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COMMUNICATIONS

In-Situ Surface Depositing of Nano–Micro-particles on Electrospun Fibers

Carlos A. Delgado[1] · Adriana Chapa[1] · Karen Lozano[1] · Arturo Fuentes[1] · Horacio Vasquez[1]

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Abstract

A novel process of in-situ production of particle decorated electrospun fibers was developed by generating, charging, and depositing micro–nano-particles onto fibers during the electro-spinning (ES) process. The generation and charge of micro–nano-graphite particles occurred in an ES setup due to the pulverization of a negatively charged carbon brush near the fiber collector. The setup includes an aluminum cylinder rotating at a constant speed and being used to collect the fibers during electrospinning. The cylinder is negatively charged to attract the fibers from a positively charged needle, both charged with high voltages. A carbon brush contacts the cylinder to apply and maintain it connected to the negative voltage while it is rotating. Due to specific orientation and surface roughness, the carbon brush suffered wear which produced a graphite dust cloud around the collector. Nanofiber mats were produced with a unique characteristic appearance, creating as a result graphite coated fiber mat. These fiber mats were analyzed using scanning electron microscopy characterization and imaging. Results led to the discovery of coarse graphite particles embedded uniformly and in great quantities along the produced fibers. Therefore, fiber mats covered with graphite particles in a single-step electrospinning process were created and the method could be expanded to other material systems. This newly discovered in-situ deposition method could be beneficial to future studies about the effects of particle additives on the morphology and properties of the fiber mats for different applications.

Keywords Surface deposition · Electrospinning · In-Situ · PVDF · Fibers · Polymers

1 Introduction

Creating nanofiber mats from a polymeric solution is the first step toward achieving desired material composition and properties required to form layers for scaffolds, membranes, tissues, and similar applications. After fabrication, various processes can be applied to these nanofiber mats, depending on the desired properties of the resulting fibers. In this study, a newly developed method focuses on the addition of additives on the surface of the fibers, this is known as fiber decoration. This method of coating or decorating fibers was obtained through electrospinning by adding a cloud of negatively charged particles near the electrospinning fiber collector. Fiber decoration usually makes use of an external element not present in the solution, and it becomes engrained onto the surface of the nanofiber to form part of the new composition of the nanofibers and creating desired asperity or roughness properties.

Electrospinning is a process based on creating fine fibers through the use of differential high voltage polarities. During the fiber making process, dark spots were noticed on the resulting fibers. Upon closer inspection of the fibers, graphite particles from a worn carbon brush that rubs against the rotating fiber collector were identified. Given the contact of the carbon brush with the rotating cylinder, it started to wear out and carbon particles became airborne. These airborne particles were negatively charged and attracted to the positively charged fibers resulting in carbon decorated polymeric fibers.

The most used method for fiber decoration is through immersion, where the fibers are submerged in a solution holding the desired elements for decoration [1–3, 17]. In such a process, the decorating elements stick to the fibers, and the excess is removed, which results in coated fibers with new desired properties. Immersion has high reproducibility

✉ Carlos A. Delgado
carlos.delgado02@utrgv.edu

[1] Department of Mechanical Engineering, College of Engineering and Computer Science, The University of Texas Rio Grande Valley, 1201 W. University Drive, Edinburg, TX 78539, USA

characteristics, as different experiments have resulted in similar coated nanofiber morphology. Nonetheless, sometimes additives can take on different types of morphology depending on the nature of the material and the type of dispersion it goes through. Other techniques of coating fibers for decoration are through chemical and thermal procedures. These thermal techniques often recur to calcination of the produced fibers to obtain carbon coatings on the fiber surface [4, 5]. Chemical processes might involve nucleation processes, as well as phase separation processes, and chemical vapor deposition, which help the additives to engrain into the fiber surface [6–8, 16, 19].

The resultant changes of these additives on the fibers are not only esthetical, but the coating also improves the mechanical, electrical, chemical, and other properties of the original fibers. For instance, numerous studies have shown that carbon nanotubes (CNT) added onto fibers have a beneficial change of mechanical properties [9, 20]. CNT additives make fibers capable of withstanding higher amount of stress, as well as being able to strain further than non-decorated fibers [9, 20]. The CNT additives create a type of composite matrix attached to the polymers, and as a result they can withstand higher tensile and compressive stresses.

In the experiments performed by the authors, a solution of polyvinylidene fluoride (PVDF) was used to create fiber mats. An important aspect of PVDF is its piezoelectrical properties, meaning its ability to create an electrical charge when mechanical force is applied to it. PVDF is one of the most researched polymers for the optimization and creation of piezoelectric devices. These properties are primarily affected due to the crystallization phase of the resulting fibers. It has been documented that the optimal phase for piezoelectric applications for PVDF to be its beta phase [10, 11] which due to its symmetrical polymer chain morphology, conducts electricity more efficiently. However, the crystallinity phase of PVDF is commonly recognized to be affected primarily by the rate of evaporation of the solvent, during the creation of the nanofiber [12].

Various methods of fiber decoration are actively being researched, such as chemical vapor deposition, phase shifting, and chronoamperometric deposition [5, 7, 8]. However, all these methods take place after the fibers have been produced and are considered as an extra step for fiber treatment and modification. The purpose of this paper is to demonstrate a novel process of fiber decorating through in-situ deposition of nano- and micro-particles simultaneously happening during the electrospinning method of fiber production.

2 Materials and Methods

PVDF was used as the solute, while N-dimethyl acetamide (DMA) and acetone were used as the solvents in our samples. A solution with a concentration of 11 wt% PVDF, with solvents at a 1:1 v/v mixture of DMA and acetone was prepared. DMA is a strong solvent needed to dissolve PVDF, whereas acetone acts as an additive decreasing viscosity, which contributes to maintain diameter uniformity of the produced nanofibers. Additionally, the polymer was heated in an oil bath at 75 ℃, while a magnetic plate constantly stirred the solution at a rate of 400 rpm, with a duration of 1 h and 30 min. Finally, the solution was placed in a sonication bath to further homogenize the solution, for a duration of 5 min. The solution was then returned to the magnetic plate for a 24-h stirring.

Numerous polymers and solutions can be used to create fibers through electrospinning. In our lab, PVDF has been extensively used to create piezoelectric nanofibers through electrospinning and centrifugal spinning methods [13, 14]. PVDF is a semi-crystalline polymer possessing high piezoelectric properties due to its β-phase crystalline structure. Electrospinning utilizes an electric field which charges and fabricates fibers with diameters in the nano- and micrometer scales. Electrospinning can be considered as one of the best methods for the creation of piezoelectric PVDF fibers, which could be optimally fabricated for energy-harvesting applications. PVDF fibers could also be used in many other applications, such as fuel cells and tribology applications.

The in-situ deposition setup comprised a syringe pump, an aluminum cylinder acting as a collector, a variable speed motor that rotates the collecting cylinder, two power supplies of opposite high voltage polarities, and a soft carbon brush which touches a side of the cylinder to apply the negative voltage to the fiber collector. This soft carbon brush is inserted in a protective plastic case for its safety as well as to keep it aligned and touching the cylinder. The carbon brush was attached to the negative high voltage power source. The end of the protective case of the carbon brush was placed about half an inch from the cylinder's center. The carbon brush sticks out of it due to a spring that pushes it against the cylinder to maintain them in contact at all times even when the cylinder rotates. This soft carbon brush wears out because of its contact with the rotating cylinder. The rate of wear depends on the surface roughness of the section of the cylinder in contact with the brush, the force of the spring, and the alignment of the carbon brush. Through this process, the wear of the carbon brush creates a cloud of negatively charged graphite powder, which interacts with the positively charged polymeric fiber jet, decorating the fibers just before they

are deposited on the collector. It was determined that the negatively charged graphite particles travel toward the fibers being created. It is assumed that they travel toward the opposite polarity, thus in direction of the positively charged needle and polymeric jet of fibers. Figure 1 shows a top view of the in-situ setup that was custom made to create decorated fibers mats.

A cloud of carbon particles is generated due to the misaligned carbon brush. Figure 2a and b shows the state of the carbon brush when used. From these pictures, a slant in the carbon brush can be identified, which allowed a higher surface area to be in constant wear. The geometry of the piece, with added spring force, alignment, and roughness of the carbon brush, led to the creation of an excess of carbon particles. This can be directly compared with Fig. 2c, which shows a brand-new carbon brush with its original length and geometry.

For the electrospinning process, an electrical field of ± 15 kV was used. One milliliter of the solution was placed in the syringe. The syringe was then placed in a pump which constantly applied pressure onto the syringe, for a solution volumetric flow rate of 0.25 mL/h. A value of 3500 rpm was set to the collecting cylinder, which also contacted the carbon brush with the negative high voltage applied to it. An 18-gage steel needle was used as a nozzle for fibers to come out of the syringe, while also applying a positive high voltage to the needle. The cloud of graphite particles surrounding the collector occurred due to the accelerated wear of the soft carbon brush. Therefore, due to the electrospinning process and the negatively charged cloud of graphite powder, a novel method for the creation of decorated–functionalized fiber mats was developed. Other materials could be used to create the particle cloud, but they need to be negatively charged to be attracted toward the jet of fibers coming from the needle.

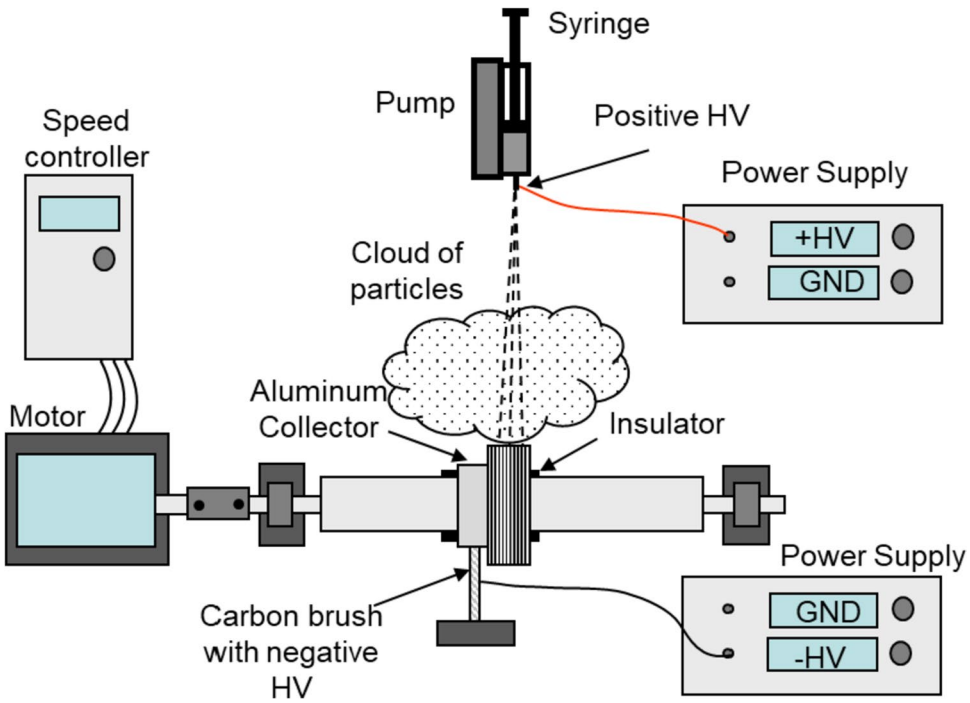

Fig. 1 Electrospinning setup used for in-situ deposition of particles on fibers

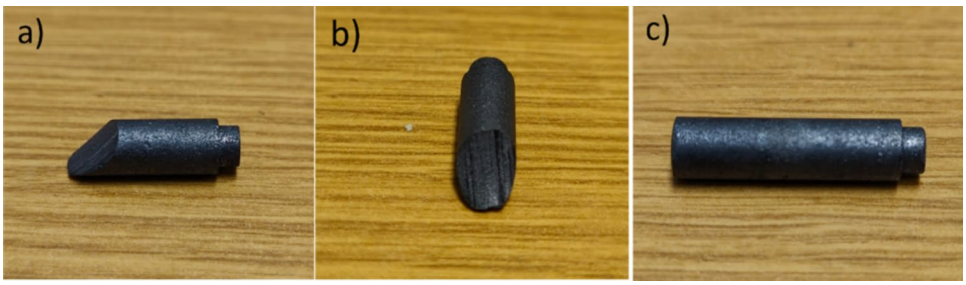

Fig. 2 **a** Side view of worn-out carbon brush, **b** Front view of worn-out carbon brush, **c** Side view of original carbon brush

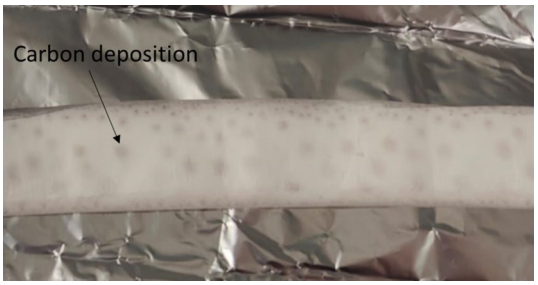

Fig. 3 Fiber mat created with in-situ deposition of graphite particles

3 Results

Figure 3 shows the resulting fiber mats obtained from the electrospinning and the in-situ deposition of carbon particle elements. Here it can be seen how certain spots in the fiber have a higher conglomeration of carbon particles, distinguished by a dark color. These spots had a higher concentration of carbon particles deposited on it, whereas the rest of the fiber has a white color representative of the PVDF polymer.

Figure 4 shows SEM micrographs of the obtained fibers. These images were specifically taken to show the deposition of carbon particles. From these images, the heterogeneity on carbon particle size can be observed, as well as the distribution and dispersion of the carbon particles on the surface of the fiber. Figure 4a and b shows the initial SEM images representing the morphology of the obtained fibers through electrospinning. These images are focused on the areas with higher graphite concentration which are noticed as darker spots in the resulting fiber mat. In these first set of graphs, it is possible to get a grasp of the overall morphology of this section of the fiber mat. From these images, it can be concluded that an additive was inserted onto the fibers, and this can be said from the high amount of graphite present in the overall structure of the sample. Figure 4c and d shows images focused on the same section of these deposited graphite elements, causing an outstanding level of decoration in the system since there isn't a single fiber from this black spotted surface area without a well-distributed amount of graphite on its surface. From this magnification, it is possible to see a tendency of alignment in the nanofiber mats, thus denoting that the in-situ deposition of the graphite did not affect the resulting morphology of the nanofibers. Finally in Figs. 4e and f, it is possible to examine both the size of the micro–nano-particles of graphite engrained into the surface of the nanofibers. Comparisons in size of both graphite particles relative to the size of the individual fibers can be observed in these images, where the nanoparticles of graphite seem to be uneven in size. However, the distribution of these along the individual fibers themselves shows a uniform amount of graphite present in all the fibers. Visually represented as big coarse particles or finer ones, at any rate it can be determined that the deposited elements are engrained in the fibers itself. A higher variety of sizes of graphite are located within this small surface area of the overall nanofiber mat.

To further analyze the morphology of these graphite nano–micro-particles, the SEM images were measured using ImageJ software to calculate the diameter of the graphite particles. A set of arbitrarily measurements was taken from these images. Figure 5 shows a histogram representing the recorded cross-sectional graphite particle size. The graph shows an average in diameter of approximately 0.50 μm and a standard deviation of 0.21 μm. These particles vary from a wide variety of diameters due to how these particles are created. The high-velocity collector wears out the carbon brush which generates negatively charged graphite particles that direct themselves toward the positively charged fibers.

The chemical composition of the observed spots on the developed fibers was analyzed using energy-dispersive X-ray (EDAX) characterization where a rich carbon presence was expected to be observed. Figure 6 shows an SEM image of the sample that was characterized by the EDAX. Various areas were selected to compare results. However, the most interesting areas were 2, 6, and 8. Areas 2 and 6 encompass a cumulus of graphite particles, whereas area 8 represents the overall surrounding area of these accumulated particles, as well as the particles themselves. Selected areas represent an area on the sample that was chosen for an isolated elemental composition characterization, such are the cases of areas 2, 6, and 8.

From the analysis of each of these selected areas, it was possible to identify a high carbon elemental composition. Figure 7 shows the results obtained from the EDAX on the three different aforementioned areas of interest. Area 2 represents a small cumulus of what it was originally thought to be graphite particles. However, with its high fluorine composition, it can be determined that these are embedded beads of the PVDF fibers. Nonetheless, Fig. 7 shows the results of area 6, which can be identified as a graphite particle agglomerate, due to high carbon composition shown in the graph. Finally, area 8 shows an elemental composition similar to that of area 2 since the area chosen for this analysis encompasses both fibers and graphite particles. However, since the fibers have a high fluorine composition compared to the number of particles present in the analyzed area, the carbon composition displayed is lower than that of fluorine.

4 Discussion

Due to a poorly adjusted carbon brush that was in close contact with the rotating cylinder, the brush experienced constant wear, creating a negatively charged graphite

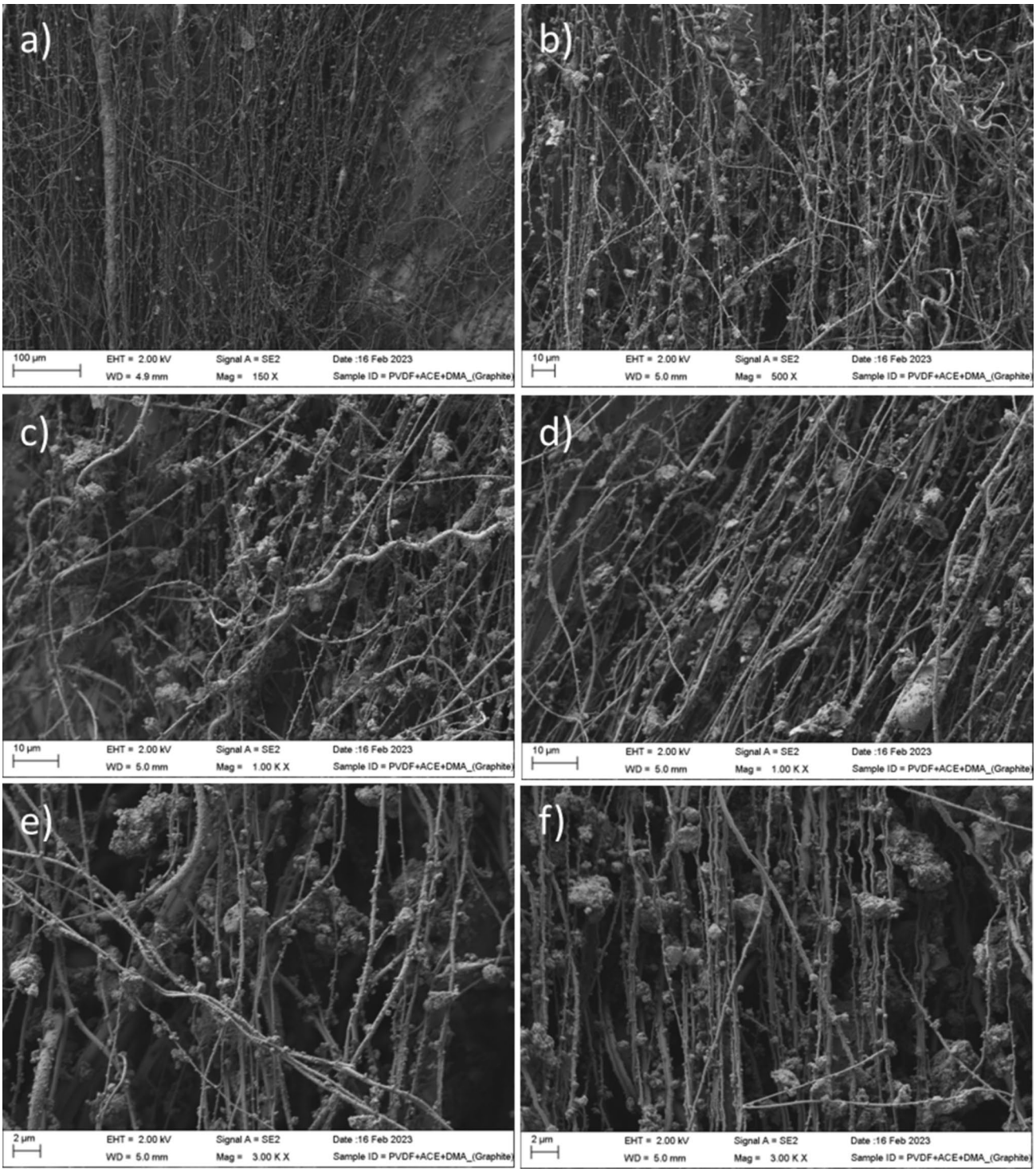

Fig. 4 SEM of PVDF + ACE + DMA + Graphite (Particles), **a** Magnification of 150 X, **b** Magnification of 500 X, **c** Magnification of 1000 X, **d** Magnification of 1000 X, **e** Magnification of 3000 X, **f** Magnification of 3000 X

particle cloud, which ultimately surrounded the collector. As the fibers were being ejected from the nozzle, the negatively charged carbon particles were deposited on the surface of the fibers. The number of particles can be increased by changing the contact area, the force of the spring, the alignment of the carbon brush and its roughness. The resulting fiber mat consisted of a morphology of two distinct colors, represented with predominant white

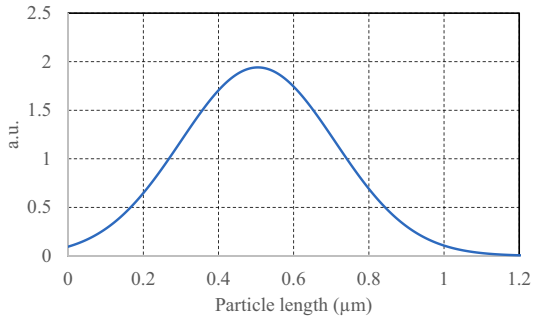

Fig. 5 Histogram depicting graphite particle diameter distribution

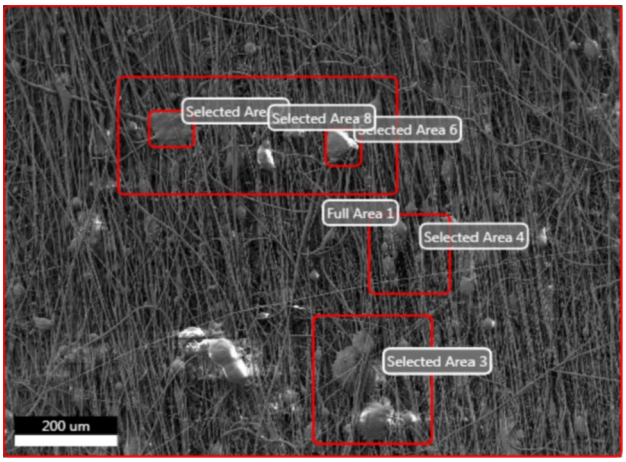

Fig. 6 EDAX Area Selection for Elemental Composition Analysis

PVDF fibers and dark graphite particles coating the fibers. The graphite particles concentrate in specific areas around the fibers in the form of black spots. This claim can be supported through the results shown previously in Fig. 4. Area 6 is specifically selected for elemental composition in which morphology is shown in Fig. 6, and its elemental composition in Fig. 7. The amount of carbon detected in area 6 is substantially higher than the carbon found in the other two areas, which are not dominated by the presence of graphite particles. For example, results from area 2 in Fig. 7 where the primary element detected is fluorine, characteristic of PVDF's chemical composition.

This novel in-situ coating technique, along with the results analyzed can be identified as an effective method, open to further optimization and development, aimed toward the use and testing of alternate additives onto different polymeric nanofibers. This method may resemble other post-fiber method for decorating fibers and for deposition of an additive through polarity [15]. Nevertheless, other methods are only performed after the fibers are produced and extracted. This method decorates the fibers in situ, during the process of fiber formation.

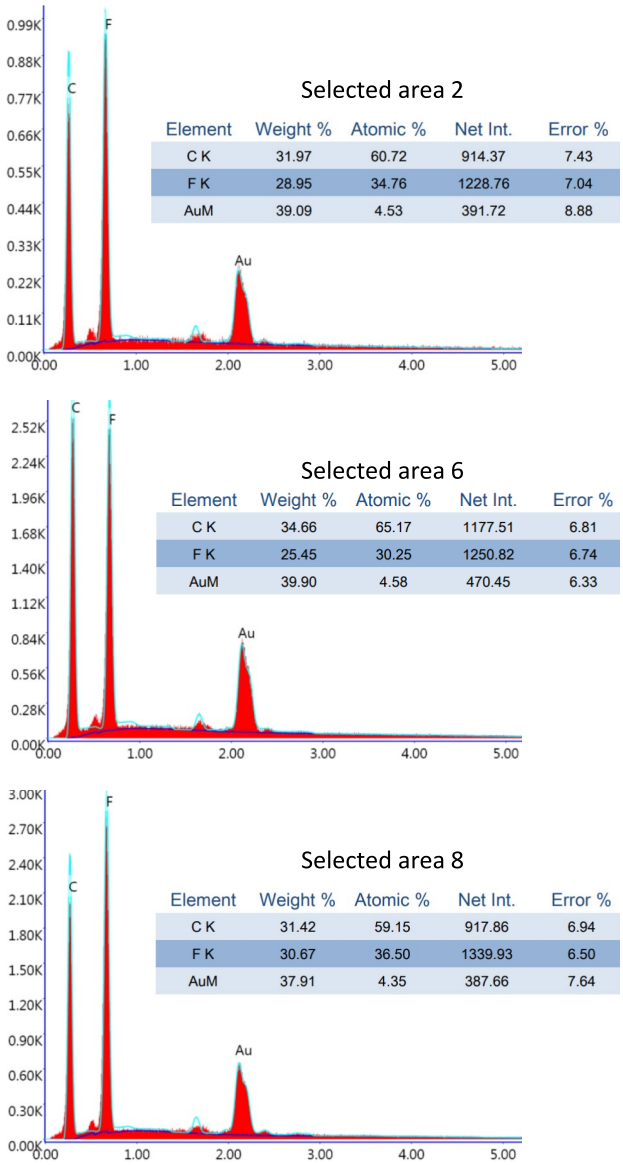

Fig. 7 EDAX Results in selected areas 2, 6, and 8

In this experiment, a control optimization was not implemented to select and evenly distribute the deposited elements onto the electrospun fibers. However, this experiment provides a foundation for the design of a control mechanism that can charge and evenly distribute the deposited elements onto the fiber actively being electrospun. This optimization would allow the deposition of different elements onto the fibers, which could open a new area of research dedicated to the effects of the in-situ deposition of elements onto electrospun fibers. The setup for this future procedure includes a dispenser of particles. This dispenser is situated above the area between the needle and the rotating cylinder. Charged particles will then deposit themselves to the fiber being created with a positive polarity. These particles could be charged

inside this chamber, or could be pre-charged through other processes, and then placed inside the chamber. This process could then be extended to the use of other materials, in the form of powders or with the ability to be ground into a powder-like state, then be charged and deposited into any type of fiber being created through electrospinning. The in-situ deposition of elements onto electrospun fibers has the potential to create new materials with unique properties. For example, the deposition of metal nanoparticles onto electrospun fibers could create materials with enhanced electrical conductivity. The deposition of biomolecules onto electrospun fibers could create materials with enhanced biocompatibility. The development of a control mechanism for the in-situ deposition of elements onto electrospun fibers would enable the creation of new materials with tailored properties, which could have a wide range of applications.

This process can be quickly adapted to work in other types of additives, such as CNT's, graphene, and even other polymers. The important aspect of this in-situ process is how the additive can be easily added and affect the final morphology of the produced fiber mats, during its creation process. Not only could the coatings affect the morphology of the fibers and their thermo-physical and electrical properties, but definitively also the mechanical properties of the fibers are also expected to be influenced by the coatings [9, 18]. Future work will be focused on the systematization of this novel methodology to decorate fibers, to be able to experiment with other types of materials, as well as creating a process that could be easily reproducible and simple to operate. With this process setup, it will be possible to use different particle-like materials for coatings, such as nanoparticles of different elements that could benefit the fibers being produced by this in-situ deposition method.

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Data Availability All experimental data were processed using Microsoft Excel and Image J. Experimental data will be made available upon reasonable request.

Declarations

Conflict of Interests On behalf of all the authors, the corresponding author states that there is no conflict of interest.

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