

# Fabrication and Characterization of polyamide-66 Nanofibers Via Electrospinning technique: Effect of Concentration and viscosity

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**Abstract:** polyamide-66 continuous Polymer nanofibers webs were produced by using conventional single needle electrospinning jets technique. In this paper solution parameters such concentration and/or viscosity were investigated to optimize fiber morphology. The first morphological and structure properties of the fiber (average diameter, height, length, surface roughness and fiber shape) are visualized by Atomic Force Microscopy. Good alignment and small of polymer nanofibers was confirmed by AFM. Low Polymer concentrations 7 wt% was the best conditions to produce the smallest nanofibers ( $d=125$  nm). We investigated that fiber diameter decreases with decreasing polyamide-66 concentration. This study shows that modifying solution's concentration provides a straightforward method for changing morphological properties of electrospun nanofibers for specific applications.

**Key Words :** ElectroSpinning (ES), Polymer NanoFibers (PNF), Nanotechnology (NT), polyamide-66 (PA66), Atomic Force Microscopy (AFM).

## 1. Introduction

The electrospinning form mechanical, electrical and physical techniques which stem from atoms or molecules leading to the nano size of the material so it is (bottom-up) way that has many important properties and multi applications. Electrospinning technique is very simple, that does not require any sophisticated and expensive equipment - comparing with other physical techniques like Epitaxy- and that can be easily scaled-up for mass production. Has recently, regained importance as an efficient and straightforward technique to produce of different materials such as metallic, ceramics and polymeric fibers in nanoscale. ES has been demonstrated to be an extremely versatile technology able to produce fibers with diameters ranging from few nanometers to several microns [1], from over two hundred synthetic and natural polymers, in the form of plain fibers, blends and organic-inorganic composite fibers [2]. Nanomaterials especially nanofibers possess superior structural and physical properties not found in conventional fibers (bulk materials) e.g. they have a high porosities, high surface areas, large volume-to-mass ratios, this will increase the capability of nanofibers to react with the solution or air treated, also this allows a higher adsorption rate of various trace organics and bacteria for improving water quality. The size of the fiber has a nanoscale surface texture, leading to different modes of interaction with other materials compared with macroscale materials. These aspects and a wide variety of pure and blended, natural and synthetic, organic as well as inorganic polymers have already been successfully electrospun into fibers allowing the production of tailored nanofibrous webs for multiple applications, e.g. in filtration, membranes [3], sensors [4], catalysis, ultra-strong composites, optical devices, conductive thin films [5], functional textiles, Protective or smart clothing [6], (bio-)medicine [7], drug encapsulation, wound dressing, vascular grafts, stent manufacture, tissue engineering [8] and blood vessel engineering [9-10]. The morphology and diameter of electrospun nanofibers are dependent on a number of processing parameters that include. (a) the intrinsic properties of the solution such as the type of polymer and solvent, polymer molecular weight [11], viscosity (or concentration), elasticity, conductivity, and surface tension [12]. (b) the operational conditions such as the applied voltage, the distance between spinneret and collector (tip-target distance), and the feeding rate of the polymer solution [13]. In addition to these variables, the humidity and temperature of the

surroundings may also play an important role in determining the morphology and diameter of electrospun nanofibers [14]. For instance, the polymer solution must have a concentration high enough to cause polymer entanglements yet not so high that the viscosity prevents polymer motion induced by the electric field. The solution must also have a surface tension low enough, a charge density high enough, and a viscosity high enough to prevent the jet from collapsing into droplets before the solvent has evaporated [15].

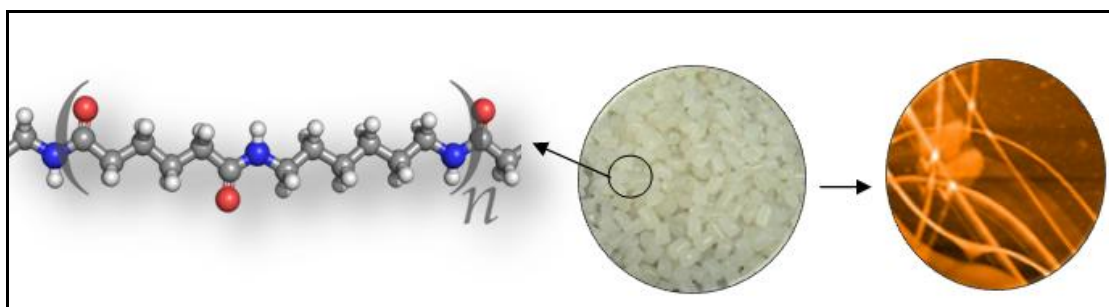
## 2. Experimental materials and methods

### 2.1 Materials

For the experiments, we have worked with a Polyamide-66 (PA66) polymer (Mw 262,35 g/mol) was received from Sigma Aldrich Co. The formic acid (FA) was purchased from Sham-LAB with corporation I-Fisher Technology-Germany, which was used directly without further purification.

#### PA66 solution preparation:

The PA66 solution was prepared by dissolving PA66 granules (see figure 1) in pre-determined proportions in formic acid (85 wt%). Various polymer PA66/FA solution with concentrations ranging from 4 to 17 wt%. PA66/FA solution viscosities were determined by Viscologic TI1 viscometer. The solution was prepared at room temperature and gently stirred by magnetic force for 3 h to expedite the dissolution. A homogeneous solution was achieved by slow agitation. The agitation was kept slow to avoid mechanical degradation of the polymer chains. After the PA66 had completely dissolved and cooling it to room temperature, the PA66/FA solution was then placed inside a 10 ml syringe, the excess air was removed, and the syringe was placed in the syringe pump. These solution were electrospun at different voltages 10-25 kV and needle tip-to-collector distance 15-25 cm.



**Figure 1. The formation of nanofibers from granules of polyamide-66**

PA66 nanofibers are prepared by ES method on glass substrates (26mm×38mm×1 mm). The glass substrates are dipped during 5 min into hydrochloric acid, ultrasonically cleaned with double distilled water, immersed into methanol solution, rinsed again with double distilled water and then rinsed and stored in dried box during 10 min.

### 2.2 Electrospinning

In electrospinning process, the setup consisted of a DC high voltage power supply seen in Figure1 from HV-PHYWE, (Order no: 13671.93, Type: Hochsp .Netzger) with an electrical potential range from 0 to 30 kV, and a tow-syringe pump seen in Figure1 (Dual Channel syringe pump Systems. Model HO-SP-2DH from Holmarc Opto-Mechatronic (p) Ltd., India). The flow rate can range from 55μL/hr to 37 ml/min (using a 20 ml syringe with 19.05mm diameter). We have used 10 ml syringe connected to metallic needle with an internal diameter (ID) of 0.6 mm. All experiments were carried out under atmospheric pressure and at room temperature. The positive electrode wire was hooked at the metal part of the needle and negative part of the electrode was attached to the metal collector. Tow to five minutes of operation time was sufficient for the deposition of fibers on glass substrates. A horizontal setup was chosen for electrospinning process. A picture that was captured during electrospinning is illustrated in Figure 2.

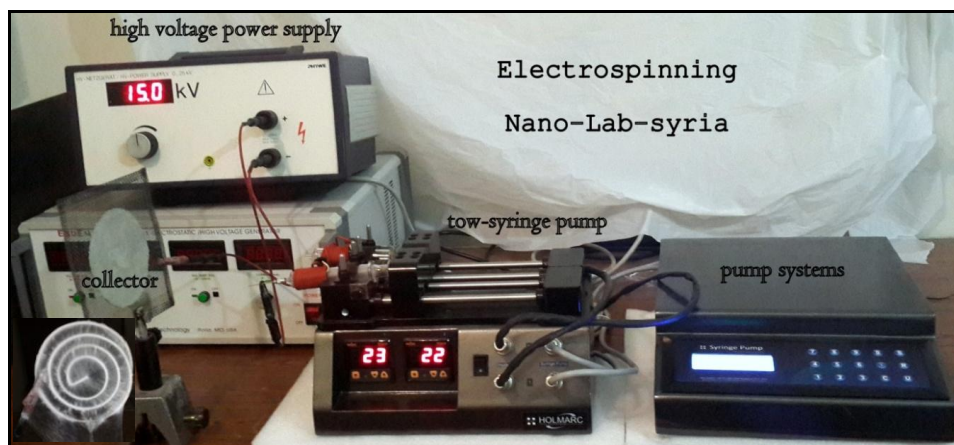


Figure 2. Photograph of the electrospinning apparatus used in this work.

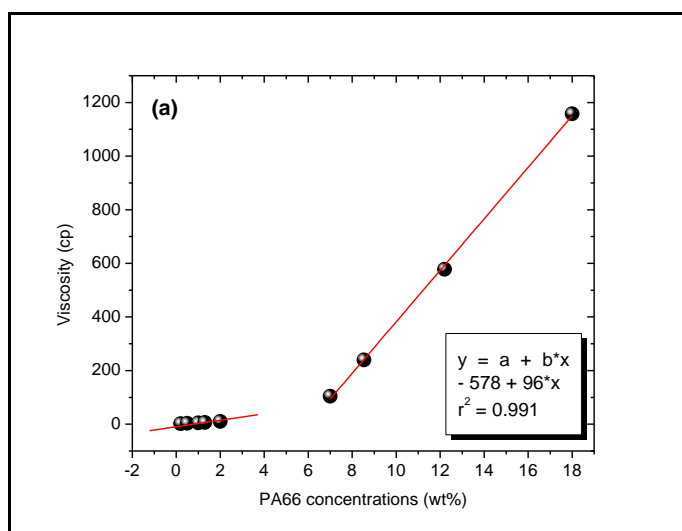
## 2.2 Characterization of electrospun fiber

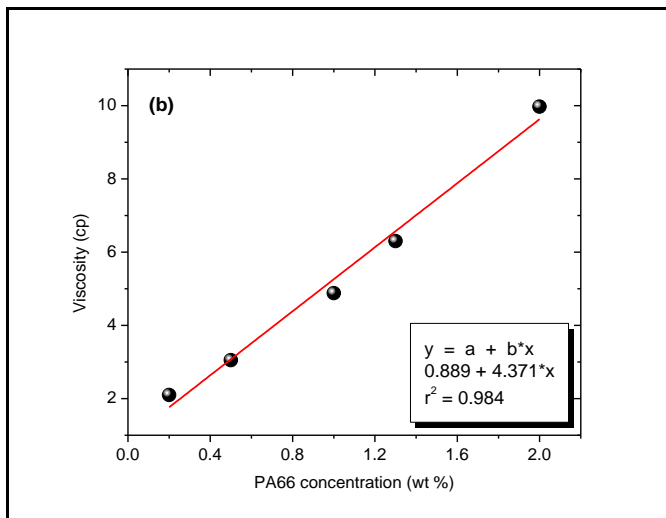
The results obtained from the qualitative and quantitative analyses of the Atomic Force Microscopy. The AFM is able to physically examine structural fibers surfaces without a conductive coating. AFM imaging is performed on the Nanosurf system (easyScan2) operating in a tapping mode where is not contact between the sample and the tip. Silicon cantilevers (Tap190 Al-G, NanoSensors) are used. Each image was then processed using AFM Software (Nanosurf Report Expert 5.0). All samples were scanned at room temperature in normal atmosphere. The scanning size was  $10\ \mu\text{m} \times 10\ \mu\text{m}$  and the images are captured in the medium mode with  $256 \times 256$  pixels. A many measurements were taken and the highest and lowest values discarded prior to calculating the average diameter.

## 3. Results and discussion

### 3.1 Concentration and viscosity of polymer solution

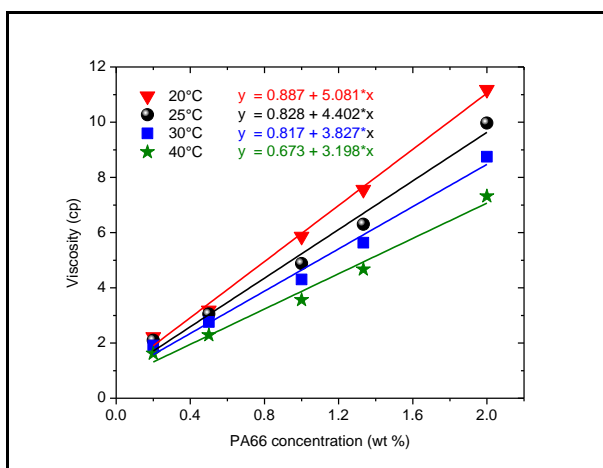
The concentration of solutions is a variable that has a dramatic effect on the results of electrospinning trials. In this work, the influence of the concentration and/or viscosity on the average diameters of electrospun nanofibers of PA66 will be investigated. Viscosity of a material can be defined as the measure of the resistance to flow. There are several factors affecting solution viscosity. Molecular weight, polymer chain entanglement, concentration, and temperature are accepted as the main factors. The solution viscosity can be controlled by the solution concentration. Hence, polymer concentration has tremendous effect on the viscoelastic jets of nanofibers. In order to control the fiber diameters formed by electrospinning method, we studied the relationship between the viscosity and concentration of PA66 solution. Viscosity versus concentration of PA66 solution in the range investigated is plotted in figure 3.





**Figure 3. Viscosity Vs low and high concentration of PA66 solutions in formic acid at T=25°C, (a) 0.2 - 18 wt% and (b) 0.2 - 2 wt%.**

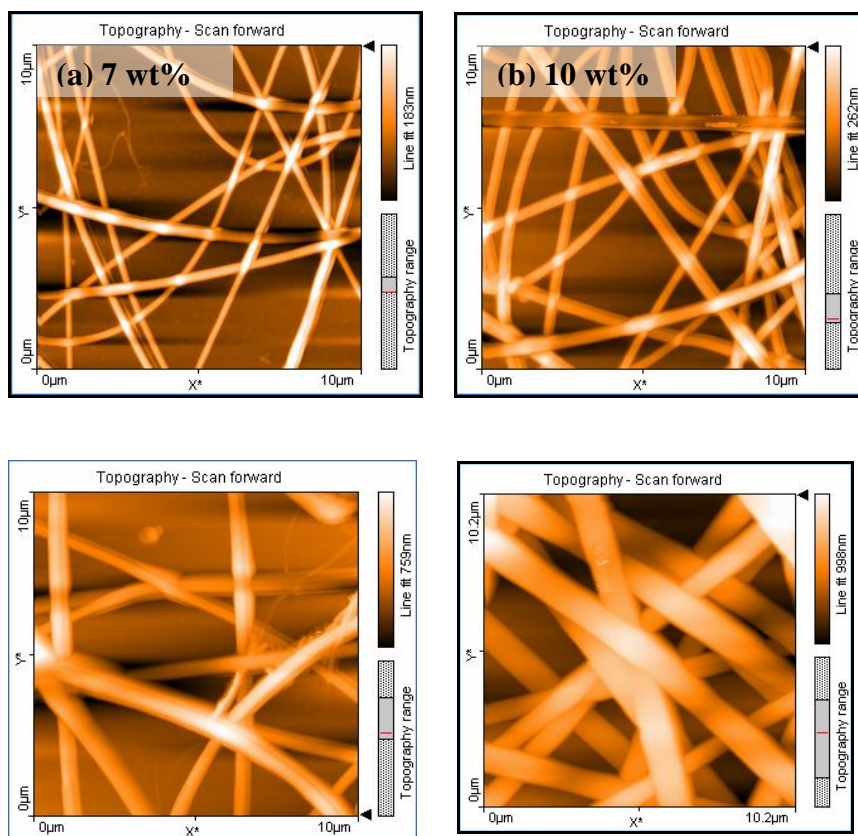
We found that this relationship is linear for the concentrations ranged between 7-18 wt% [Fig 3(a)]. While this linear relationship almost be neglected for low concentrations ranged between 0.2-2 wt%, (slight difference in viscosity of polymer was noticed at this very low concentration) as shown in [Fig 3(b)], therefore we are not worked in this range of concentration which was too low to make fibers. The viscosity of the solution was found to be dependent on PA66 concentration. However, when a solid polymer is dissolved in a solvent, the solution viscosity is proportional to the polymer concentration. Thus, at the higher polymer concentration, the larger resulting nanofibers diameters could be gained. Whereas, the concentration of PA66 was increased above 18 wt%, the fluidity of the solution decreased tremendously and the syringe pump could not feed the solution with at a constant rate (0.25 mL/hr). Under these conditions, electrospinning experiments could not be carried out. There is also a lower limit for the concentration of PA66. For the solutions with a PA66 concentration less than 7 wt %, the solution viscosity was found to be very low for the realization of electrospinning. We also studied the effect of temperature on the viscosity of the solution for different concentrations of PA/FA polymer solution. Higher temperature lowers the viscosity of the solution, increases the solubility of the polymer and raises the polymer chain mobility. This greater solubility, low viscosity of the polymer jet and enhanced mobility of the polymer chains strengthen the stretching of the polymer jet and finally more uniform fibers can be produced. In order to clarify the effect of temperature on viscosity of PA66 solution, we tested the effect of PA66 concentration ranged between 0.2 - 2 wt% on solution viscosity at versus temperature (20 °C, 25 °C, 30 °C, 40 °C). The results can be found in Figure 4.



**Figure 4. Effect of PA66 Polymer concentration on solution viscosity at different values of temperature (T= 20°C, 25°C, 30°C, 25°C) of polymer solution.**

### Morphology of the electrospun polyamide-66 nanofibers:

Polymer concentration seems to be one of the most effective parameters determining the morphology of the electrospun fibers. In order to study the effect of concentration of the PA66 solution on morphology and diameter of the fiber formed, we have prepared several solutions of PA66/FA with different PA66 concentrations ranging from 2 wt% to 18 wt%. The applied voltage at a value of 25 kV, the flow rate of 0.25 mL/hr, the inner diameter 20-gauge needle of (20G = 0.603 mm) and the distance from the capillary to the target (20 cm) were kept constant throughout the experiment. At low polymer concentrations, surface tension is the dominant effect on fiber morphology. Below a certain concentration (2 to 4 wt%), drop and small grains have been formed instead of fibers with average diameter of 228 nm and a height of 94 nm, likely due to the low viscosity. The relationship between the concentration of PA66 and the diameter of fibers is shown in Figure.5. It shows the AFM microphotographs (10 $\mu$ m x 10 $\mu$ m) images of ultrafine PA66 fibers electrospun deposited onto glass substrate at different concentration values ranging from 7 to 18wt%. However, PA66 fiber can hardly be obtained beyond this range. These AFM micrographs were then used to analyze the average diameter, height and surface roughness as shown table 1. The AFM image shows that as the concentration is increased than 4 wt% (7 wt%), the morphology was changed from drops to uniform and smooth nanofibers structure, the average diameters, height of PA66 fibers electrospun was 125 nm and 59 nm respectively. PA66 nanofibers show a fully homogeneous and randomly oriented web composed of relatively straight fibers and the pores with varying sizes are formed. On the other hand, PA66 grain or beads do not appear and this leads to optimum surface efficiency of PA66 webs since the surface/volume ratio is remarkably increased. We can see also from AFM images; particularly at low concentrations, the presence of some fibres doublets or fibres fused together partially. With increasing concentration of PA66 solution to 10 wt% (Fig 5(b)), the average diameter and height of NFs increased to 273 nm and 73 nm respectively. At 14 wt % PA66 concentration (Fig 5(c)), cylindrical electrospun fibres were observed with the average diameter of 490 nm and height of 189 nm. An increase of the concentration of the solution more and more until we get to 18 wt % (Fig 5(d)), the average fibre diameter (713 nm) and height (307 nm) becomes gradually large. This is probably because a higher viscosity results in a larger fibers diameter and the solution viscosity is proportional to the polymer concentration.

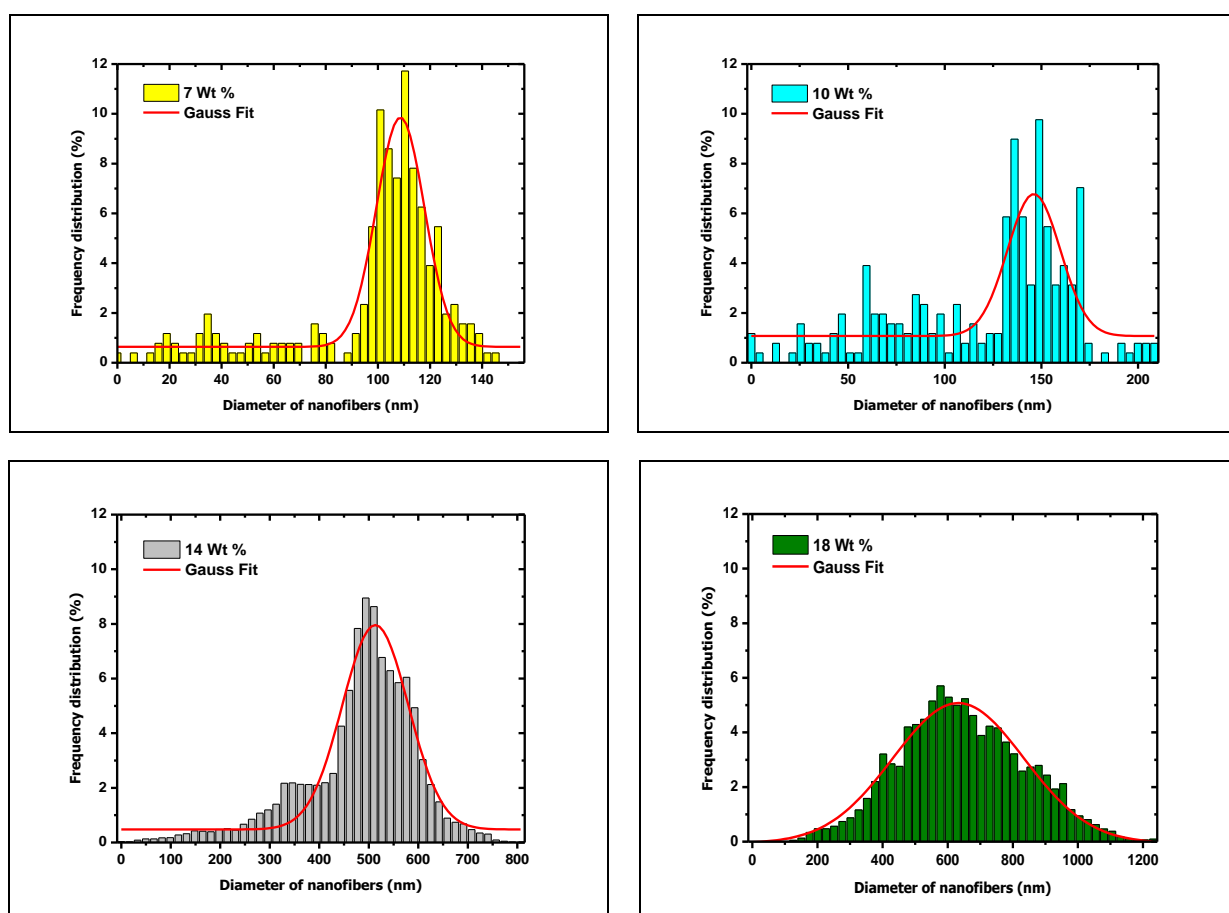


**Figure 5. Two-dimensional (2D) AFM surface images of PA66 nanofibers at a constant voltage 25 kV, flow rate of 0.25 mL/hr, tip to target distance 25 cm, and 20-gauge needle, with varying concentration: (a) 7wt%; (b) 10wt%; (c) 14wt%; (d) 18 wt%.**

**Table 1. The mean fiber diameters, heights and Roughness as a function of the concentration.**

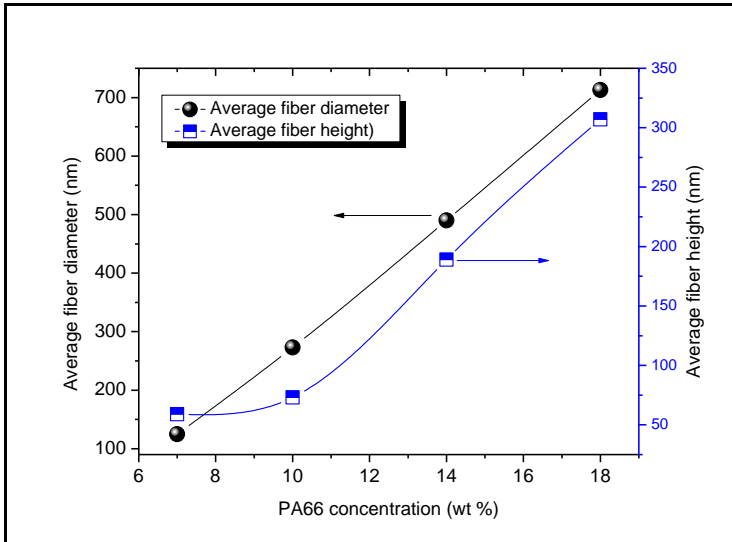
Number of experiments	Concentration	Average fiber diameter	Average fiber height	Mean roughness
S1	7wt%	125 nm	59 nm	41 nm
S2	10 wt%	273 nm	73 nm	46 nm
S3	14 wt%	490 nm	189 nm	177 nm
S4	18 wt%	713 nm	307 nm	207 nm

According to figure 6, the distribution of fiber diameters was measured for each concentration. A narrow distribution of nanofiber diameters were observed at a lower concentrations of 7 wt %, while broader distribution in the fibre diameter was obtained at higher concentrations of 18 wt %.



**Figure 6. The effect of concentrations on the fiber diameter distribution at 20 kV, 0.25 mL/hr, 25 cm and 20G according to AFM photographs.**

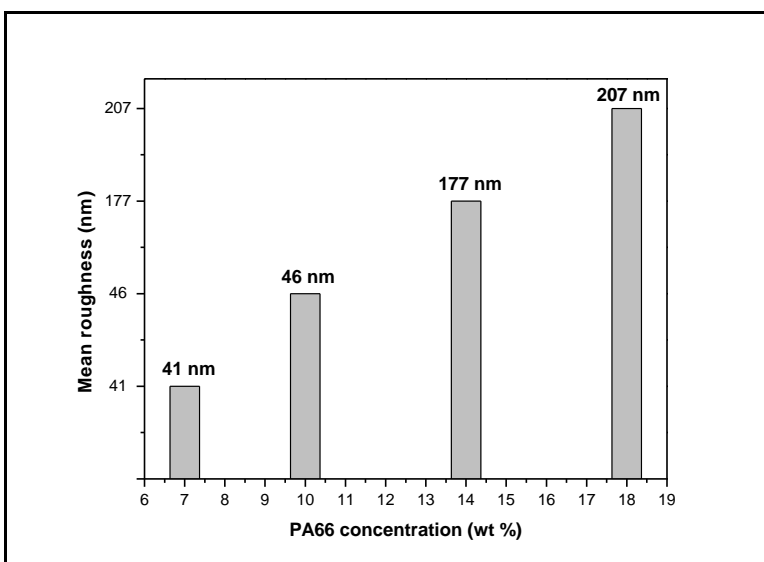
We show also in figure.7 the average fibers diameter and height calculated as a function of the concentration. Evidently, when the polymer concentration increased, the nanofibers diameter and height increased exponentially. It can be found that much finer fiber could be gained when the concentration of the solution is much lower.



**Figure 7. Effect of concentrations of on the diameter and height of fibers electrospun from PA66/FA**

at a constant voltage of 20 kV, flow rate of 0.25 mL/hr, nozzle to collector distance of 25 cm and diameter gauge needle 20G.

We can see in that curves a clear change in the average diameter and height as a function of the concentration, in the case of high concentrations (18 wt%) the average diameter of 713 nm, height of 307 nm, while when using the low concentration (7 wt%), the average percent reduction of fibers diameters, heights was calculated to be 83%, 81% respectively. The result showed that increasing the concentration while keeping other parameters constant significantly increases the size of the fibers. To explain the concentration effect on fibres morphology, we argue that the lower is the concentration, the more difficult is to dry the electrospun fibers before they reach the collector. Where, there will be less amount of chain entanglement in polymer solution. The forces from surface tension become dominant and smaller fibres formation occurs along the string of electrospun fibers. In contrast, at higher concentrations, the electrospun fibers are mostly dried by the time they are collected. During electrospinning of higher concentration solutions, the jet would not split due to the sufficient chain entanglement, and this single jet gets to target to form larger diameter fibers. Also, at higher concentrations, viscosity of the solution becomes higher and it prevents the jet having larger bending instabilities. This causes small deposition of fibers on the collector and the resultant fibers with large diameters. Therefore, PA66 concentrations in formic acid between 7-18 wt% were the best electrospinning conditions to produce the smallest nanofibers. This result is compatible with previous studies of reference [11]. Also the mean surface roughness determined from AFM images (Fig 8).



**Figure 8. Diameters distribution histograms of fiber diameters measured for each concentration.**

For 18 wt% PA66 concentration was 207 nm and 41 nm for 7 wt%, the average percent reduction of surface roughness was also calculated to be 80%. This indicates quantitatively that the mean surface roughness does indeed decrease with lower concentrations.

#### 4. Conclusion

In this study, the effect of concentration of the solution on the morphology of electrospun polyamide-66 nanofibers was investigated and characterized. Atomic Force Microscopy were used to study the web morphology, sizes and diameter distribution of produced nanofibers. Straighter and ultrafine PA66 nanofibers were produced by electrospinning technique. It was found, that the average of nanofibers diameter decreases and the distribution became wider with decreasing PA66 concentration. PA66 nanofibers with smooth surface and small diameter of 125 nm were successfully obtained using low concentration of the PA66 solution.

#### 5. References

1. Baji A, Mai Y W, Wong S C, Abtahi M and Chen P 2010 *Compos. Sci. Technol.* 70 703- 18.
2. Bhattarai S, Bhattarai N, Yi H, Hwang P, Cha D and Kim H. Novel biodegradable electrospun membrane: Scaffold for tissue engineering. *Biomaterials* 2004; 25: 2595–2602.
3. Yan Li, Zhengmaing Huang, Yandong Lu, “electrospinning of nylon-6, 66, 1010 terpolymer”, *European polymer Journal* 42 (2006) 1696-1704.
4. Dapeng Li, Margaret W. Frey, Antje J. Baeumner “Electrospun polylactic acid nanofiber membranes as substrates for biosensor assemblies” *Journal of Membrane Science* 279 (2006) 354–363.
5. Yuan-Li Huang, Avinash Baji, Hsi-Wen Tien, Ying-Kui Yang, Shin-Yi Yang, Chen-ChiMMA, Hong-Yuan Liu, Yiu-WingMai and Nian-HauWang, “Self-assembly of grapheme onto electrospun polyamide 66 nanofibers as transparent conductive thin films” *Nanotechnology* 22 (2011) 475603 (7pp).
6. Nattanmai Raman Dhineshababu, Gopalu Karunakaran, Rangaraj Suriyaprabha, Palanisamy Manivasakan, Venkatachalam Rajendran, " Electrospun MgO/Nylon 6 Hybrid Nanofibers for Protective Clothing", *Nano-Micro Lett.* 6(1), 46-54 (2014).
7. Mohamed H. El-Newehy, Salem S. Al-Deyab, El-RefaieKenawy, and Ahmed Abdel-Megeed, “Nanospider Technology for the Production of Nylon-6 Nanofibers for Biomedical Applications” *Journal of Nanomaterials* Volume 2011, Article ID 626589, 8 pages doi:10.1155/2011/626589.
8. Archana Mishraa,1, Yihua Looa,1, Rensheng Denga,1, Yon Jin Chuahb, Hwan Tak Heeb, Jackie Y. ing a, Charlotte A.E. Hausera, “Ultrasml natural peptides self-assemble to strong temperature-resistant helical fibers in scaffolds suitable for tissue engineering—239” *Nano Today* (2011) 6, 232.
9. Frenot, A., Chronakis, Ioannis S. (2003) “Polymer nanofibers assembled by electrospinning”, *Current Opinion in Colloid and Interface Science*, 8(1), 64-75.
10. Huang Z-M.; Zhang Y-Z.; Kotaki M.; Ramakrishna S. *Composites Science and Technology* 2003, 63, 2223-2253.
11. Lilia Muller Guerrini, Marcia Cristin Branciforti, Thomas Canov, Rosario Elid Suman Bretas, “ Electrospinning and Characterization of Polyamide 66 Nanofibers With Different Molecular Weights”, *Materials Research*, Vol. 12, No. 2, 181-190, 2009.
12. Jarusuwannapoom T., Hongrojjanawiwat W., Jitjaicham S., Wannatong L., Nithitanakul M., Pattamaprom C., Koombhongse P., Rangkupan R., Supaphol P., Effect of solvents on electrospinnability of polystyrene solutions and morphological appearance of resulting electrospun polystyrene fibres, *Eur. Polym. J.*, 41, 409-421 (2005). [9]
13. Zhang C., Yuan X., Wu L., Han Y., Sheng J., Study on morphology of electrospun poly(vinyl alcohol) mats, *Eur. Polym. J.*, 41, 423-432 (2005).
14. Li D., Xia Y., “Electrospinning of nanofibres: Reinventing the wheel”, *Adv. Mater.*, 16, 1151-1170 (2004).
15. Frenot A., Chronakis I.S., “Polymer nanofibres assembled by Electrospinning”, *Curr. Opini. Coll. Interf. Sci.*, 8, 64-75 (2003).

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