Electrospinning of Nanofiber Composite from Solution of Poly(vinylidene fluoride) / Carbon Nanotube

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Resumen: *El artículo se dispone a tratar la inclusión de nanotubos de carbono como adictivo en una solución polimérica de poli(fluoruro de vinilideno) para ser utilizada en "electrospinning". La manta obtenida fue analizada morfológicamente por microscopia electrónica de barrido (SEM). La conductividad de la solución también es un parámetro importante que es considerado en el análisis de resultados de la manta obtenida y en el aparecimiento de "beads". La conductividad de la solución y la morfología de la manta obtenida mediante "electrospinning" están influenciados por la concentración de nanotubos de carbono.*

Palabras clave: *Electrospinning, Poli(fluoruro de vinilideno) (PVDF), Nanotubo de Carbono (CNT), Nanofibra, Morfología, Conductividad, Beads.*

Abstract: *This article proposes the inclusion of carbon nanotube additive in the polymeric solution of poly(vinylidene fluoride) to use it on the electrospinning process to obtain a mat which structure was morphologically analyzed by scanning electron microscopy (SEM). The solution conductivity is also an important considered parameter on final result analysis of the obtained mat and the appearance of beads. The conductivity of the solution and the morphology of the mat obtained by electrospinning are related by the influence of the carbon nanotube concentration.*

Keywords: *Electrospinning, Poly(Vinylidene Fluoride) (PVDF), Carbon Nanotube (CNT), Nanofiber, Morphology, Conductivity, Beads.*

1. INTRODUCTION

Electrospinning is a methodology to obtain nanofibers, inducing the stream solution to form jets due to high voltage applied [18]. Polymer from different molecular weight or composite are used and they can influence the formation of the droplet on the tip of the needle and Taylor´s cone, and the characteristics of the mat. When a high voltage is applied, the electrical force (F_E) and the gravitational force (F_G) work against the surface tension (F_γ) [2]:

$$F_\gamma = F_E + F_G \quad (1)$$

A problem that occasionally happens is the whipping instability that increases the surface area of the jet and decrease the charge density over the surface, caused by stronger fields. Stable regime can be obtained when electrical repulsive force overcomes weaker forces of surface tension, forming the jet toward the collector [2].

The experimental diagram (see Fig. 1) shows as a didactic way the scheme in the Fig. 3. The obtained fibers at the collector mainly depend on the parameters of the polymeric solution in the syringe, which will form the jet, and the parameters of the electrospinning process, which involve solution feed rate, diameter of the needle, distance between the collector and the tip of needle, applied voltage, and environment conditions during the test [9],[22].

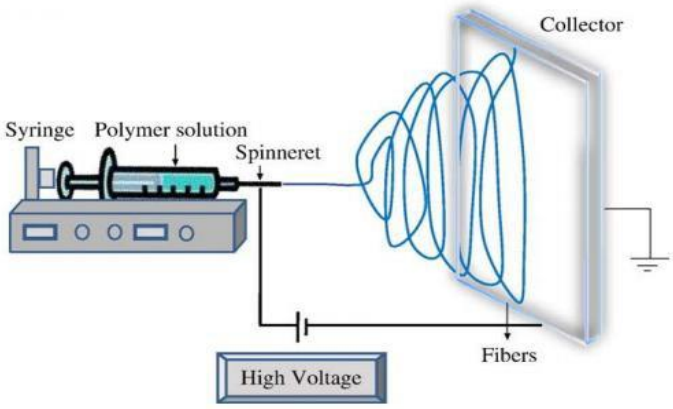


Figure 1. Diagram of electrospinning apparatus [3].

The polymeric solution is inserted in the syringe. The pump is responsible to push it against the collector and input the solution feed rate, the diameters of the syringe and the needle.

The spinneret is formed due to high potential difference between the tip of the needle (positively charge electrode) and the collector (negatively charge electrode), when finally the fibers will be collected, forming a mat (see Fig. 2).

Although it is known for years, the recent development and study could obtain different applications using polymer nanofibers, as piezoelectric and biochemical sensors, and industrial application with nano electronic devices, with capacity to generate electrical charges when stress is applied [4],[16].

The conductivity of PVDF is one of the most important characteristics of this polymer because of the piezoelectric property, innumerous applications developed as medical and sensor devices [10]. There are four possible formed phases at the crystallization of the PVDF can form. Non-polar α phase can be transformed into the polar β phase through mechanical stretching at elevated temperature. Phases β, γ, and δ are polar, and β form is the most important phase for piezoelectric, suitable for sensor application due to its low density, flexibility and elastic modulus [1].

Figure 2. Mat formed through electrospinnig test.

Carbon nanotubes have been used as medical as microelectronic applications [20]. They can be differenced by the number of walls which compose their structure (SWCNT, DWCNT, MWCNT), the inner and outer diameters, factors that influence their weight and density [17]. Electrospinning of PVDF/CNT can result in interfacial interaction, and lead to β phase effect and change in the orientation of crystalline phase [12].

The effect of solutions with different concentrations of PVDF with Dimethylformamide (DMF) and DMF/Acetone were verified on the electrospinning, indicating a fiber diameter decrease with addition of acetone to the solution [6].

The formation mechanism of β-phase in PVDF/CNT composite was studied, using sonication proceeding, based on theoretical calculations and experimental results [23].

Some imperfections on the morphology of the mats influenced by solution or process parameters can be detected. One of the most common is the beads formation, caused by lower concentration of polymer in the solution, or the composition of the solvents [11],[13].

Electrospun structure properties of PVDF/DMF with carbon nanotubes were analyzed and the percolation threshold for the insulator-to-conductor transition defined [21].

The parameters of solution such as the ratio of DMF/acetone and polymer concentration, and process parameters influence the formation of nanofibers [7].

In the present work, the morphological characterization of a nanostructure membrane of a composite Poly(vinylidene fluoride) / Carbon Nanotube nanofiber obtained from electrospinning method and the conductivity of its solution are studied. The effect of the addition of CNT on the composite is verified by measuring the conductivity of the solution and analyzing the morphology of the mat formed by nanoscale fibers, influenced by defined electrospinning process parameters.

2. MATERIALS AND METHODS

Materials

It was used poly(vinylidene fluoride) (PVDF), supplied by Solef 11010/1001, Solvay do Brasil Ltda, and solvents Dimethylformamide (DMF) and Acetone purchased from Synth.

Multiwalled carbon nanotubes (MWCNTs) supplied from CNT Co. Ltd. (Korea) were treated by reflux technique and magnetic stirring, after cooling down to room temperature, they were vacuum-filtered and washed with deionized water until the filtrate reach a neutral pH. The treated multiwall carbon nanotubes were dried in vacuum system at room temperature for 24 hours. The morphology was obtained using Transmission Electron Microscopy (Carl Zeiss CEM-902) to determine their diameter, which varies from 10 nm to 40 nm and Scanning Electron Microscopy (FEI NanoLab200) to their length, smaller than 5 μm.

The concentration of PVDF is 16 wt %, and the proportion of solvents is 3:1 for DMF:Acetone. The CNT content was varied from 0 to 0.46 wt %, and five different solutions were obtained, according to Table 1.

Method

The first step, different concentrations of solvents and polymer for the solution of neat PVDF sample were defined. The second step, the solution was used at electrospinning test, adopting different process parameters. The analysis of the obtained mat under Scanning Electron Microscopy (SEM) indicated the successful solution and process parameters by appearance of nanofibers. The third and final step, the solutions containing CNT was also tested, maintaining the same solution and electrospinning parameters.

The sonication method (Sonics, model Vibracell, tip Hielscher UPS 200S, 750 Watt, 20 kHz, 37% amplitude) was used to obtain CNT dispersed in the solution, for 15 minutes. Afterwards, the polymer was dissolved in a magnetic shaker for 4 hours. This solution was sonicatted for 5 minutes more, then it was shaked for 14 hours [12].

Finally the solution was put in a 10 mL syringe, with a mm needle for the electrospinning test. The parameters

of the process are feed rate 0.4 mL/h, the needle tip to the collector is 18 cm, voltage of 18 kV. A schematic electrospinning test is shown in Fig. 3.

Figure 3. Scheme of electrospinning test.

Table 1. Samples of PVDF/CNT.

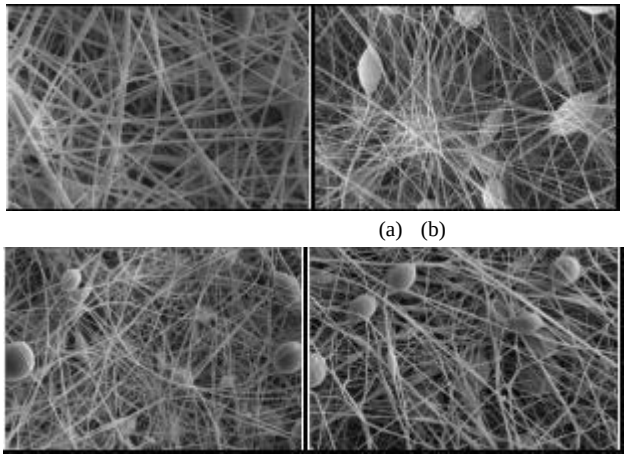
Sample	Compound
Sample 01	Neat PVDF
Sample 02	PVDF+0.05 wt% CNT
Sample 03	PVDF+0.11 wt% CNT
Sample 04	PVDF+0.23 wt% CNT
Sample 05	PVDF+0.46 wt% CNT

3. ANALYSIS

As a result, images of the mats (see Fig. 4) obtained by electrospinning from five different concentration of CNT are introduced by utilizing the Scanning Electron Microscopy (SEM) (Zeiss, model EVO/MA 15).

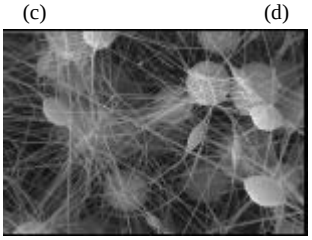
From the images (see Fig. 4) and the utilization of Image J software is possible to introduce an average and standard deviation of nanofiber diameters from the mats produced (see Fig. 5).

Higher CNT concentration in polymeric solution is a cause factor to fiber diameter reduction because of its conductivity increase (Table 3), as also discussed in [8].



(a) (b)

(c) (d)



(e)

Figure 4. Micrograph of the morphology of PVDF/CNT with different concentrations of carbon nanotube (a) neat PVDF; (b) 0.05% CNT; (c) 0.10% CNT; (d) 0.23% CNT; (e) 0.46% CNT. The length of the horizontal edge of each of the images is 1 μm long.

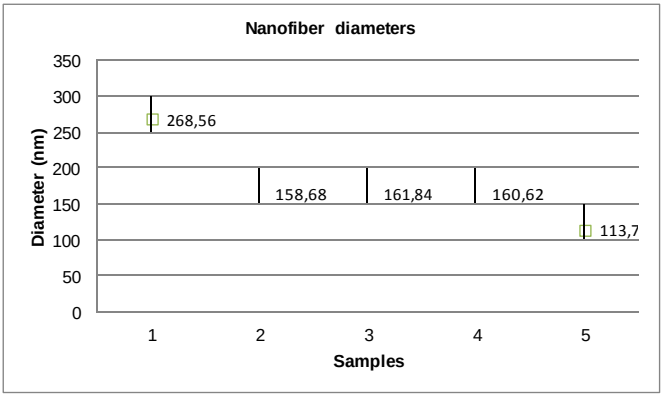


Figure 5. Diameters of fiber mat of PVDF/CNT samples.

The solution of each sample (Table 1) was then characterized, defined its density, surface tension and conductivity. The densities were obtained through a 5 mL pycnometer, taking its empty weight and with the solution.

The surface tension test was done at the tensiometer Attension Theta, and the values were obtained (see Table 2).

CNT density is a function of its number of walls and outer diameter [17], in this case between 10 nm and 40 nm. The final solution density is composed of solvents density, 0.79 g/cm^3 of acetone and 0.94 g/cm^3 of DMF based on [2], CNT density, around 1.74 g/cm^3 as in [15] and PVDF which is very close to the CNT. Low variation of solution density measurements is due to pycnometer use uncertainty and low CNT concentration in solution.

The solution conductivity varies with the temperature. At ambient temperature, these values vary with different nanotube concentrations.

The electric conductive test was done with the conductivimeter Analion C708 – PLUS, 0.1 μS resolution, 200 μS scale, ±1.5% reading precision, using the cell C801/1 Analion, with constant 1 cm^{-1}, building of boron silicate and with electrodes of platinum. First of all, verification was done with KCl standard solution, obtaining conductivity of 1.413 μS. The mean conductivity values from three different measures, as shown in Table 3.

The functionalized carbon nanotube used in the experiments is a factor that can be considered to no significant increase of solution conductivity because of its high oxidation treatment.

Due to its functionalization, CNT shows higher superficial area caused by defects. Besides that, this factor also influences the percolation threshold increase, shifting it to higher concentrations [5]. The electrical behavior can be explained by percolation theory [10] and CNT exhibit low

dispersibility in organic solvents, in this case acetone and DMF [19]. Including that, no significant CNT agglomeration at fiber surface was observed, though obtained by [14].

Table 2. Solution density and surface tension of different CNT concentrations.

Solution	Density (g/mL)	Surface tension(mN/m)
Neat PVDF	0.9769	30.60±0.08
PVDF+0.05 wt% CNT	1.0178	31.53±0.08
PVDF+0.11 wt% CNT	1.0134	31.45±0.17
PVDF+0.23 wt% CNT	1.0317	31.89±0.06
PVDF+0.46 wt% CNT	1.0042	31.05±0.06

Table 3. Solution electrical conductivity of different NTC concentrations.

Solution	Condutivity (μS/cm)
Neat PVDF	2.7
PVDF+0.05 wt% CNT	2.6
PVDF+0.11 wt% CNT	3.0
PVDF+0.23 wt% CNT	3.4
PVDF+0.46 wt% CNT	3.7

4. CONCLUSION

It was adopted defined conditions to electrospinning mats, so the V/d (tension/distance) is equal to 1 (18kV/18cm) to the samples. The surface tension and gravity forces didn´t vary significantly, so the formed jet during the electrospinning was basically influenced by electrical force due to introduction of CNT in the solution and its increased conductivity.

The determination of the electrospinning parameters and the related instability of the jet of polymer solution vary according to solution parameters. The charge of the electrospinning liquid jet, present on its surface, can influence the diameter of the fiber, taking sample 1 as a reference. The consequence of a higher electric force is a reduction of diameter mainly at higher percentage of the additive (0.46wt% CNT concentration) sample 5, although a decrease of diameters also can be verified at sample 2 to sample 4.

Beads are observed whatever the percentage of nanotubes in the solution, increasing with its concentration, indicating instability of the jet because of the voltage applied, which can be reduced, adjusting electrospinning parameters. The whipping instability is one of the responsible factors involved with fiber formation, and its occasion takes a reduction on the nanofiber dimension.

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