir University of Technology, Tehran, Iran. He is also the member of Textile Research Institute (ATMT) and Center of Excellence in Textile (CENMIT). He received his Engineering Degree (B.S.) in Textile Technology from Amirkabir University of Technology in 1985 and Ph.D. in 1990 from the University of Leeds, Leeds, UK. His research areas are Nano Fibrous Structure, Smart, Technical and Conductive Textiles and Applied Image Processing with a teaching and research experience of 20 years. Sixty postgraduate students have obtained their degree under his supervision. He has authored or co-authored over 120 research papers.

Seeram Ramakrishna has been the Vice-President (Research Strategy) of the National University of Singapore since 2008. He is a Professor of Mechanical Engineering. He was a former Dean of NUS Faculty of Engineering from 2003 to 2008, and has been a founding Co-Director of NUS Nanoscience & Nanotechnology Initiative from 2003 to 2010. He received his Ph.D. in Materials Science & Engineering from the University of Cambridge and General Management Training from the Harvard University. He is an acknowledged global leader for his pioneering work on Science and Engineering of Nanofibers for Regenerative Medicine, Harvesting Solar Energy, and Water Treatment.