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Automatic Assembly and Morphological Characteristics of a Poly (Vinylidene Fluoride) and N, N-Dimethylformamide Compound "Root-Like" Fiber Structure

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Abstract

A study to describe the process to induce an automatic assembly and morphological characteristics of a Poly (Vinylidene Fluoride) and N, N-Dimethylformamide compound "root-like" fiber structure was developed. PVDF, poly (vynylidine fluoride) is a widely investigated polymer due to its excellent mechanical properties, chemical stability and ferroelectricity. The electrospining variation with two electrodes was used to collect PVDF & DMF compound "root-like" fiber structure and these were morphologically analysed using Scanning Electron Microscopy (SEM). The compound fiber structure presents porous round structures from which fibers extends and/ or aggregate to create a hollow cylinder that has a diameter of micrometers. The conditions for the automatic assembly of the PVDF &DMF compound "root-like" fiber structure appear to be a unique property of the PVDF & DMF. For the automatic assembly to occur, the distance between electrodes must be around 14.5cm, a voltage in the range of 15Kv to 30Kv and a concentration of 18%wt/wt.

Keywords: Electrospinning, Fiber, automatic assembly

1. Introduction

Electrospinning has been largely used to obtain polymeric nanofibers[1]. However, it is a technique that normally does not allow control of the position of the deposited material. The nanofibers are normally randomly deposited or deposited with some orientation using non-conventional setups[2].

In this work, we investigate a modified electrospinning process that allows automatic assembling of "root-like" polymeric structures with cylindrical branches containing micro and nanofibers and, round porous polymeric arrangements. This represents an innovative use of the electrospinning. Self-assembled structures have attracted a lot of attention due to their possible applications in several fields[3].

The developed process uses parallel macro electrodes and the solution is injected in the electrode with positive voltage. The "root-like" structures are obtained using a solution with Poly (vinydilene fluoride (PVDF) and N,N-Dimethylformamide (DMF). PVDF, is a polymer with the chemical formula $-CH_2-CF_2-$. This polymer has excellent mechanical properties, chemical stability, ferroelectricity, high dielectric permittivity and unique pyroelectric and piezoelectric properties [4]. DMF, is an excellent polar solvent for many compounds, a multipurpose reagent participating and is used as a carbonating agent [1].

The goals of this investigation are to make a detailed description of the formation process of the "root-like" structures and the future creation of a biosensor.

2. Experimental Methods

Solutions were prepared using PVDF and DMF as solvent. Different concentrations of PVDF were adopted (15 wt%, 18 wt%, 21wt% and 24 wt%) using 5 mL of DMF. All solutions were stirred during 24 hours at room temperature before deposition.

To make the "root-like" fiber structure, an electrospinning apparatus with parallel macro electrodes was used. The electrodes were made of aluminum with dimensions of 5.0 cm × 2.5 cm × 1.2 cm [2]. The distance between the electrodes varied from 14.5 cm to 30.5 cm and the voltages applied to the electrodes varied from 10 kV to 30kV. An insulin syringe (1 mL) was used for insertion of polymeric solution between electrodes. Polymer was injected close to the positive electrode keeping the syringe needle with angles between 22.5° and 67.5° with respect to the vertical wall of the electrode. The tip of the insulin syringe has to be in constant contact with the positive electrode and the deposition flow of the polymer has to be constant.

The "root-like" structures were manually collected after the deposition and were placed on top of silicon substrates with a carbon tape to improve SEM analysis. A thin layer of gold was deposited on the samples before SEM analysis.

Videos of the formation process of the "root-like" structures were taken with a Canon Powershot SD1400 IS Digital ELPH camera. Snapshots were taken using Windows Live Movie Maker. Images were obtained using an optical Microscope (Meiji Techno, Infinity Analize Software) and a Scanning Electron Microscope (JEOLJSM-6360).

3. Results and Discussion

3.1 Formation Of The Compound "Root-Like" Fiber Structure

Before the automatic assembly occurs, it is necessary an accumulation of deposited material on the negative electrode. The polymeric stream liberates fragments that follow the intense electric field lines from the positive electrode and aggregate on a border of the negative electrode. This aggregation starts to elongate following the intense electric field lines to the positive electrode, rotating and creating new ramifications. An example of a root-like structure is presented in Figure 1.

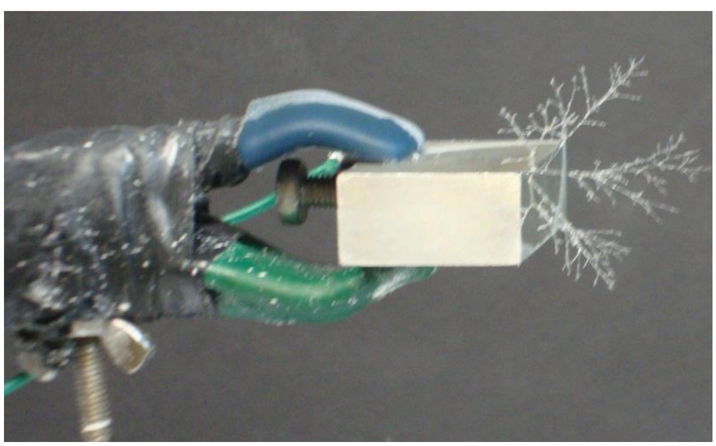

Figure1. Example of a root-like structure

3.2 Description Of The Compound "Root-Like" Fiber Structure

The compound "root-like" fiber structure is a complex organization of structures seen on traditional electrospinning process. As shown in figure 2, its surface is made of circular polymeric arrangements that have a smooth or porous surface and fibers that originate from these structures. Both the circular arrangements and fibers assemble to form a cylinder that is the compound “root-like” fiber structure. The fibers travel along the surface of the compound “root-like” fiber structure, passing on top or under the circular arrangements that aggregate. When the compound “root-like” fiber structure divides, it tends to form three new ramifications (figure 2) that go in opposite direction. This behavior shows that polymer from the streams is preferentially deposited on the extremes of the ramifications. In the ending of the compound “root-like” fiber structure, the fibers spread of with their smooth circular arrangements and stretch in all directions.

Figure2. SEM image of the ramification of the compound “root-like” fiber structure

3.3 Effect Of The Voltage, Concentration And Distance Between Electrodes On The Diameter Of The Compound “Root-Like” Fiber Structure And Fibers In The Surface

There is confirmed evidence that the voltage, distance between electrodes and concentration of the solution has an important function in the formation of fibers formed with parallel electrospinning method. For the automatic assembly to work, the maximum distance between electrodes is 30.5cm. Figure 3 shows that the greater the distance between the electrodes, the bigger the diameter of the compound “root-like” fiber structure. Similar to this tendency, it is found that the more concentrated the solution, the bigger is the diameter of the compound “root-like” fiber structure. These tendencies respond to the changes in the forces that act to elongate the compound “root-like” fiber structure. When the solution is more concentrated, the viscosity acts as a force to aggregate and the difference between opposing forces is higher, causing more deposition of material in the structure. A similar effect is observed because the forces of elongation get weaker with distance, thus the difference between opposing forces is higher, causing more deposition of material in the structure. Figure 4 shows that when the force of elongation is increased by increasing the voltage, the diameter of the structure decreases because less deposition of material occurs.

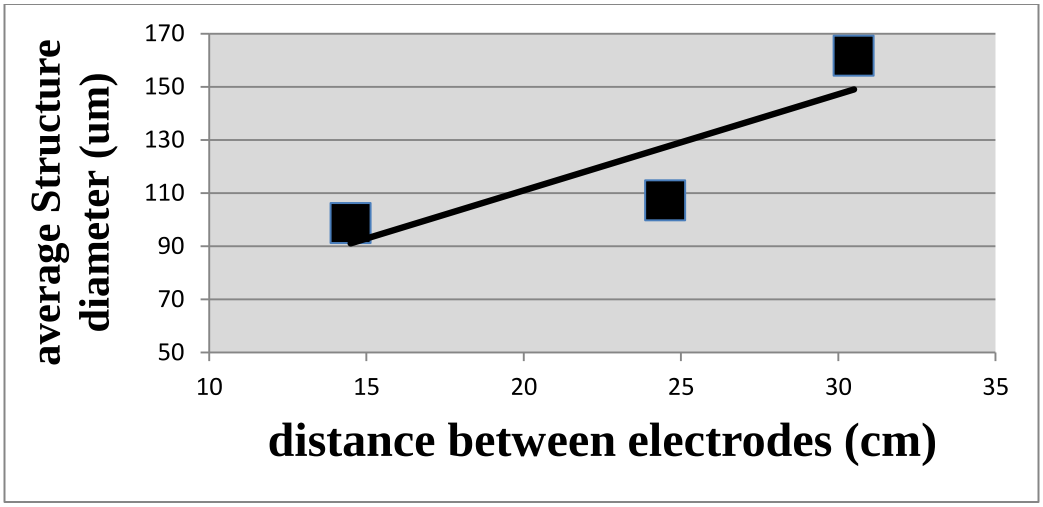

Figure3. Effect of the distance between electrodes on the diameter of the compound “root-like” fiber structure

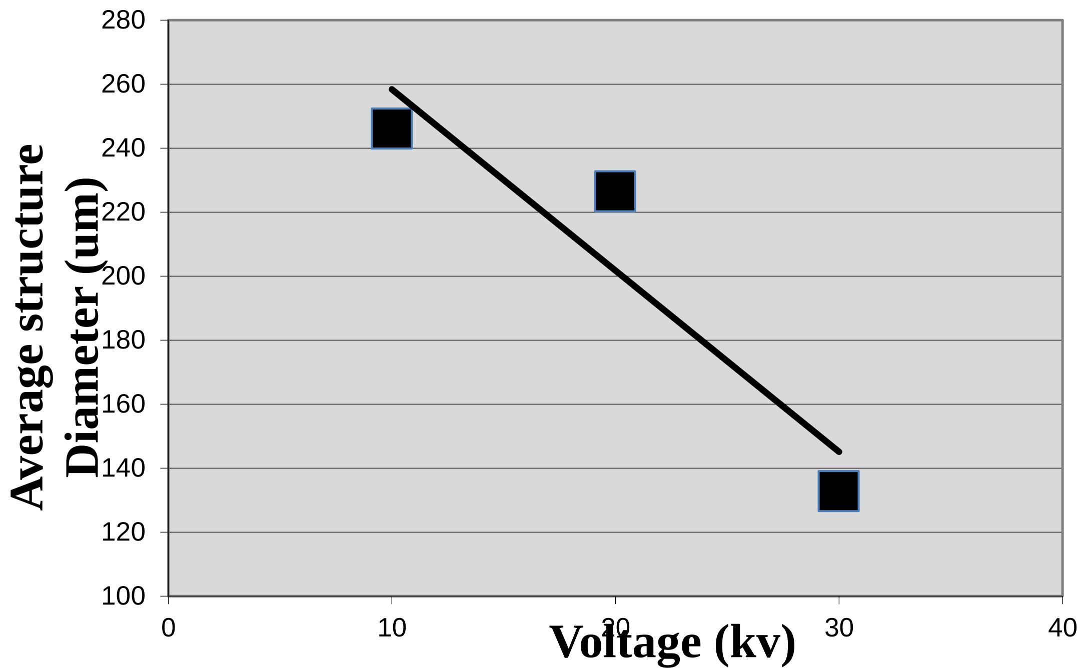

Figure4. Effect of the voltage on the diameter of the compound “root-like” fiber structure

When the fibers in the structure where observed, it was noticeable that there is a significant difference in the diameter of the fibers formed with a distance between electrodes of 30.5cm compared to the other conditions. This is observed in the figure 5, where the dispersion observed for 30.5cm does not overlap with the dispersions observed for 24.5cm and 18.5cm, and has fibers with bigger diameter. This can be related to the fact that the forces of elongation are weaker because of the distance. This causes the fiber to stretch less than when the forces are stronger (24.5cm and 18.5cm). A similar phenomenon is observed in figure 6 when there is a significant difference for the PVDF: DMF concentration of 15% wt/wt. In this case, the viscosity of the solution is less than that for concentrations of 21% wt/wt and 24% wt/wt, causing a smaller average fiber diameter because of the low viscosity.

Unfortunately, compound “root-like” fiber structure could not be created using concentrations lower than 15% or higher than 24%.

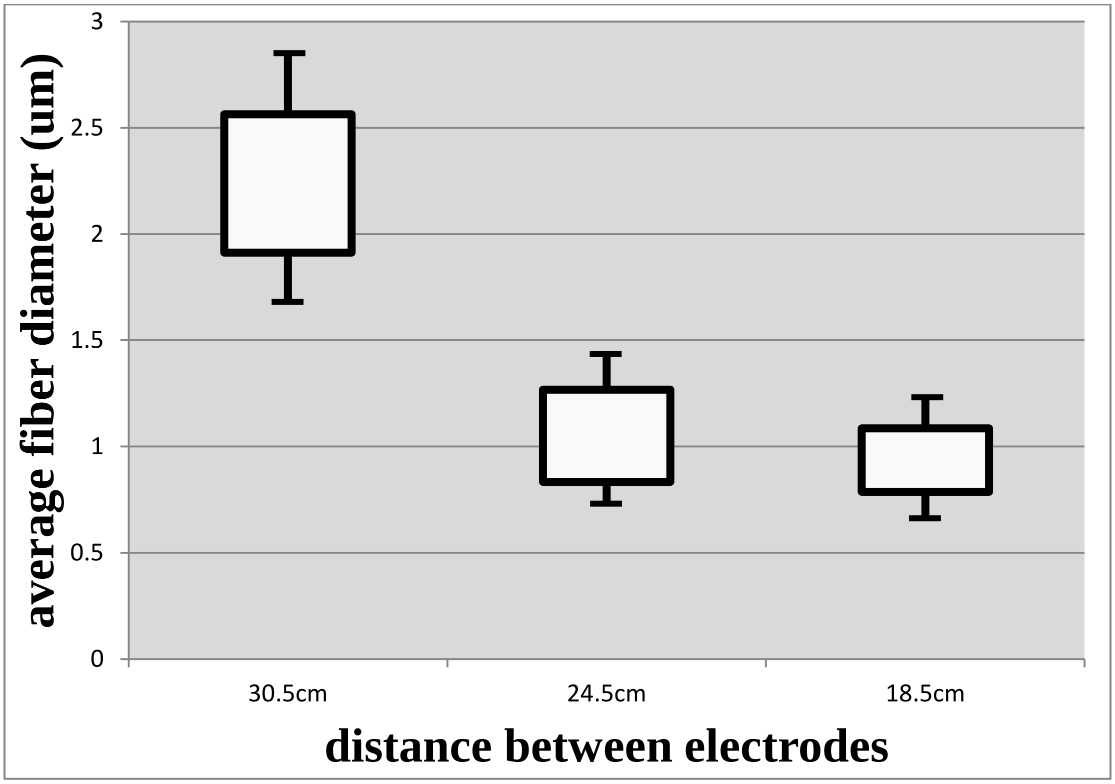

Figure5. Effect of distance between electrodes on the fibers in the surface of the compound “root-like” fiber structure

There are no significant differences between the average fiber diameters when the voltage is changed. When the tendencies for 30kv, 20kv and 10kv are analyzed, the dispersions overlap but the dispersions differ.

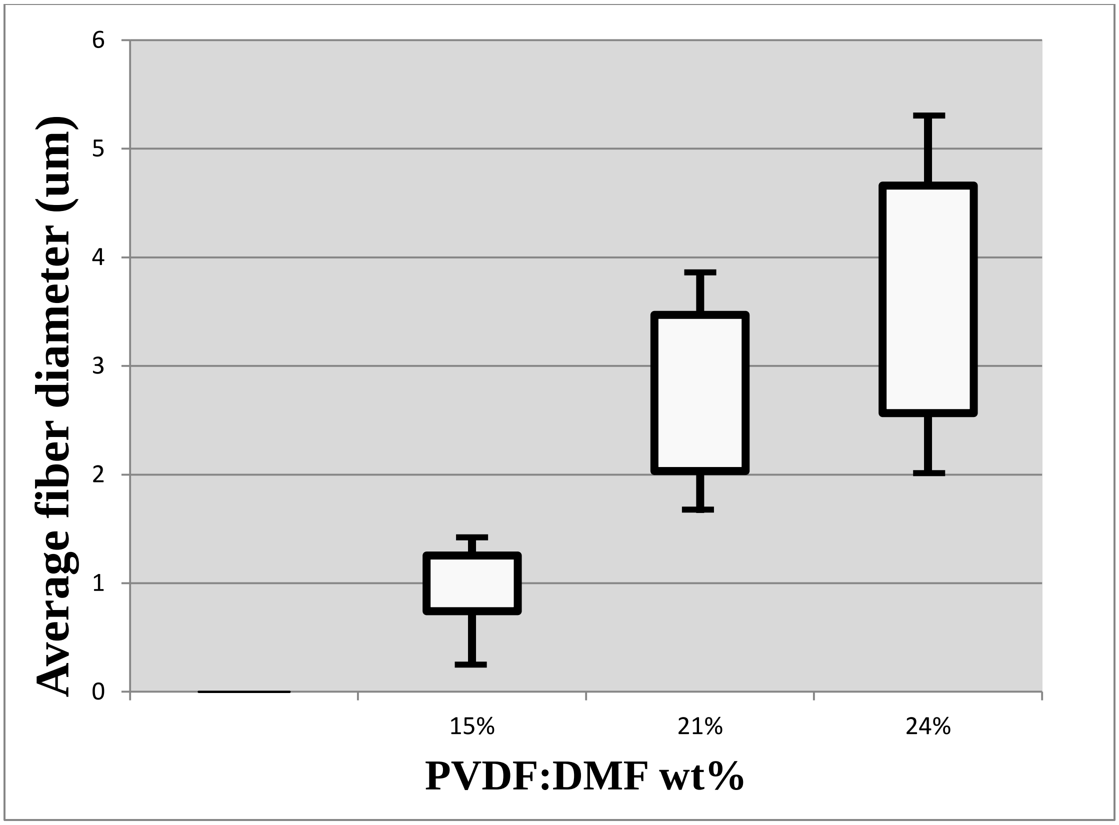

Figure 6. Effect of the concentration of the solution on the fibers in the surface of the compound “root-like” fiber structure

The influence of distance, voltage and concentration in specific locations of the compound “root-like” fiber structure was observed. When the distance is altered, the ramification cylinder of the compound “root-like” fiber structure presents the biggest average fiber diameter while the ending presents the shortest fiber diameter. This tendency could be caused by the changes in the forces of elongation present during the automatic assembly process. When the compound “root-like” fiber structure is dividing, the forces that divide the fiber pull in opposite directions, creating a zone where the material deposits. On the other hand, the fibers on the ending of the compound “root-like” fiber structure are closer to the positive electrode, making the electric forces stronger and more stretched that the rest of the fibers in the compound “root-like” fiber structure. In contrast to the tendencies for the distance between electrodes, the largest fiber diameters depending on the voltage conditions are found in the ending zone of the compound “root-like” fiber structure while the smallest ones are in the ramification position.

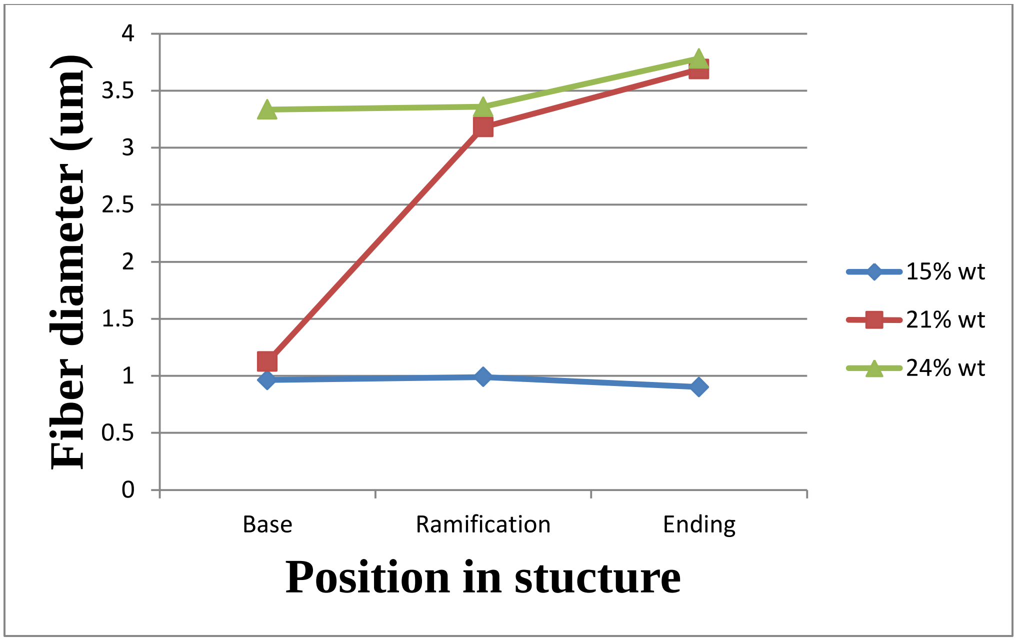

Figure6. the effect of the concentration on the average fiber diameter in specific locations of the compound "root-like" fiber structure

Finally the effects of the concentration on the average fiber diameter were the most significant. When the concentration is 15% PVDF:DMF, the smallest average fiber diameter is found in the ending of the compound "root-like" fiber structure while the biggest is found in the ramification. This is the same tendency observed when the distance between electrodes is changed. In contrast to this, the 21% and 24% PVDF:DMF concentrations demonstrate that the smallest average fiber diameter is found in the base of the structure while the biggest fiber diameter is on the ending of the fiber. This discrepancy between the 15% concentration and the other two could be explained by the fact that the 21% concentration is almost saturated solution while the 24% is saturated.

4. Conclusion

A process for the automatic assembly of the compound "root-like" fiber structure was defined. The cylindrical structures present diameters from 90um to 300um and are composed of a complex organization of circular polymeric arrangements and fibers with the range of microns. It was determined that an increase on the distance and PVDF: DMF concentration increases the compound "root-like" fiber structure diameter and its surface fibers while an increase in the voltage does the opposite.

5. Acknowledgments

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6. References

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