

Relationship between Single Walled Carbon Nanotubes Individual Dispersion Behavior and Properties of Electrospun Nanofibers

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The dispersion stability behavior of single walled carbon nanotube (SWCNT) has important effects on morphological and mechanical properties of SWCNT/polymer composite nanofibers. The effects of SWCNTs incorporation on the morphological and structural developments and the relation between this developments and mechanical properties of the polyacrylonitrile (PAN) nanofibers were demonstrated. The uniform, stable dispersion and well oriented SWCNT within the PAN matrix were achieved through using polyvinylpyrrolidone (PVP) as dispersing agent. Our data indicate that with increasing the amount of SWCNT (from 0 to 2 wt %), the average nanofiber diameter was increased from 163 ± 19 nm to 307 ± 34 nm. The analysis of the mechanical properties of the composite nanofibers displays that they exhibit an improvement in the tensile strength of $\sim 172\%$ from 3.93 ± 0.45 MPa to 10.74 ± 1.03 MPa, and the elastic modulus was increased by $\sim 885\%$ from 61.39 ± 15.58 GPa to 605.08 ± 65.55 GPa, as compared to the pure electrospun nanofibers. The optimal SWCNT concentration for electrospun nanofibers with better morphological and mechanical properties is ~ 2 wt %.

Keywords: Single walled carbon nanotube, Composite nanofiber, Morphology, Mechanical properties.

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1. INTRODUCTION

Nanocomposites are a novel class of composite materials where one of the nanomaterials has dimensions in the range of 1–100 nm. Nanocomposites with nanoparticle are considered as materials that have the propensity to show amazing mechanical, electrical and thermal properties due to the interaction between the matrix and nanoparticle. These composites were reported to have the high strength and also good electrical conductivity at comparatively low carbon nanotubes (CNTs) loading. CNTs exist in two types which depend on number of graphene layers in their structure. The single walled carbon nanotubes (SWCNTs) which known as "Russian doll" structure, consist of a single graphene layer while the multi walled carbon nanotubes (MWCNTs) consist of coaxial cylindrical graphite shells. SWCNTs extraordinary mechanical properties due to carbon-carbon sp^2 bonds and cylinder structure present comparing to many other different nanoparticles and other forms of carbon [1-3].

Polymeric nanocomposites reinforced with SWCNTs are believed to have many potential engineering applications ranging from ultra-strong materials, lithium-ion batteries, electromagnetic interference shielding devices, gas sensors, and biosensors [4]. The various applications of SWCNT/polymer composite materials considerably depend on the individual dispersion and alignment of SWCNTs in the matrix, which is considered a very difficult job to be done. The difficulty in preparing well dispersed SWCNT composite solutions has been related to their higher specific surface area

and consequently, possessing very stronger van der Waals interactions comparing to MWCNT solutions [5]. Therefore, the important challenges in electrospinning process of SWCNT/polymer nanofibers lie in preparing the uniform dispersion and oriented SWCNT within the polymer matrix structures. Non-chemical and chemical methods have been presented for preparing well dispersed SWCNT in the polymer solutions. The chemical methods presented by researchers mainly based on SWCNT oxidation [6], and situ polymerization [7]. The effective non-chemical dispersions have been described by using surfactants or amphiphilic polymers, which can be adsorbed onto the hydrophobic SWCNT surfaces, such as sodium dodecyl sulfate (SDS) [8], polyvinylpyrrolidone (PVP) and polystyrene sulfonate (PSS) [9], and natural polysaccharide Gum Arabic [10]. However, the non-chemical methods have been preferred because, chemical approaches mainly give rise to structure deterioration, non friendly environmental process, and consuming higher amounts of chemicals.

The fabrication of SWCNT reinforced nanofibers is a promising technique to advance composite materials. Among the various methods of producing SWCNT/polymer composite nanofibers, electrospinning is a novel and efficient tool for their fabrication [11-13]. In this work, SWCNTs were dispersed by a non-chemical method and then embedded and aligned in polyacrylonitrile (PAN) / PVP nanofibers by electrospinning process. Finally, the effects of SWCNTs dispersion behavior on the morphological and mechanical properties of the electrospun PAN/PVP composite nanofibers were investigated.

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2. EXPERIMENTAL

2.1 Materials

The SWCNTs were purchased from Research Institute of Petroleum Industry (purity: 95 %, diameter: 0.8-1.1 nm). PAN powder ($M_w = 100000$ g/mol), consisting of 93.7 wt % acrylonitrile and 6.3 wt % methylacrylate and PVP ($M_w = 40000$ g/mol) were supplied with Polyacryl Co. and Sigma-Aldrich, respectively. The solvent used for dissolving PAN/PVP and PAN / PVP / SWCNT dispersion was N, N-dimethylformamide (DMF, Merck).

2.2 Preparation of Composite Nanofibers

Dispersion approach was accomplished in three steps. First, the solution samples were prepared by dissolving 1 w/v % PVP in DMF using magnetic stirrer (Corning Hot Plate Stirrer PC-351) at 25 °C for 1 hr. In the second step; different weights of SWCNTs were dispersed in the PVP / DMF solutions by using a high power ultrasonic homogenizer (UP200, Germany) at 0 °C for 40 min. Finally, the electrospinning solutions were prepared by dissolving 12 w/v % of PAN in sonicated solutions by using a magnetic stirrer at 40 °C for 24 hr (see flow chart in Fig. 1). The prepared solutions were added to a glass syringe with a needle tip (22G, $L = 34$ mm, and $I.D = 0.4$ mm). The feeding rate of the polymer solutions was 0.25 ml/hr and electrospinning voltage of 16 kV was applied to the needle, while the distance between the needle tip and the drum collector was chosen at 18 cm and the take-up speed was set on 100 RPM. The electrospinning of PAN / PVP / SWCNT solutions were performed at 22 ± 2 °C and constant relative humidity (30-35 %).

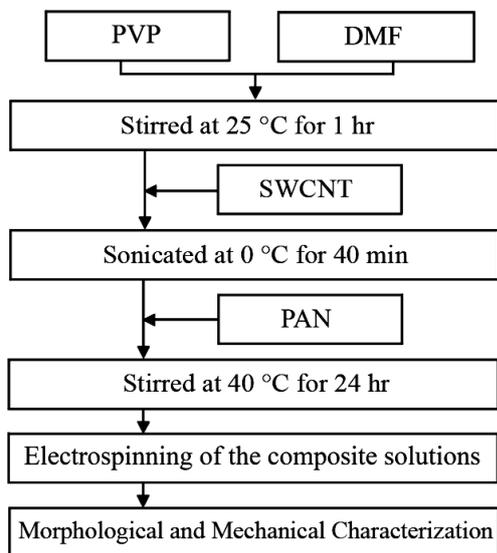


Fig. 1 – Flow chart for the synthesis of composite nanofibers

The viscosity and the conductivity of PAN / PVP / SWCNT solutions were measured by a Rheometer (Brookfield, DV-II+Programable) and by a conductivity meter (Jenway, 4010), respectively. The surface morphology of the electrospun nanofibers was examined by SEM (Philips, XL-30) at an accelerating

voltage of 25 kV under magnification of 10000X, and the average fiber diameter was measured with the SEM images using Image J software (National Institute of Health, USA) from 200 fibers/sample. The orientation of SWCNTs in the PAN / PVP / SWCNT nanofibers was characterized using a TEM (Philips, EM 208).

The mechanical properties of the electrospun PAN / PVP / SWCNT nanofibers were measured on the universal testing machine (Instron, 5566) at room temperature. The specimens of nanofiber mat were cut into 1 cm × 4 cm rectangular shapes. The resulting specimens had a planar dimension of width × gauge length = 1 cm × 3 cm. Tensile testing was performed using a 10 N load cell at extension rate of 10 mm/min. The strength of the nanofiber mat was calculated from the eq. 1. The modulus and elongation at break were obtained from the stress-strain curves. The mechanical data were acquired with five independent experiments, and all data were displayed as mean values and standard deviation.

$$\sigma(\text{MPa}) = \frac{\rho \text{ g/cm}^3 \cdot F(\text{cN})}{T(\text{cm}) \cdot A(\text{g/m}^2)} \quad (1)$$

Where, σ is tensile strength, ρ is density, F is tensile force, T is the thickness of the nanofiber sample, and A is cross-sectional area density.

3. RESULTS AND DISCUSSION

3.1 Composite Nanofibers Morphology

Fig. 2 displays SEM photographs of the electrospun composite nanofibers. The surface of the electrospun nanofibers with 0 % and 0.5 % SWCNT is very smooth, as shown in Fig. 2a and Fig. 2b, respectively. Low surface roughness and unevenness in the samples with 1 % and 2 % SWCNT were observed, while still good alignment in the sample structures can be seen (Fig. 2c and 2d). However, considerable aggregation and local irregularities were observed as the SWCNT content increased to 10 wt % (see the sample in Fig. 2e). With increasing the concentration of SWCNT in the solution from 0 to 2 wt %, the mean diameter of nanofibers increased from 163 ± 19 nm to 307 ± 34 nm. However, when SWCNT concentration was increased to 10 wt % the average diameter decreased.

In the electrospinning process, the solution viscosity and conductivity are two very important parameters, which can affect the composite nanofibers diameters. As described in the literature, mostly with increasing the viscosity and conductivity of the electrospinning solution, the average diameter of nanofibers increased [14, 15]. Variations in the conductivity and viscosity values were determined against various SWCNT concentrations (Fig. 3). These variations can be related to the polymer chain conformation changes in the solution produced due to adding SWCNT. As it can be seen from Fig. 3, with increasing of SWCNT concentration of the polymer solutions from 0 wt % to 2 wt %, a slight increase in the viscosity and conductivity were obtained. However, when the SWCNT concentration was increased to 10 wt %, the viscosity and conductivity decreased noticeably.

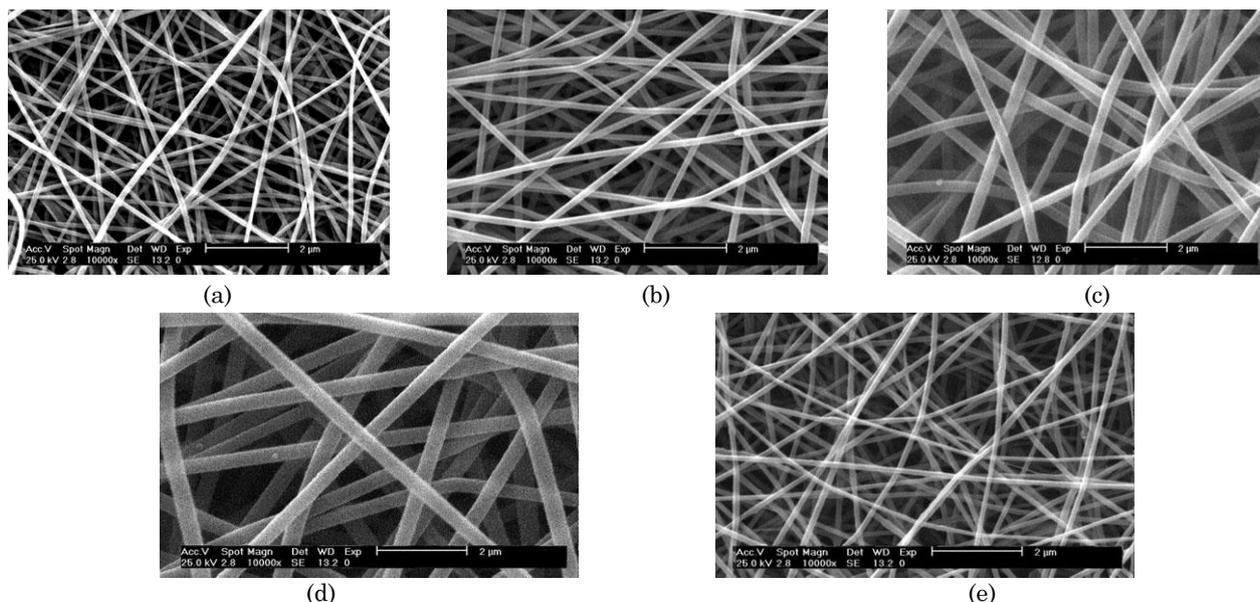


Fig. 2 – SEM photographs of composite electrospun nanofibers with various concentration of SWCNT: (a) 0 wt %, (b) 0.5 wt %, (c) 1 wt %, (d) 2 wt %, and (e) 10 wt %

3.2 Individual Dispersion

Generally, to improve the morphological properties of the fabricated composite nanofibers containing SWCNT, the dispersion condition is very critical and plays a significant role in achieving effective properties. It is important that SWCNTs can be dispersed without any breakage and aggregation.

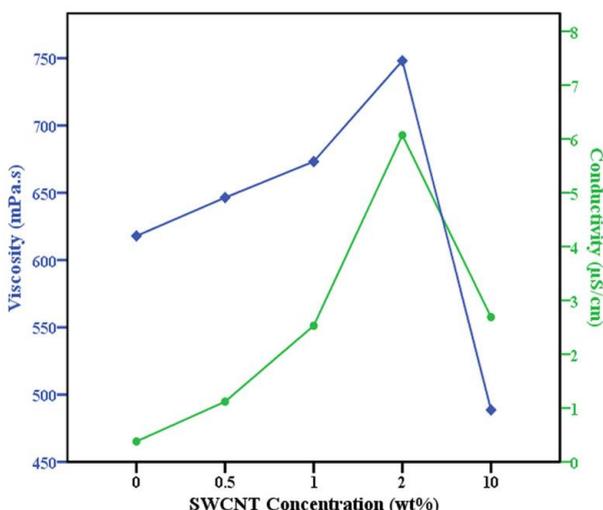


Fig. 3- The changes in viscosity and conductivity values against SWNT concentration

Accordingly, the regression relationship between the solution viscosity (η) and its SWCNT concentration in the form of $\eta=614.3+65.2C$ ($R^2=0.993$) is obtained and the relation between the solution conductivity (σ) and SWCNT concentration was in the form: $\sigma=0.31+2.83C$ ($R^2=0.976$). The regression relationship between the average diameter of composite nanofiber (d) and SWCNT concentration (C) were obtained in the form: $d=156+73C$ ($R^2=0.987$). It should be emphasized that this relation is valid only for SWCNT concentration values lower than 2 wt %. However, for values over

than 2 wt % due to instability and bundle SWCNT dispersion the mentioned relation is no longer reliable. This unconvinced behavior can be related to the weakness of the solvent to overcome on the remained and still strong van der Waals interactions among SWCNTs. The above observations and results indicate that SWCNT dispersion behavior plays a very important role in determining the morphology of composite nanofiber.

3.3 Mechanical Properties of Composite Nanofibers

Table 1 shows the changes of the strength, modulus and elongation as a function of the SWCNT concentrations in the electrospun nanofibers. By increasing the SWCNT content from 0 wt% to 2 wt% sample, obvious increase in the tensile strength and modulus can be observed. Even so, interestingly when SWCNT concentration was increased to 10 wt%, the tensile strength and modulus decreased. The yield stress of the PAN/PVP/SWCNT nanofibers containing only 2 wt% of SWCNT comparing to neat samples was increased by ~172% from 3.93 ± 0.45 MPa to 10.74 ± 1.03 MPa, and the tensile modulus is increased by ~885% from 61.39 ± 15.58 GPa to 605.08 ± 65.55 GPa. Meanwhile, the highest increase in the tensile strength and modulus occurs when the SWCNT concentration is increased from 1 wt% to 2 wt%. The values of both elastic modulus and tensile stress for sample with 2% SWCNT was significantly larger than the other groups ($P<0.01$).

According to the Table 1, by addition of SWCNT to the electrospun nanofibers structure from 0 wt % to 10 wt %, obvious decreases in the elongation at break were observed. The decrease in the elongation at break for all composite samples comparing to neat sample implies that incorporation of SWCNT in nanofiber polymer structure generally can give rise to be stronger but fewer flexible nanofiber layers. The obtained elongation at break for 2 and 10 wt % SWCNT samples were significantly different from all other groups ($P<0.01$) but

not significantly different from each other. The increase in tensile strength and modulus and drop in elongation at break have been also reported by Saeed and Park [7] and Mercader et al.[8] where the latter group incorporated SWCNT into polyvinyl alcohol nanofibers and the former incorporated MWCNT into poly(ethylene oxide).

Thus, based on the experimental results presented in the Table 1 and the regression relations obtained from the statistical analyses the optimal SWCNT concentration for the composite PAN/PVP nanofibers having convenient morphology with highest mechanical characteristics can be suggested at nearly 2 wt %.

Table 1 – Tensile Strength, Modulus, and Elongation at break as a Function of SWCNT Concentration (Mechanical properties data are expressed as means \pm SD, $n = 5$)

Sample	Tensile strength (MPa)	Modulus (GPa)	Elongation at break (%)
0% SWCNT	3.93 \pm 0.45	61.39 \pm 15.58	43.70 \pm 4.26
0.5% SWCNT	5.07 \pm 0.51**	94.89 \pm 19.23	37.39 \pm 4.28*
1% SWCNT	7.23 \pm 0.73*	217.37 \pm 30.24*	25.88 \pm 4.78*
2% SWCNT	10.74 \pm 1.03*	605.08 \pm 65.55*	16.78 \pm 3.06*
10% SWCNT	6.40 \pm 1.35*	179.46 \pm 31.19*	15.73 \pm 4.44

*: $P < 0.01$; **: $P < 0.05$, values are significantly different from the previous group compared

4. CONCLUSION

In the present work, nanofibers mats of PAN/PVP and PAN/PVP/SWCNT were fabricated by electrospinning process. The SWCNT concentration was varied from ~0.5 wt % to 10 wt %. With the addition of SWCNT to the polymer solutions from 0.5 wt % to 2 wt %, considerable increase in the viscosity and conductivity was observed. Moreover, with increasing the concentration of SWCNT in the solution from 0 to 2 wt %, the average nanofibers diameter increased from 163 \pm 19 nm to 307 \pm 34 nm. By increasing the amount of SWCNTs in composite, the surface roughness of nanofibers was increased. Tensile results showed that only 2

wt % SWCNT loading to the electrospun composite nanofibers gave rise to 10-fold and 3-fold increase in the tensile modulus and tenacity of nanofiber layers, respectively. The morphological and mechanical properties of SWCNT/polymer composite nanofibers depend on the dispersion stability and orientation of SWCNTs in the matrix. Essentially, high mechanical properties and uniform morphology of the composite nanofibers were found at SWCNT concentration of ~2 wt % due to their stable and individual dispersion. Thus, it can be seen that the homogeneous dispersion of SWCNTs is comparably important for an excellent SWCNT/polymer composite nanofiber.

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