The electro-spinning devices the opened door to the nano dimension

Prof. **Dominique C. Adolphe**, Ph.D
University of Haute-Alsace, Ecole Nationale Supérieure d'Ingénieurs Sud-Alsace, Laboratoire de Physique et Mécanique Textiles
Mulhouse cedex, France
e-mail: dominique.adolphe@uha.fr

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Since 2004, the Nano-team of LPMT has developed and investigated the electro-spinning facilities in order to produce products made of filament presenting a nano-size in diameters. In order to achieve these goals, the following studies have been carried out in different directions, one on the electro-spinning devices, one on the electro-spinning conditions and their optimisation and the last area to be studied has been the development of product with specific properties in terms of structure and filament orientations. These products are mainly developed for medical purposes.

Key words: *electro-spining, optimisation, nano dimension.*

1. Introduction

Since 2004, LPMT is involved in the production of objects made of electro-spun nano-web. To achieve these goals, different studies have been carried out on different directions. The first study focuses on the development of the lab-scale electro-spinning booth. 3 generations of booths have been developed and a safe, secured and automatized one has been finally built and used for all the researches that have been carried out in this field. In parallel, a study on the evaluation of the electro-spinnability of the polymer/solvent solutions has been conducted. This study is crucial as soon as you would like to test new polymers even with a low amount of material. Concerning the object (product) developments, following the request of our colleagues from different areas (Electrical faculty, Chemistry department, Medical Faculty), functionalized objects are requested and it appears that some objects have to present differential structure within the object, therefore investigations have been carried out in order to be able to produce these objects with the required properties.

2. Electro spinning booth

As told in the introduction, different booths have been built in the laboratory, horizontal production bottom up vertical production and top down vertical production, the last one illustrated on Fig.1 is a top down vertical production, it presents the more reliable security device in order to be used by all the researchers without any risks [1, 2].
This booth is composed of:

- A computer driven XY motion device to handle the collector plate,
- A high voltage power supply (from 0 to 30 kV),
- A pump to deliver the solution polymer-solvent
- A security system to avoid any accident.
- A needle holder that can be rotated in regard to the production desired.

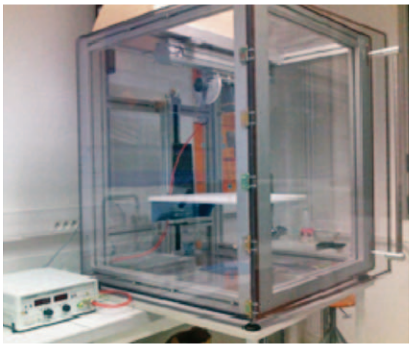
Fig.1 Third electro-spinning booth

3. Developed products

In this paper, 2 different products are presented, the first product is an elec-

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*Preliminary lecture on 8th INTERNATIONAL TEXTILE, CLOTHING & DESIGN CONFERENCE – Magic World of Textiles, October 2nd to 5th 2016, Dubrovnik, Croatia tro- spun nano-web made of PAN and functionalized with carbon nanotubes, the second product is a structured layer dedicated to the scaffold applications and the tissue engineering.

3.1. Electro-spun nano web made of PAN functionalized with carbon nano tubes

The application for this object is focused on electronic applications such as super capacitor or sensor development [3]. The desired properties are good electrical conductivities in surface and/or in volume or a variable resistance depending on the pressure applied. Polyacrylonitrile (PAN) with molecular weight Mw = 150000 gmol^{-1}, N, N-Dimethylformamide pure (DMF), purified multi-wall carbon nanotubes prepared by vapor deposition on a catalytic support, supplied by Arkema, mean external diameter of 11 nm and a thickness of about 3.2 ± 1 nm have been used for this study.

As soon as you introduce particles in the electro-spinning process the main problem is the good dispersion of the particles in order to avoid the aggregates. Six dispersions of multi-wall carbon nanotubes in DMF with different loading percentages (0.2, 0.4, 0.5, 0.7, 1.0 and 1.5 wt. %) were prepared using high shear homogenizer (18000 rpm during 15 min). In order to avoid over heating of nanotubes resulting from high shear mixing, an aqueous bath was used for this purpose. Then, samples were ultrasonicated for 30 min at 50 ˚C.

To prepare the charged colloids to be electro-spun, proper quantities of PAN equivalent to a concentration of 10 wt. % were added to the treated dispersions of MWNT in DMF. Samples were stirred for 24 h at 70 ˚C to insure the homogeneity of the final spinning polymeric solutions.

The prepared solution was, then, electro-spun by means of an electrospinning set-up manufactured at LPMT (cf. Fig.1). Based on the production procedure, previously detailed the following sample has been produced.

The Fig. 2 to 7 represent the SEM micrographs of the different produced samples.

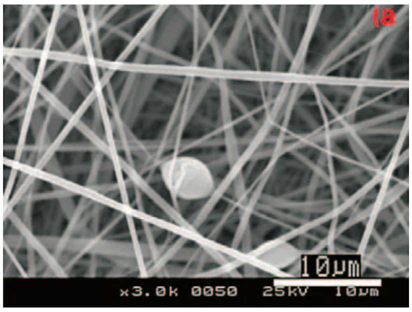
It can be noticed that the CNT are visible on the shape of the nano-fimanents. More the concentration, more the CNT are visible in the shape. This visualization is due to the CNT aggregates.

On these photos, 50 different fibers of each specimen have been measured, using Photoshop 6.0 ME, in order to evaluate their diameters.

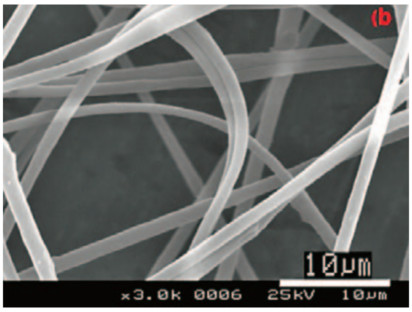
The Fig.8 displays the results of these diameter measurements. Based on these measurements it can be assumed that CNT addition increases the conductivity of the solution, therefore the obtained filaments be-

Tab.1 Electro spinning conditions (needle - collector distance: 30 cm, spinning time: 60 min)

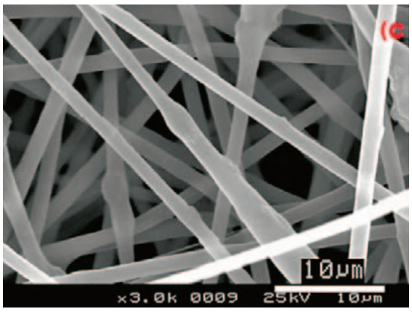
	10% PAN	10% PAN 0.2% CNT	10% PAN 0.4% CNT	10% PAN 0.5 % CNT	10% PAN 0.7 % CNT	10% PAN 1.0% CNT	10% PAN 1.5% CNT
Voltage (kV)	11	12	12.5	11	14	14	12
Feed rate (mL/h)	0.354	0.212	0.212	0.283	0.424	0.424	0.283



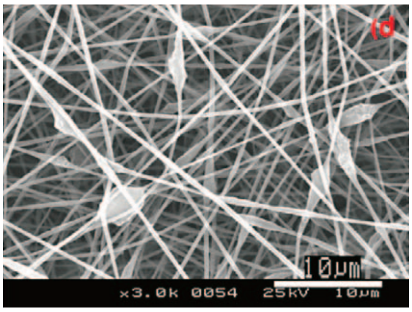
Sl.2 10% PAN



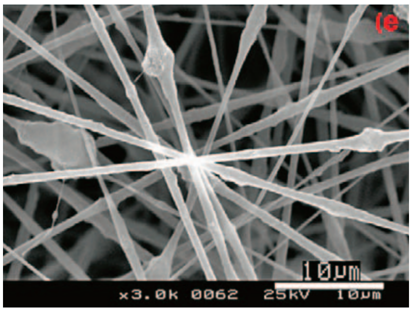
Sl.3 10% PAN – 0.2% CNT



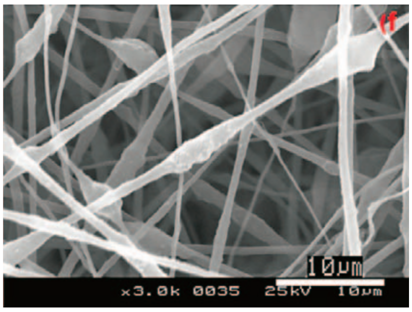
Sl.4 10% PAN – 0.4% CNT



Sl.5 10% PAN – 0.5% CNT



Sl.6 10% PAN - 0.7% CNT



Sl.7 10% PAN – 1.0 CNT

come, in a first time, thinner. When the CNT percentage increases, the aggregates become more frequent and induce an increase of the diameter. The inclusion of the CNT has been decided for improving the samples conductivity, this conductivity will be tested in different manner resumed in the Tab.2.

Two kinds of measurement are realized, the measurement of the volume and surface resistance. The measurement set-up are presented in Fig.9 and 10.

The obtained results are resumed in the following Fig.11, 12 and 13.

It can be observed that:

- The percolation threshold of CNT, for volume electrical conductivity is located between 0.4 to 0.5 wt.%.
- The volume electrical resistivity is directly influence by the applied pressure whatever the CNT concentration is.
- The current content of CNT do not permit to find the percolation threshold for the surface electrical resistivity and the pressure applied do not change the value of the resistivity. It is proven by the constant value of the electrical resistivity whatever the percentage of CNT and the applied pressures are.

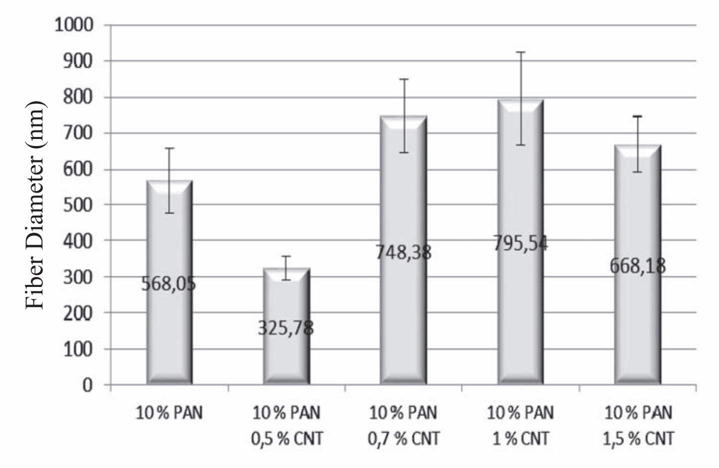


Fig.8 Diameters of the electro-spun filaments

Tab.2 Parameters of electrical resistance measurements

Shape & dimensions of sample	Type & dimensions of electrodes	Conditioning of specimen	Test conditions	Applied voltage	Time of electrification
Square 2 × 2 cm² Rectangular 2 x 6 cm²	Plates of copper metalized by gold 2 × 2 cm²	No cleaning No pre-drying 24 h of conditioning	20 ± 2 °C 60 ± 2 %RH	Surface Resistance: 500 V Volume Resistance: 10 V	2 min

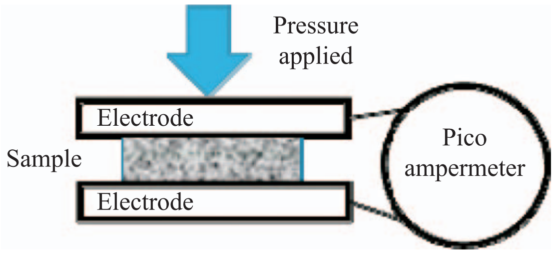


Fig.9 Volume conductivity measurement

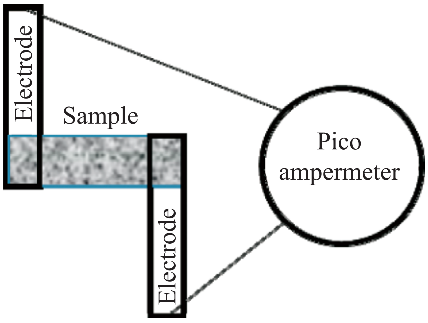


Fig.10 Surface conductivity measurement

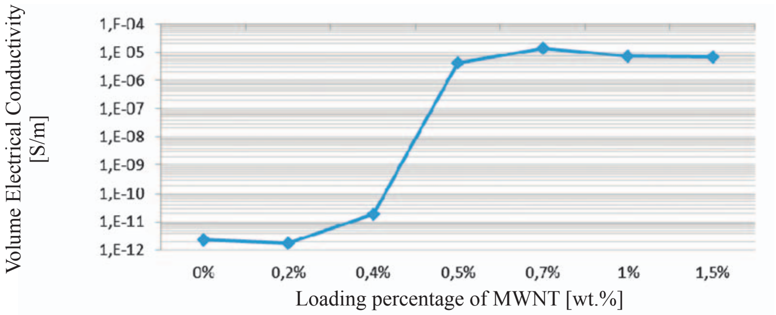


Fig.11 Volume electrical conductivity vs the multi-wall carbon nanotubes percentage

3.2. Novel 3D structured Electrospun Polyamide Scaffolds

The electro-spun substrates, due to their main interesting property, large surface area to volume ratio, attract more and more the interest of the biomedical scientific community. One of the most important areas is tissue engineering in which it is needed to provide a scaffold to mim-

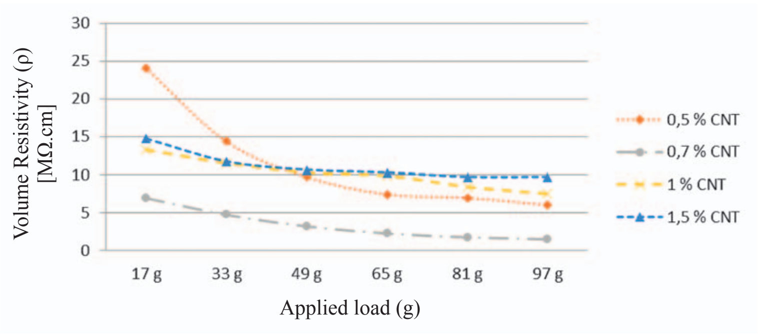


Fig.12 Volume electrical conductivity vs applied pressure

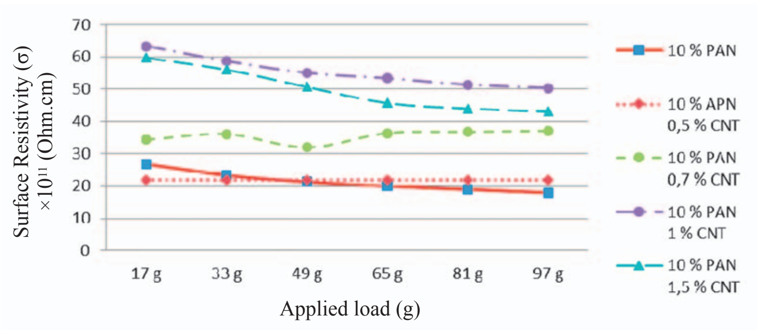


Fig.13 Surface electrical conductivity vs applied pressure and CNT percentage

ic the natural Extra Cellular Matrix (ECM) for cell growth and new tissue formation [5, 6]. Nano-fibrous materials are good candidates for this kind of application and fiber orientation plays an important role in cell attachment and proliferation [7].

Collector design is one of the most important parameters of electrospinning process which affects the structure and orientation of nanofibers in electrospun nanoweb. There are different collector types with different designs such as static plate, rotating drum, parallel electrode, rotating disc, etc. which have been developed [8]. Depending on collector type, nanofibers orientation can be changed from totally random to highly oriented arrangement [9, 10].

In this study, different 3D collectors has been produced thanks to 3D printing technique. This collectors were used in electrospinning system (Fig.1) to produce Polyamide-66 (PA-66) scaffold. A design of the frames also proposed to be produced by the 3D printer to keep the scaffold fix to characterize easily. As mentioned in the literature, cells have different growth behaviour on an electro-spun nanoweb scaffold depending on orientation of nanofibers. In order to validate the efficiency of this method a cell culture tests were performed using Chondrocyte cells. It is expected that the performed biological experiments in this study could indicate the ability of the PA-66 3D scaffold to support cell activities.

Tab.3 The different dimension of grooves

Samples Grooves	Width (W) [mm]	Distance between Grooves (D) [mm]
Small (S1)	0.2	0.4
Small (S2)	0.2	0.6
Small (S3)	0.2	0.8
Medium (M1)	0.4	0.4
Medium (M2)	0.4	0.6
Medium (M3)	0.4	0.8

6 collectors having different patterns were produced to investigate the effect of collector geometry on nanofibers orientation and architecture.

The Tab.3 described the different geometry of the collectors.

To validate the precision (0.1 mm) of 3D printing, collectors were observed by Scanning Electron Microscope (Quanta 400F Field Emisson, USA) of 50kV and surface and side view photos of collectors were recorded and analyzed. These observation are presented in Fig.14, 15, 16 and 17.

Polyamide 6.6 (PA-66) was selected because of its good mechanical and physical properties. Moreover, it has been proven that PA-66 has good biocompatibility with human tissue [15, 16]. Commercially available Polyamide-66 was dissolved in formic acid to produce polymeric solution with four different concentrations; 15, 17, 20 and 25wt.%. Then, stirring was applied by using a magnetic stirrer for 24 h at 53 ºC.

Tab.2 shows the result of nanofibers' diameter versus polymer solution concentration and needle tip to collector distance. According to the nanofibers characterization, as shown below, two conditions were chosen; 17 % (w/w) concentration with 30 cm needle-collector distance and 20 % (w/w) concentration with 10 cm needle-collector distance. These conditions and parameters were selected according to the smallest standard deviation (SD) and the smallest diameter of nanofibers.

SEM images presented in Fig.16; 17, 18, 19 indicate the morphological properties of nanofibers and their structure in the produced scaffolds. In Fig.16; 17, 18, 19, the images clearly showed the oriented and non-oriented parts in the scaffold. The results show that structured collectors allow producing nanowebs templates made of nanofibers with alter-

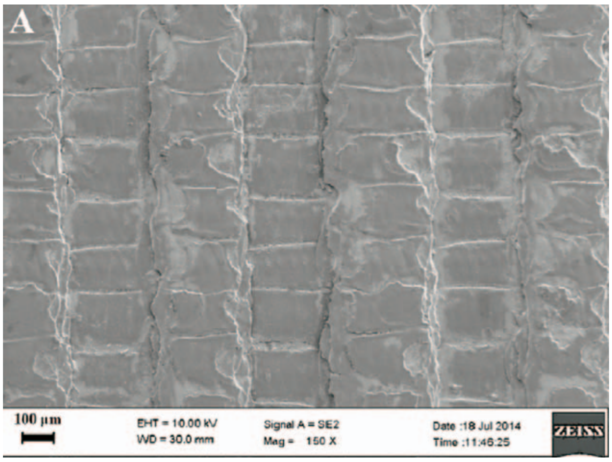


Fig.14 SEM image of collector S1

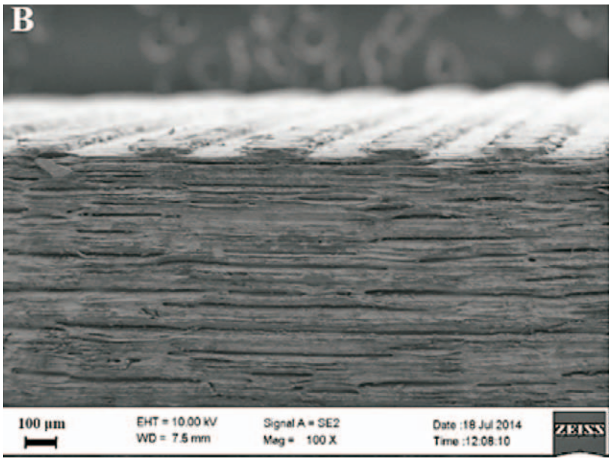


Fig.15 SEM side view of collector S1

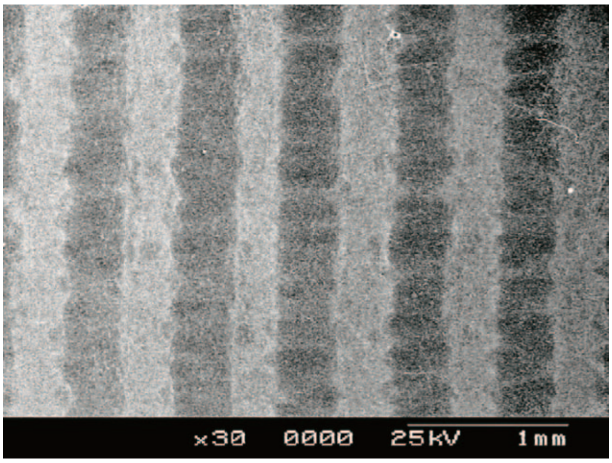


Fig.16 SEM images of PA-66 20% (w/w) nanoweb

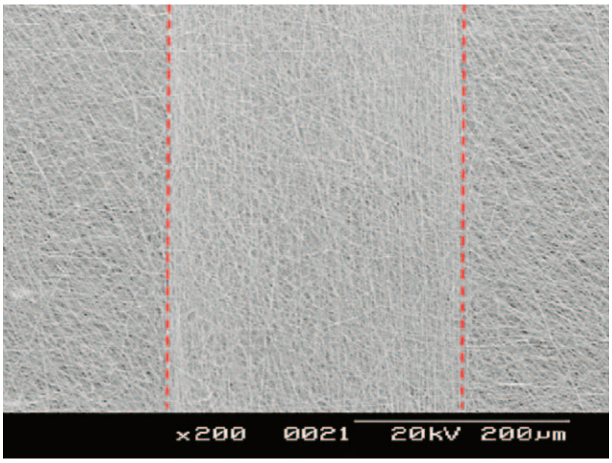


Fig.17 Oriented and non-oriented parts of scaffold nanofiber

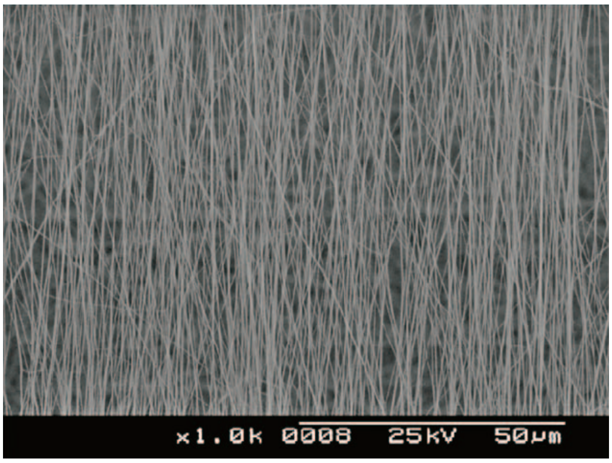


Fig.18 Oriented nanofibers

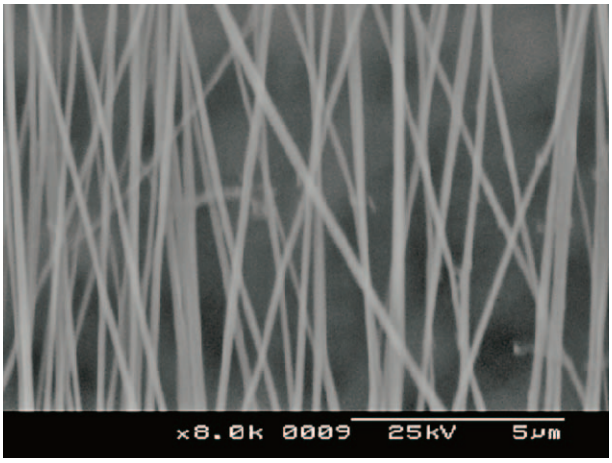


Fig.19 Oriented nanofibers

native pattern of oriented and non-oriented area.

As it was mentioned previously, by changing the design of the collector in the electrospinning process, we can achieve different rates of alignment and orientation of the electrospun nanofibers. This geometry changes in the fiber orientations could influence the cells growth in the case of scaffold and tissue engineering applications.

After characterization by SEM (Fig.16-19), the findings clearly show that, the PA-66 nanofibers followed both the geometries and dimensions of the fabricated 3D collectors. The random nanofibers

Tab.4 Result of nanofibers' diameter versus polymer solution concentration and needle tip to collector distance - two chosen conditions for electrospinning

Concentration (%)	15	**17**	**20**	**25**
Needle tip to collector distance 30 cm				
Average diameter (nm)	98	**98**	118	129
SD	26.6	18.8	25.1	24.4
CV%	27%	19.20%	21.30%	18.90%
Needle tip to collector distance 10 cm				
Average diameter (nm)	135	190	**194**	226
SD	39.9	62.9	59.3	101.6
CV%	29.50%	33.20%	30.50%	44.90%

were found mostly on the top of the grooves and on the edge, but the oriented nanofibers are observed in the valley.

4. Conclusions

This paper has highlighted the huge number of possible applications of the electro spun material thanks to 2 specific examples, one in electrical engineering and sensor development and the second in medical application, scaffold design and ECM production. By adding functionalized material inside the nano filament, new functionalities could be added to this one and specific behaviour can be achieved. By playing on the shape of the collector, complex filament orientation can be obtained; this complex filament structure can be customized in order to facilitate the cell growth and the cell colonization.

Future studies could run on different directions, the first one, by including some other nano particles such as clay, meso-porous material, MOF, etc. Every added particle will generate specific functionalities that could be customized regarding consumer requirements. Another direction could be to shape the electro-spun layer in order to achieve special applications where the shape and the structure are crucial in the success of the product development.

Acknowledgement

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