# An Innovative Development Towards The Industrialization of Electrospinning Process - Hybrid Electrospinning Technology

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## PURPOSE

Early discoveries about the electrospinning process date back to the 1930s. Since then, thousands of scientific papers and patents have been published on electrospinning processes, nanofibers and their application areas. The advantages offered by nanofibers for different applications have been scientifically proven and accepted by all concerned. In spite of the enormous application potential, electrospun nanofibers have not been widely used in practice. The main reason is that the fiber production rate of conventional systems is far lower than the requirement for commercial usage. In this context, it is possible to find investigations on many different system designs for high speed application of the process in the literature. In this context, many studies have been made to increase the production speed and different system configurations have been tried. In this paper we will focus on a new approach, which is defined as hybrid electrospinning technology.

## INTRODUCTION

Although it is possible to encounter different definitions in the literature, nanofibers are generally defined as fibers under 1-micron diameter. With their unique properties like surface area and volume ratios, porosity, mechanical characteristics, usability of a wide range of materials, ease of the production methods, nanofibers are considered as an advantageous material by the actors of science and technology areas.

The simplicity of the fabrication scheme, the diversity of materials suitable for use with electrospinning, as well as the unique and interesting features associated with electrospun nanofibers, make them attractive for many different applications like; tissue engineering scaffolds, wound dressing and healing materials, advanced air filters, water and wastewater filtration membranes, sensors, battery separators, supports for catalysis, regenerative medicine materials etc.

There are several methods to produce nanofibers from different polymers, such as drawing, phase separation, template synthesis, self-assembly, island-in-the-sea, centrifugal spinning and electrospinning. Among those methods, electrospinning has been accepted as the most effective and versatile technology for producing nanofibers from various polymeric materials [1].

Figure 1. Application areas of nanofibers (Inovenso, 2019)

The electrospinning process is an excellent method for the formation of nano-sized polymeric or composite fibrous structures, allowing the control of fiber orientations. Easily changing the effective parameters on the electrospinning process makes it possible to control the fiber properties[2]. These parameters can be summarized as solution parameters, operation parameters and environmental conditions.

The history of the electrospining process is based on the practice of the British physicist William Gilbert in the 1600s by applying a controlled electric field to a drop of liquid. The first patents were granted by Anton Formhals between 1934 and 1944 in the process of developing electrospining as a commercial value generating method. In the same period, the work of producing fiber from melt C.L. Norton and patented in 1936[3].

The theoretical background of the process was built by Sir Geoffrey Ingram Taylor between 1964 and 19694. In his studies, Taylor examined the shape behavior of the cone formed by liquid droplet under the influence of an electric field with mathematical model studies. This characteristic droplet shape is now known as Taylor cone.

A simple electrospining assembly consists of three different components (Figure-2). These are the pump used to feed the solution into the medium and the nozzle at the end of the feed line (usually a syringe needle, although different feeding systems may be used), a grounded (or opposite charged load) conductor collector, a high voltage power source for generating an electric field between the collector and the nozzle.

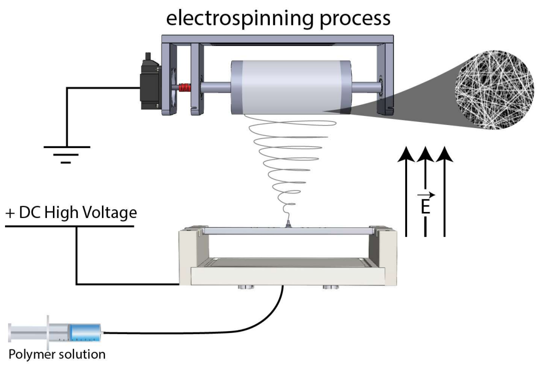


Figure 2: A basic scheme of electrospinning process (Inovenso, 2019).

Electrospinning is an electro-hydrodynamic process by working systematic. In electro-hydrodynamics (EHD), electrical charges enable any fluid to move within an electric field. During the process, the transport and distribution of these charges generate stresses that result in the movement of the fluid. The driving force in the electrospinning process is the potential difference of the static electric field. With this force, the electrically charged polymer solution or melt is pushed into a grounded collector assembly, where a dry membrane structure is formed[5].

The solution droplet at the top of the electrospinning needle is held by the surface tension forces that it has when electrospinning forces in the electrospinning area is not enough. As the voltage increased (by decreasing collector and spinneret distance of increasing the applying high voltage to the system). As the voltage is increased, the solution droplet at the tip elongates and a conical shape is formed. When the applied voltage reaches a critical value $V_c$, the electrostatic forces overcomes the surface tension and consequently a thin electrically charged jet is stretched from the apex of the cone (Figure-3)[6].

As mentioned before, there are several parameters affecting the characteristics of nanofiber medium. Solution properties are the most important. The solution parameters are the most effective in determining fiber properties. These are viscosity of polymer solution, solvent selection, surface tension and conductivity of solution. The most critical factor in controlling the structural morphology of the nanofibrous structure is polymer solution viscosity. For obtaining nanofibers, the viscosity must be in a range. That means there is a minimum and maximum value for viscosity to produce nanofibers. Below that minimum value, beaded fibers or just particles can be obtained. Increasing viscosity of solution increases polymer chain entanglements in the solution. After increasing viscosity more than maximum value, the surface tension becomes so high and it becomes impossible to jet formation from tip to collector. It is understood that a specific level of solution viscosity depending on the types of polymer-solvent system is necessary to counteract the electrostatic forces and produce a uniform electrospun jet during electrospinning. Hence this would lead eventually to the collection of defect-free nanofibres[6].

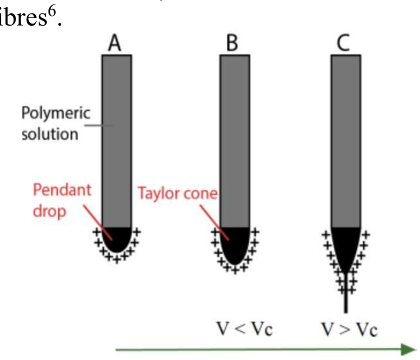


Figure 3: Schematic illustration of the Taylor cone and jet formation: (A) the applied electric field creates surface charges in the polymeric solution; (B) increasing the voltage causes change in the shape of droplet (C) The VC is critical voltage where the electrostatic force becomes equal to surface tension force. when the current voltage is higher than VC, the polymeric jet is formed and travels towards the collector due to the charge repulsion[6].

Another important solution parameter is the conductivity. The solution stretches and forms nanofibers by the repulsion of the electrical charges at the surface of the electrospinning jet. The electrospinning jet carries more charges when the solution has higher conductivity, as a result A significant reduction in the diameter of the electrospun nanofibers can be observed. When the conductivity of the polymer solution is high, the enormous tensile force will be created with respect to the voltage applied. This, in turn, helps in the formation of nanofibers with a reduced diameter[7].

Applied voltage, electrospinning process distance and flow rate are the most important operation parameters. Increasing the applied voltage reduces the drawing stress and hence decreases the diameter of the resultant fibers. However, maintenance of the control over the electrospun fibers is highly challenging at high voltage. Because increased drawing stress can result in the breakage of fibers. So for obtaining defectless fibers, applying optimal voltage during the spinning process becomes important[8].

To increase the productivity increasing flow rate is a solution in electrospinning. Higher flow rates will increase the production rate of the electrospinning process but can have adverse effects on the morphology of the fibers if not properly controlled[9]. The electrospinning system has to be designed for this purpose to obtain good fibers.

Similar to the high voltage that is applied to the system, the flow rate of the polymer solution, spinneret type; the electrospinning process distance (the distance between collector and spinneret). Nanofiber morphology is affected by the distance, because the distance is directly related with the deposition time, evaporation rate, and whipping or instability interval[10]. In their study Matabola et. al[10] observed that, with an increase in the distance, the fiber diameter decreased from 397 to 314 nm with improved uniformity. This change is attributed to the complete solvent evaporation of the solvent, more stretching and thinning which favors the formation of thinner fiber[10].

A schematic diagram of a typical electrospinning apparatus is given with Figure 2. That type of one-nozzle system is a good solution for researchers. Although many researchers have used single-needle schemes for electrospinning, the low fluid throughput in spinning has limited the industrial use of single-needle systems[7].

Besides the conventional electrospinning technique, different variations of the well-known mechanism of process have been developed. These include the multi-needle and needleless or open surface electrospinning. Both multi-needle and needleless electrospinning techniques comes with multi-jet formation to enhance the productivity of the conventional electrospinning[11].

Application of electrospinning process via multijet ejection is the technique for improving the productivity of nanofibers. But the most important question that comes to mind here is the possibility of the electrical interferences between charged jets, the instabilities are enhanced further, which can become problematic for the mass production of uniform nanofibrous membrane. So, high efficiency production of uniform nanofibers through multiple jets is of great importance to the industrial applications of electrospinning technique[12].

To meet the high liquid throughput requirements, several multi-jet systems have recently been tested. Several methods have been developed to enhance the electrospinning production rate. They can be classified as multi-needle and needleless methods.

Several researchers have tried to mass-produce nanofibers by using a free surface of polymer solution, including electrospinning based on a two-layer system, bubble electrospinning, spider spinning, ball electrospinning, disc electrospinning, cleft electrospinning, porous tube electrospinning, porous electrospinning with drilled hole, ring electrospinning, stepped pyramid stage, wire electrode, and etc[13].

Multi-nozzle electrospinning has been under ongoing investigation, since not only is it an easy method for enhancing productivity but it is also a simple technique for producing composite fibers from polymers which cannot provide a solution in a common solvent. The disadvantage of the multi-nozzle system is repulsion by adjacent jets and the non-uniform electrical field at each nozzle tip of the spinneret[14].

Conventional multi-needle electrospinning systems has a good process control, but they have a very limited production rate. Needleless systems can overcome that problem with their modified spinnerets, but needleless systems have open surface solution feeding system and that can cause a big problem to maintain consistent solution concentration and viscosity. Those changes can cause big differences on the fiber morphology during the production. On the other hand, it is almost impossible to work with rapid evaporating solvents with the needleless systems. Fiber morphology and quality are not precisely controlled, the raw materials that can be utilized are limited, which in turn limits versatile fiber production and process parameters such as flow rate, cannot be controlled.

In recent years, Inovenso made a lot of innovations for pilot and industrial systems. One of the most important innovations is a hybrid electrospinning nozzle which can increase production rate 3-4 times than conventional needles. Advantages of Inovenso's industrial system starts with a homogeneous distribution of solution to the spinnerets. That gives a uniform solution feeding capability, on the other hand the homogeny distribution of electric field in the process area is not affected. Higher production rates can be obtained by making a little increase on high voltage value. Almost same flow rates values can be seen with open surface needleless systems, while the high voltage is quite lower than them. The production rate can be increased by increasing high voltage a little. In that stronger electrical power, almost five jets can be obtained from modified nozzles. In Table-1 there is a comparison of different systems.

Table-1: Comparison of different Industrial electrospinning systems.

| Conventional Needle Based Systems | Hybrid Electrospinning Technology | Needleless Electrospinning Systems |
|---|---|---|
| Easy to Set-up | Easy to set-up | Complex set-up procedure |
| Fast evaporating solvents can be a problem with needle clogging. | Possible to work with each kind of solutions like conventional needles | Not available for working with fast evaporating solvents |
| Normal electrical power like laboratory scale electrospinning systems. (e.g. 15-20 kV) | Relatively higher electrical power than conventional needle base systems, but lower than the open surface needleless systems. (e.g. 35-45 kV) | Very high electrical power required to start electrospinning process. (e.g. 70-90 kV) |
| Uniform jet distribution | Uniform and stable jet distribution | Non-controllable jet during operation |
| Low production rates | Higher production rate | Higher production rate |
| Uniform fiber morphology | Uniform fiber morphology | Non-uniform fiber morphology |
| Fully control of electrospinning | Precise and full control of the process | Not a complete control on all of the process parameters. |
| Defectless nanofibers | Defectless nanofibers | Generally beaded and defected nanofibers |
| Control of solution concentration | Full control of solution concentration and viscosity | Difficult to maintain consistent solution concentration and viscosity |

**EXPERIMENTAL**
**Materials and Methods**

PVDF (Arkema, Kynar-761) was used as polymeric material. The solvents for the experiment were DMF and Acetone of Merck. LiCl was used for increasing the conductivity of solution. Ingredients and the properties of the solution is given in Table-2.

Table-2: Solution properties

| PVDF (%w/w) | DMF(%w/w) | Acetone(%w/w) |
|---|---|---|
| 14 | 60 | 26 |
| LiCl (gr) | Viscosity (mPa.s) | Conductivity (µS) |
| 0,05 | 1910 | 445 |

In order to improve the production capacity, different spinneret designs were made and the effect of each on the capacity was examined by applying different solutions. In this paper only the data related to the design with the highest efficiency is presented.

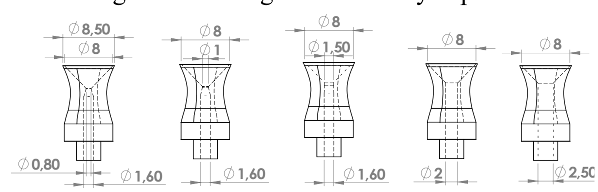


Figure 4: Used hybrid nozzles during operation. From left to right outer diameter for each nozzles are same and inner diameters are 0,8mm, 1mm, 1,5mm, 2mm and 2,5mm)

For this experiment, PE 550 model pilot scale electrospinning system of Inovenso was used. That system has 55 nozzles on it and it can coat surfaces of 550 mm width and continuous substrate by roll-roll collector. The high voltage during process was 40 kV.
System was operated under same ambient conditions. For each type of nozzles maximum achievable flow rate was checked. The distance between nozzle and collector was 140 cm.
For defect control on coated nanofiber layer, SEM images were taken by Semoscope (by Inovenso) Scanning Electron Microscope.

**EXPERIMENTAL RESULTS AND DISCUSSIONS**

In order to improve the production capacity of electrospining, some of the design-performance studies carried out in the inovenso laboratory were evaluated here. In Table 2, maximum achievable flow rates can be seen for each nozzle type and as control nozzle 18G blunt syringe nozzle was used.

Table-2: Maximum achievable flow rates for each nozzles.

| **Outer Diameter** | | **2.8 mm** | **4.0 mm** | **6.0 mm** | **8.0 mm** | **18G** |
|---|---|---|---|---|---|---|
| Inner Diameter | **1.0 mm** | 16 ml/h | 16,5 ml/h | 16,5 ml/h | 21 ml/h | 4 ml/h |
| | **1.5 mm** | 16,5 ml/h | 16,5 ml/h | 17 ml/h | 21,5 ml/h | |
| | **2.0 mm** | 16,5 ml/h | 17 ml/h | 17 ml/h | 24 ml/h | |
| | **2.5 mm** | | 17 ml/h | 17,5 ml/h | 28,5 ml/h | |

The most efficient design can be seen at Fig-5. Achieved flow rate value for this nozzle is 28,5 ml/h.

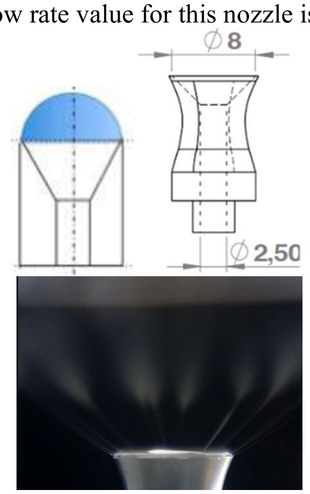


Figure 5: Hybrid electrospinning spinneret.

SEM images for all of the nozzles on this experiment were taken. But here only for the nozzle which gave the highest performance is given. SEM images are given with Fig-6

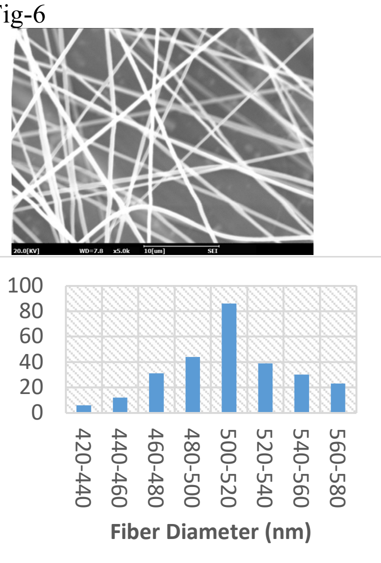


Figure 6: SEM image and fiber diameter distribution for the nozzle which has OD:8mm and ID:2,5mm

For making comparison SEM image for standard syringe needle is given at Figure-7. In this image it can be clearly seen that nanofiber layer has defects.

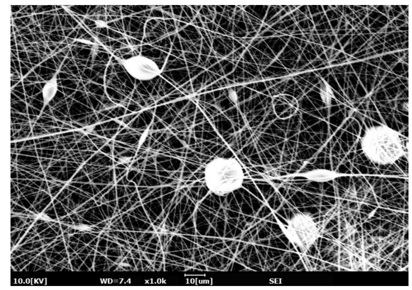

Figure 7: SEM image for 18G blunt standard syringe needle

**CONCLUSIONS**

In this study, the effect of various nozzle designs, which were developed to increase nanofiber production speed, on the effect of feed flow was investigated. When the inner and outer diameters of the hybrid nozzles were examined, the highest yield was obtained with nozzle which has an ID of 2.5mm and an OD of 8mm.

The morphology of the nanofiber coating produced was examined by SEM and no serious defect affecting the coating quality was observed.

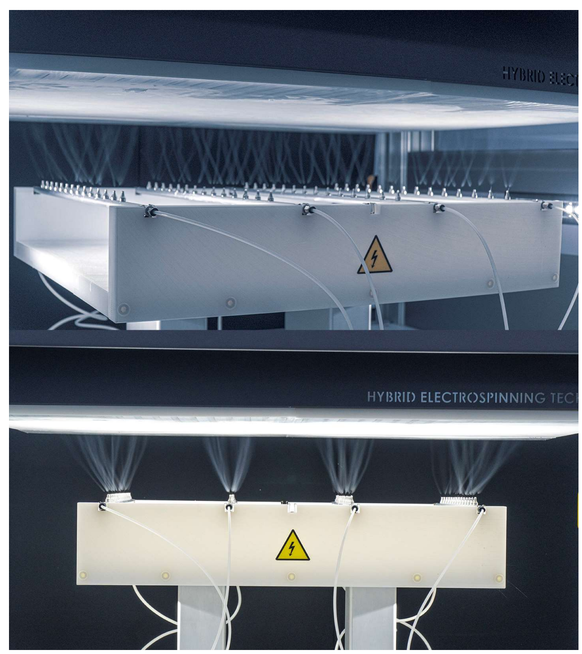

Figure: Electrospinning process area of PE300.

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