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RESEARCH ARTICLE - MECHANICAL ENGINEERING

Mechanical Properties and the Characterization of Polyacrylonitrile/Carbon Nanotube Composite Nanofiber

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Abstract
This work describes the fabrication of the composite nanofibers containing polyacrylonitrile polymer (PAN) and different weight percentage of carbon nanotubes (CNTs) using electrospinning technique which is simplest and highly versatile method to enhance the mechanical properties by removing the surface defects of the composite nanofibers. The tensile test, X-ray diffraction, scanning electron microscopy and Fourier transform infrared spectroscopy measurements are used to find the mechanical properties and the characterization of PAN/CNT composite nanofibers. The result demonstrated that adding CNTs to the polymer enhances the mechanical properties like tensile strengths and Young's modulus with an average 55 and 60 %, respectively at only 0.1 wt% of CNTs.

Keywords Composite nanofibers · Mechanical properties · Electrospinning · Tensile strengths · Young's modulus

1 Introduction

Electrospinning is the simplest technique that is used in producing the nanofibers [1,2]. The principle of this technique is based on generating high voltage and when the surface tension is overcome by the electrostatic forces, a charged polymer jet is ejected from the tip of the needle [3]. The mechanisms of the electrospinning technique are complicated, and the production of the fiber formation process has been nowadays the topic of global research [4,5]. It is easy to get electrospun nanofibers from many synthetic polymer types such as polyesters, nylon, polyurethane as well as from natural polymers such as silk, chitosan, collagen, alginate, cellulose [6]. Polyacrylonitrile (PAN) has a very good chemical and physical characteristics that make it very easily electrospinning into nanofibers morphology like a good commercial availability, mechanical properties and environmental stability [7]. PAN contains also an anionic group which adsorbs the cationic dye molecules very fast. There are some researcher's works on the electrospun PAN composite nanofiber and its applications [8,9].

Composite materials are generated from the combination of two or more constitutive materials which are prominent materials with multifunctional properties like chemical and physical property. The composite nanofibers have an important role in material science due to their properties (optical, mechanical, catalytic, thermal, electrochemical and electrical properties) that can be implemented in specific areas such as catalysis, filtration, nanocomposites, protective textiles, nanofibrous structures, drug delivery systems and tissue scaffolds [10,11]. In this regard, carbon nanotubes are found to be an ideal reinforcement of choice due to their superior mechanical properties caused by the unique structures made of hexagonal rings. In addition, CNTs improves the mechanical, electrical, and thermal conductivity of the fibers and thereby can potentially enhance the applications of the electrospun fibers [12,13]. Many reports had studied the added of CNTs into a polymer to produce a composite nanofiber by electrospinning technique [14]. Therefore, the inclusion of CNTs could be a promising strategy for improving the mechanical properties of PAN nanofibers [15,16]. Moreover, adding a high concentration of CNTs make a higher resistance from heat shrinkage during carbonization processes and make a better growth of carbon crystal during the carbonization of PAN [17]. Electrospun composite nanofiber

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was used in several applications like optical fiber, sensors, fuel cells, water treatment and filtration [18,19]. Therefore, the membrane should be stable at high stresses like (compression, tensile and shear) and high strain to avoid the mechanical failure during the filtration process. In this regard, adding the nanoparticles for strengthening the composite nanofiber membrane and helping for removing the heavy metals and degradation the organic dyes from aqueous solution [20].

The main objective of this work is to propose a strategy for enhancing the mechanical properties of PAN nanofibers by the addition of CNTs fillers. Therefore, in this work, we studied the characterization and the mechanical properties of the pure PAN and the PAN with different concentration of CNTs (0.05, 0.1, 0.5 and 1 wt%) to prepare the composite nanofiber by electrospinning technique. Scanning electron microscopy and Fourier transform infrared spectroscopy were employed to validate the good dispersion of PAN into CNTs NPs. The morphology and structure of the electrospun nanofiber membranes were examined by SEM, FTIR, and XRD techniques. The mechanical properties of PAN and PAN/CNT nanofiber membranes were evaluated by the tensile tests. Five samples of PAN and PAN/CNT with different CNTs concentration have been prepared.

2 Experimental

2.1 Material

Polyacrylonitrile, PAN (MW = 150,000) and *N*, *N*-dimethylformamide (DMF) were purchased from Sigma Aldrich, Sweden. Multi-walled carbon nanotubes (MWNTs) (purity 95 wt%; diameter: 10–30 nm; length: 20 μm) were synthesized, and the procedure is described elsewhere [21,22].

2.2 Composite Nanofibers Formation

The synthesis process of PAN/CNT nanocomposites was prepared in following steps first, 0.5 g of PAN was dissolved in 4.5 g of DMF, at 50 °C for 4 h. Second, functionalized CNTs with different concentration were added to the solution. MWCNTs were oxidized by refluxing at 120 °C in mixed acid (H_2SO_4:HNO_3 = 3:1) for 30 min and then the mixture was diluted with water and filtered. The obtained samples were washed by distilled water and dried in an oven at 60 °C for 12 h [23,24]. Subsequently, the mixture of the PAN/CNT was magnetically stirred at 40 °C for 20 min at room temperature. Afterward, the mixture was kept in ultrasonication for 30 min to dissolve the CNT into the PAN. After preparing the PAN/CNT solution, the electrospinning process will be achieved by putting the solution in the syringe with a flow rate 0.4 ml/h at room temperature. The two cables of the power supply put at the needle tip and the collector. The operation was synthesized at a high voltage 28 kV. That high voltage generates a horizontal electric force between the needle tip and the collector. The distance between the tip and the collector in a range of 15–20 cm with 1 ml/h feeding rate. The produced composite nanofiber was collected on the aluminum foil. Then, the composite nanofiber web was left at 70°C to remove the solvent residues for 24 h. Figure 1 showed the schematic illustration of the whole experimental process of the composite nanofibers.

2.3 Characterization

Scanning Electron Microscopy (SEM, Ametek FEG 250) was used for measuring the morphology of the composite nanofibers. The X-ray diffraction (XRD) in a Rigaku X-ray diffractometer operated with Cu K α radiation ($\alpha = 1.540$ Å) is used for examined the structural characterization. Fourier transform infrared (FTIR) spectroscopy is used to make a characterization of the configuration bonding of the com-

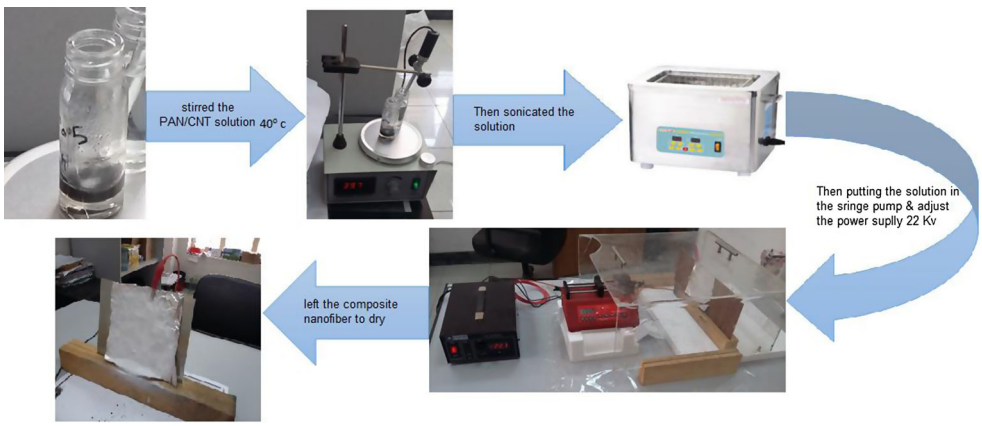

Fig. 1 Schematic illustration the preparation of electrospun PAN/CNT composite nanofibers

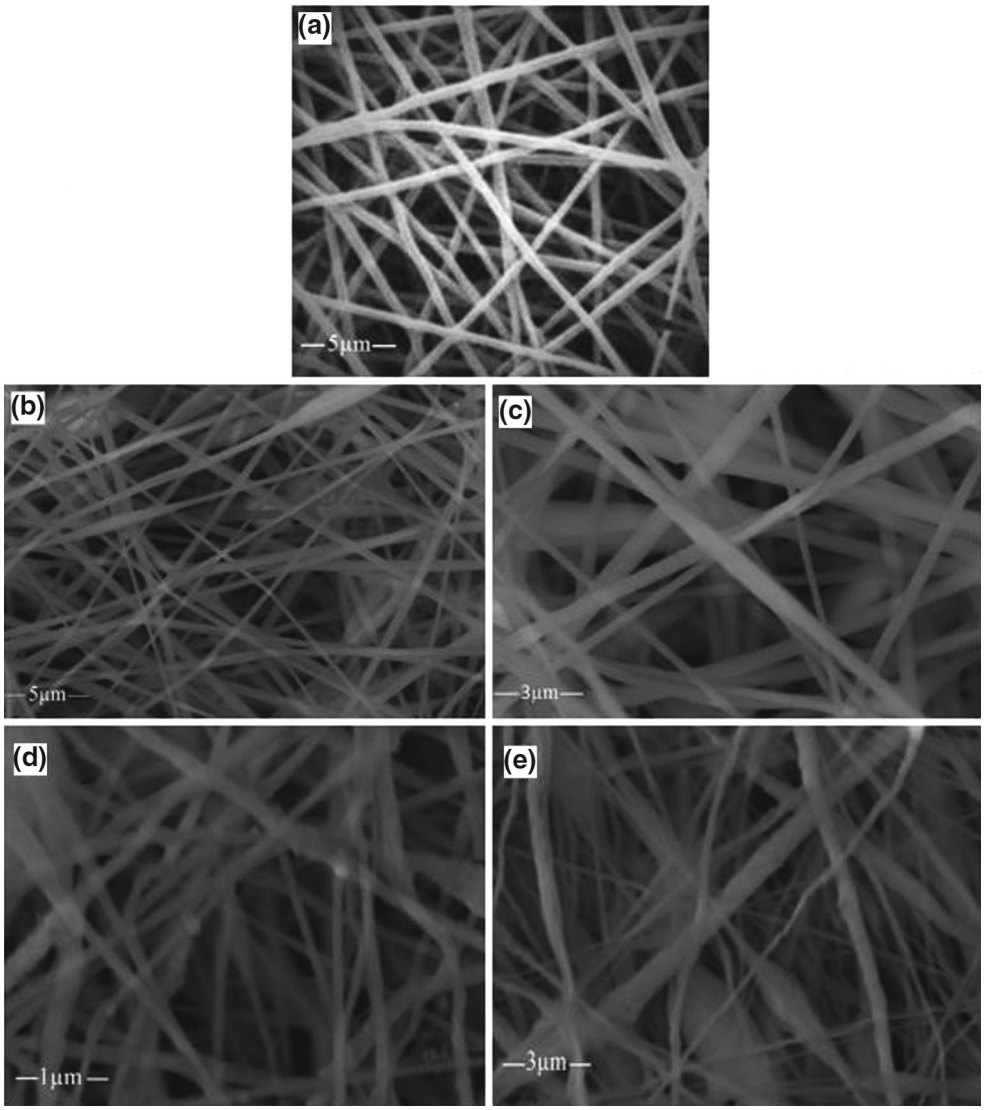

Fig. 2 SEM image of **a** PAN nanofiber web, **b** PAN/CNT (0.05%wt) composite nanofiber web, **c** PAN/CNT (0.1%wt) composite nanofiber web, **d** PAN/CNT (0.5%wt) composite nanofiber web, **e** PAN/CNT (1%wt) composite nanofiber web

posite nanofibers. Image processing software (ImageJ) was used to measure the diameters of the fiber.

3 Mechanical Testing

The tensile properties of the PAN/CNT composite nanofibers were determined by a tensile tester (Tensometer type"w" by Monsanto, U.K) according to ASTM D3039 at a 5 mm gauge length and a 5 mm/min cross-head speed [25]. The specimens were cut along the vertical direction of the electrospun fibrous membranes to a 20 mm wide and 60 mm length size. For each nanofibers mat, five samples were used for tensile measurements to obtain the average values. The Young's modulus of the samples is derived from the slope of the initial linear part of the stress–strain curves.

4 Results and Discussion

4.1 The Formation of the Composite Nanofiber Web

The size of the particles and the surface morphology of the composite nanofiber film can be observed by using the scanning electron microscopy. Figure 2 shows the SEM images of PAN and PAN/CNT composite nanofibers with different concentration of CNT. Figure 2a shows a very smooth, uniform and clear surface of PAN nanofiber with a spun fiber diameters range between from 100 to 185 nm. In Fig. 2(b–d), there are a different concentration of CNT in PAN composite nanofiber, a small beads and groups of CNT on the fiber was observed in Fig. 2(b–c). Moreover, Figure 2d and e shows that there are bulges and many groves in the fiber web and it has been found that a group of CNTs pulled out of the fiber

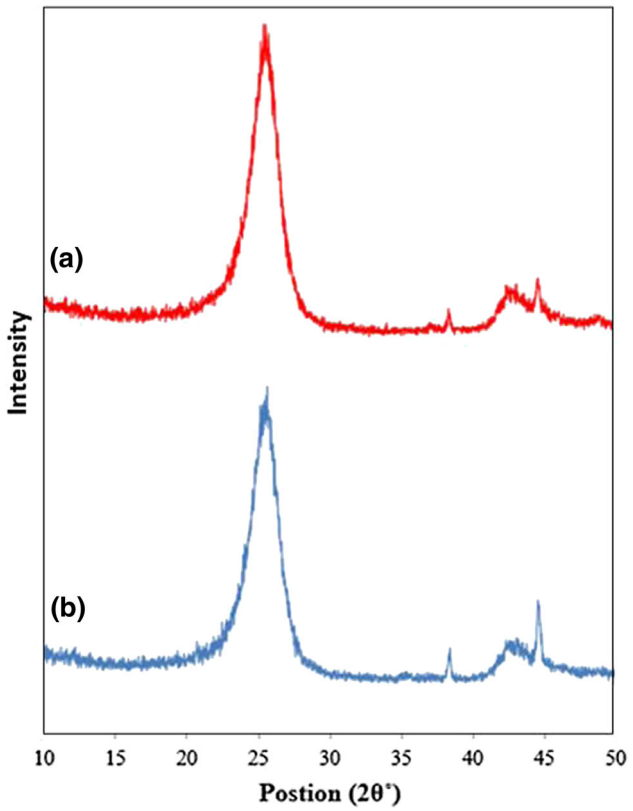

Fig. 3 XRD patterns *a* PAN nanofibers, *b* PAN/CNT nanofibers

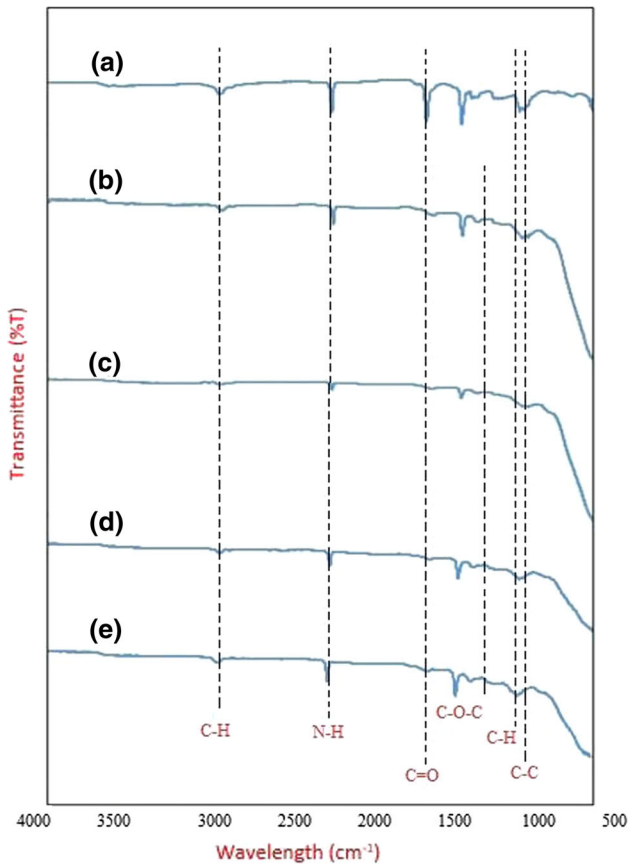

Fig. 4 FTIR spectra of *a* PAN, *b* PAN/CNT(0.05%), *c* PAN/CNT(0.1%), *d* PAN/CNT(0.5%) and *e* PAN/CNT(1%)

surface. The spun fiber diameters ranged in Fig. 1b from 155 to 215 nm, Fig. 1c ranged from 170 to 340 nm, Fig. 1d ranged from 185 to 460 nm and Fig. 1e ranged from 190 to 530 nm. As observed, the fiber diameters are small which give a high porosity and high mechanical properties that is required in various application.

Furthermore, XRD analysis was used to examine the phase structures of the composite nanofiber and the main PAN nanofibers. As shown in Fig. 3a, the main PAN nanofiber found that the broad diffraction peak centered at 25.74°. The composite nanofibers in Fig. 3b have become sharper when increasing the percentage of content of CNT in the PAN/CNT composite nanofiber. The diffraction peak of PAN/CNT appeared at $2\theta°$ value of 25.86; these results cleared that the electrospun nanofiber is a high structural quality because there are not any significant diffraction peaks of any phases are appeared in the XRD patterns.

Moreover, the FTIR spectroscopy was used to know the spectral differences between the PAN and PAN/CNT composite nanofibers. Figure 4a shows the PAN nanofiber spectrum displaying the characteristics peaks of methylene (C–H) group at 1190–1390 and 3195 $cm^{-1,}$ the nitrile (N–H) group at 2342 cm^{-1} and carbonyl stretching vibration (C=O) at 1700 cm^{-1} [21]. Figure 4(b–e) also shows a different weight percentage of PAN/CNT nanofiber spectrum displayed the characteristics peaks of nitrile (N–H) group at 2342 cm^{-1}, carbonyl (C=O) group at 1700 cm^{-1}, methylene (C-H) group at 3159 cm^{-1} and the C–O–C stretching vibrations of CNT group at 1290 cm^{-1}.

The mechanical properties of the electrospun fibers are important for their successful application to tissue engineering, material composites, filtration and drug delivery. In this regard, tensile test and elastic modulus were used to evaluate the mechanical properties of the composite nanofibers. The mechanical properties of the CNTs transferred to the polymer fiber matrix during the electrospinning process were investigated at different concentration of CNTs (0.05, 0.01, 0.5 and 1 wt%). Figure 5 shows the stress–strain behavior of the composite nanofiber. It can be shown that the addition of CNTs to the PAN nanofiber enhanced the mechanical properties of the tensile strengths and the Young's modulus about 55 and 60 %, respectively. The result indicated that the incorporation of CNTs fillers has a large influence on the mechanical properties of the composite nanofiber. This enhancement may be due to the aspect ratio of the CNT that causes an increase in the strength and the stiffness of the interfacial bonding of the PAN/CNT. In addition, to the hydrogen bonding, that occurs between the groups of the CNTs surface (carboxylic

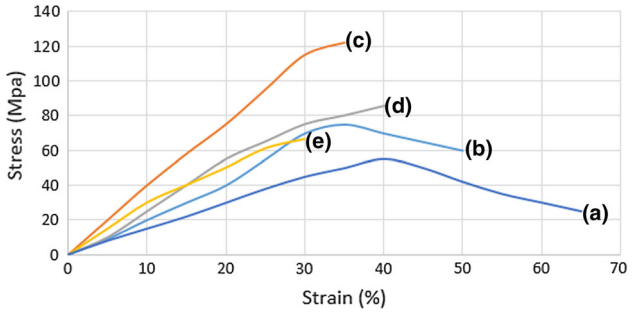

Fig. 5 The stress–strain curve of *a* PAN nanofiber, *b* PAN/CNT (0.05%), *c* PAN/CNT (0.1%), *d* PAN/CNT (0.5%) and *e* PAN/CNT (1%) composite nanofiber

Table 1 List of Young's modulus and tensile strength of the PAN/CNT composite nanofiber

Sample (MWNT) wt%	Young's modulus (MPa)	Tensile strength (MPa)
0	160 ± 8	55.2 ± 2.2
0.05	180 ± 9	75.15 ± 3
0.1	400 ± 20	122 ± 4.8
0.5	200 ± 10	85.5 ± 3.4
1	300 ± 15	66.4 ± 2.7

and the amino groups of PAN chain). Moreover, the bond in the PAN is a triple bond (C_3H_3N) that contains nitrogen causing an increase in the number of triple bonds in the composite nanofiber which makes the PAN/CNT stronger. Moreover, adding an excess percentage of CNT to the polymer make the triple bonds become too much in PAN/CNT that is lead to decrease the tensile strength of it. Table 1 provides the detailed information about the tensile strength and Young's modulus of PAN nanofiber and PAN/CNT composite nanofiber. As observed at a low concentration of CNTs, the PAN/CNTs composite nanofibers give better mechanical properties. On the other hand, at high concentration of CNTs, the tensile strength and Young's modulus was reduced.

Moreover, Table 2 lists the maximum tensile strength and Young's modulus of PAN/CNT composite nanofiber as reported in the literatures. The data indicates that our PAN/CNT composite nanofiber shows higher tensile strength and Young's modulus than many other reported PAN/CNT. Therefore, it is concluded that the PAN/CNT nanofibers could be used as an effective filtration for removal of organic dyes and heavy metals in an aqueous solution.

5 Conclusions

Successful fabrication of composite nanofibers with different concentration of CNT (0.05, 0.1, 0.5 and 1%) was achieved using electrospinning technique. The result indicated that the tensile test shows a great enhancement in the mechanical properties of the nanofiber web when adding a small amount of CNT. The tensile strength and Young's modulus of the composite nanofibers were enhanced about 55 and 60 %, respectively, at 0.1 wt% of CNTs. SEM images appeared that the average composite fiber diameter from 155 to 440 nm and the diameter pristine nanofiber have become very smooth and clear and ranged between 100 to 185 nm.

Table 2 Comparison of tensile strength and Young's modulus of the PAN/CNT composite nanofiber

Material	MWCNTs loading (wt%)	Tensile strength (MPa)	Young's modulus (MPa)	Ref.
PAN/CNT	0.3	130	470	[26]
PAN/CNT	0.2	109.2 ± 1.2	180 ± 0.2	[27]
PAN/CNT	5	80	310	[15]
	20	37.1	440	
PAN/CNT	0.55	40.7 ± 2.7	1144.4 ± 37	[28]
	0.11	29.7 ± 1.2	937 ± 12	
PAN/CNT	0.1	122 ± 4.8	400 ± 20	This work

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