HIGH THROUGHPUT NANOFIBER PRODUCTION BY ROTATION-AIDED NEEDLELESS ELECTROSPINNING

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ABSTRACT

Our research group has elaborated a needleless electrospinning technology that operates with a rotating circular electrode. The rotating electrode includes a thin circular orifice where the solution is continuously supplied. The Taylor-cones are formed from the liquid meniscus. Rotation plays an important role in the process as it helps to dispense the solution along the thin gap and moreover the acceleration caused can help to facilitate the formation and initiation of the jets. The current study introduces the method itself, the operation detailed and shows the comparison of fiber morphology to that of the classical, single capillary setup.

1 INTRODUCTION

Electrospinning is an emerging technology as it makes available to generate ultra-fine fibers with a diameter of typically in a range of a few hundred nanometers. Many different materials can be used for the process including a wide variety of polymer solutions. The advantage of electrospun nanofibers is their high specific surface and high flexibility, therefore these fibers could be potentially used as composite reinforcements. Nanofibers have appropriate properties to use them as reinforcement of composites [1]. However, it is still a challenge to predictably realize improved performance.

There are many factors affecting the fiber formation, such as ambient conditions, electrode configuration including the distance of the electrodes, the surface tension, the electric conductivity of the liquid, etc. Because of the many stochastic parameters, electrospinning technique is still based on a 'trial and error' approach. In the 'classical' setup the electrospinning technology operates with a single capillary and forces acting in a high voltage electric field draw the fibers.

The thinning jet typically has a travel speed of only around 3-5 m/s [1] that is quite low assuming that we have only a few jets and the jets are having a small diameter and the amount of the solvent within the jet is approximately 80-95 weight%. This results in a productivity rate of only 0.01-0.5 g/h for a single capillary. Maybe that is the crucial issue that hinders the emerging of industrial applications of the technology in the composites industry. Increasing the number of capillaries does not seem to be a feasible way as clogging of the needles can occur, reaching a constant flow rate is challenging, while cleaning and maintaining such a system is also an issue [2,3,4].

There are therefore efforts to avoid the application of needles or capillary holes, these techniques are called needleless electrospinning. Several types of these have been developed previously. Different conductive magnetic particles [5], cylinders [6,7], discs [8], wires [9], or even balls [10] can be rotated in a polymer solution and many self-organized Taylor-cones can be formed from the surface of them which can result in high throughput production. With the aid of conducting gas into a polymer solution results in bubbles that are also capable for electrospinning [11-14]. All these techniques are capable to increase the production rate of nanofibers. The main disadvantage of these needleless electrospinning methods is the large free liquid surface of the solution reservoir that is open for the electrospinning space. Continuous evaporation of the solvent, water adsorption, segregation of additives can occur, and as the solvents are often flammable, their ignition can take place in extreme cases in the high voltage environment. In our study we were dealing with a novel method that eliminates the problem of such a free open liquid surface, but still has a high productivity rate.

2 TECHNOLOGY

Our research group has elaborated a needleless electrospinning system that operates with a rotating circular electrode. This technology offers high throughput and continuous production. The schematics of the process can be seen in Figure 1.

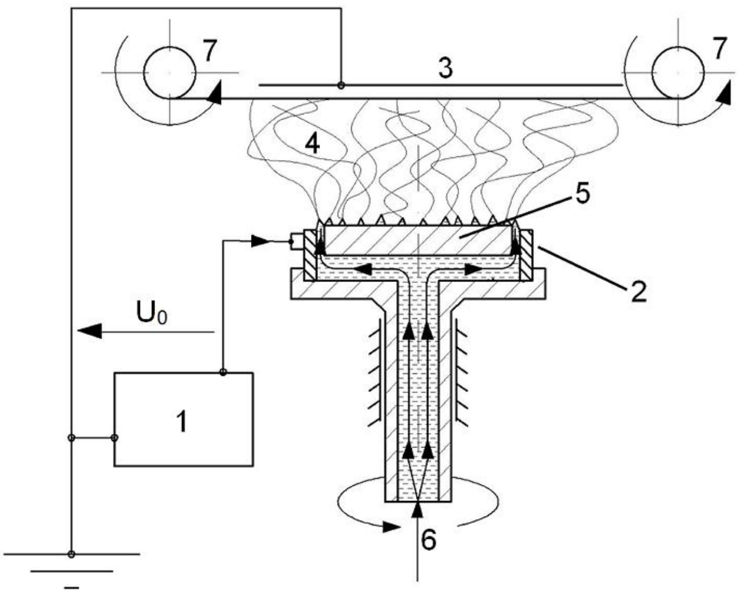


Figure 1: Scheme of the novel electrospinning method. 1: High voltage power supply, 2: Electrode (sharp edge), 3: Collector (grounded aluminum plate), 4: Forming nanofibers, 5: Blunt cylindrical part (*i.e.* lid), 6: Solution feed, 7: Traction of the textile collector substrate

The polymer solution is fed through a thin, but long circular orifice, bounded by a blunt cylindrical part from the inside and a sharp edge (electrode) from the outside. The polymer solution flowing through the orifice gets into contact with the sharp electrode and Taylor-cones are formed along the edge. Many of these Taylor-cones are formed simultaneously and in equal distances – as we found. The rotation has two roles: it helps to dispense the solution along the long electrode edge (aided by the fine vibration) and it also possibly helps in drawing the fibers. When working with high throughput volumes the evaporation rate of the solvent and adequate ventilation begins to play an important role. We designed a metal construction of the spinneret. The more detailed scheme of the design can be seen in Figure 2. which includes all important parts.

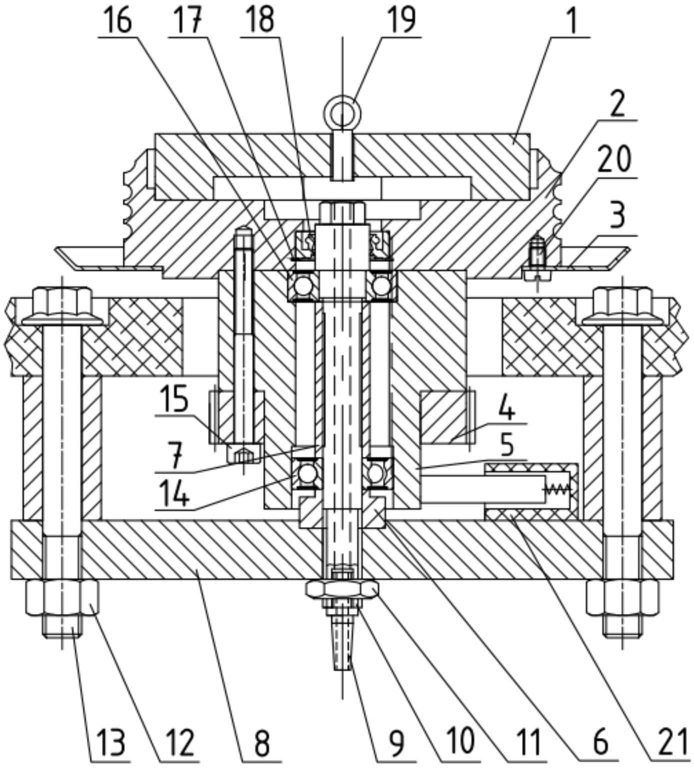


Figure 2. Engineering draft of the spinneret, 1: lid, 2: spinneret, 3: overflow collecting plate, 4: belt drive, 5-7: bearing holders, 8: base platform, 9: solution inlet, 10: shaft, 11-13: hex nuts and screws, 14: deep groove roller bearing, 15: holder screws, 16: deep groove roller bearing, 17-18: sealing and holder, 19: lid screw, 20: screws, 21: carbon brush

Figure 3. shows images of the spinneret machined from aluminum. The diameter of the spinneret at the circular orifice (a gap between 1 & 2 of Figure 2.) is 110 mm. As one can see the orifice is bounded by a sharp edge from the outside causing charge concentration. The possibly overflowing solution is collected by a plate. There are more edges formed between the plate and the edge so the overflowing solution can also undergo electrospinning from these edges. The spinneret is rotating continuously with the aid of a belt drive from the bottom.

Figure 3. The machined spinneret

3. MATERIALS AND METHODS

Polyacrylonitrile (PAN) filament fibers acquired from a carbon fiber manufacturing company (wished to remain anonymous) were dissolved in dimethyl-formamide (DMF, Aldrich) as a 12 wt% solution. The solution was fed by an Aitecs SEP-10S plus (Lithuania) syringe pump with the maximum flow rate which produced permanent fiber formation without overflow. For the electrospinning the voltage of the MA2000 NT 65/P (Hungary) type power supply was set to 60 kV, the spinneret-collector distance was 150 mm, the rotation speed was approximately 200 rpm, while the feed rate was set up to 45 ml/h that resulted in continuous and stable fiber formation.

In this study we compared the spinneret to the classical setup. There a single, hypodermic needle with an inner diameter of 0.8 mm was applied and the electrospinning was carried out vertically. The needle-collector distance was the same, the feed rate was 1 ml/h, the voltage was set to 25 kV.

Scanning electron microscopy (SEM) was carried out by JEOL 6380 LA (Japan) device. The surface of the samples was coated by JEOL JFC-1200 fine coater with fine gold-palladium (Au-Pd) alloy layer in order to avoid their charging. The determination of the average diameter and fiber orientation of 200-200 fibers was performed by using UTHSCSA Image Tool image processing software.

4. RESULTS AND DISCUSSION

Figure 4. shows a picture taken during the electrospinning process. The image shows some beard formation. As electrospinning goes with a high throughput, the solvent evaporates and the electrospinning space itself becomes enriched in it. By using continuous transversal ventilation this can be avoided efficiently. The nanofibers are collected at the top, where a PP nonwoven substrate is placed right in front of the aluminum collector screen. The textile substrate can be moved with an arbitrary traction speed within wide limits. The nanofiber mesh can be produced as an approximately 250 mm wide (depending on collector-spinneret distance and other parameters) continuous stripe. The thickness can be set easily, making available to use these nanofibers as reinforcements or interlayers of laminated composites [15].

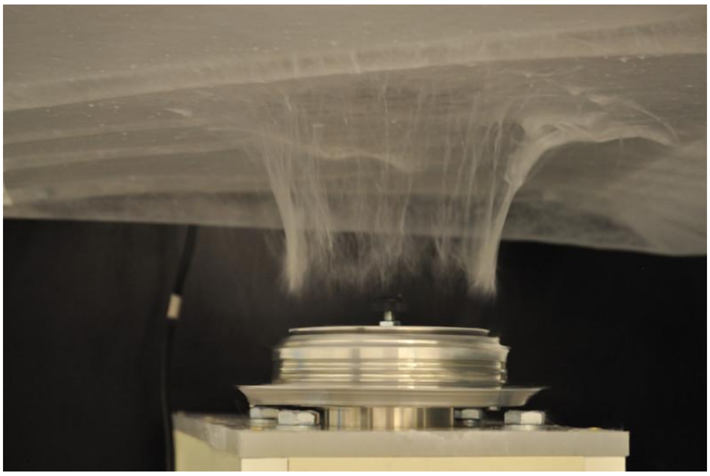


Figure 4. Electrospinning device at work

In the process the rotation plays an important role. On one hand it causes some continuous vibration of the spinneret resulting in better dispensing of the fluid along the edge. On the other hand the radial forces can help in the initiation of the jets. Usually higher rpm leads to better stability of the process. The productivity rate is 10 to 100 times higher than that of the capillary setup in general. In our case the productivity rate could be raised from 1 ml/h (capillary) up to 45 ml/h (needleless) without overflowing the solution. SEM images of the fibers can be seen in Figure 5 (classical setup) and 6 (needleless setup). One can see the morphology looks quite the same: homogeneously deposed flawless fibers could be generated in the diameter range of a few hundred nanometers.

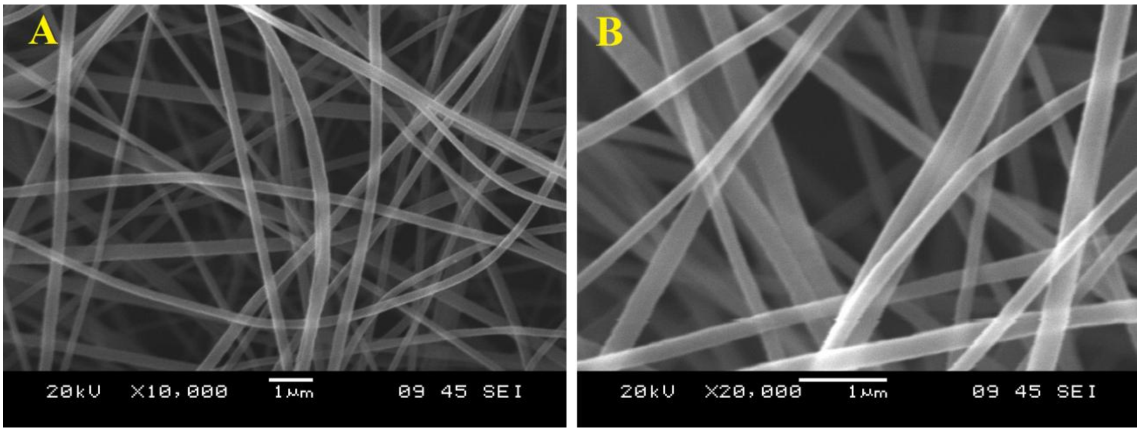


Figure 5. SEM images of the nanofibers made by the classical setup in A:10,000x and B) 20,000x magnifications

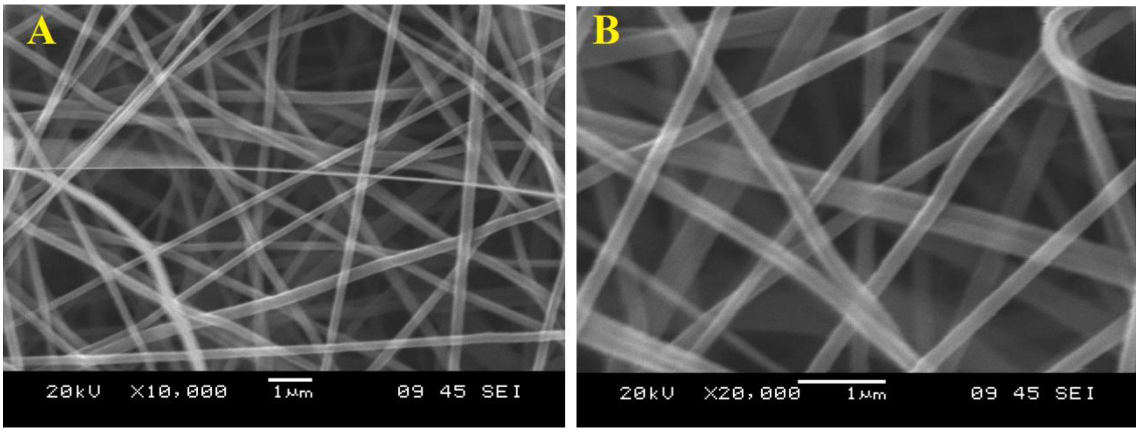
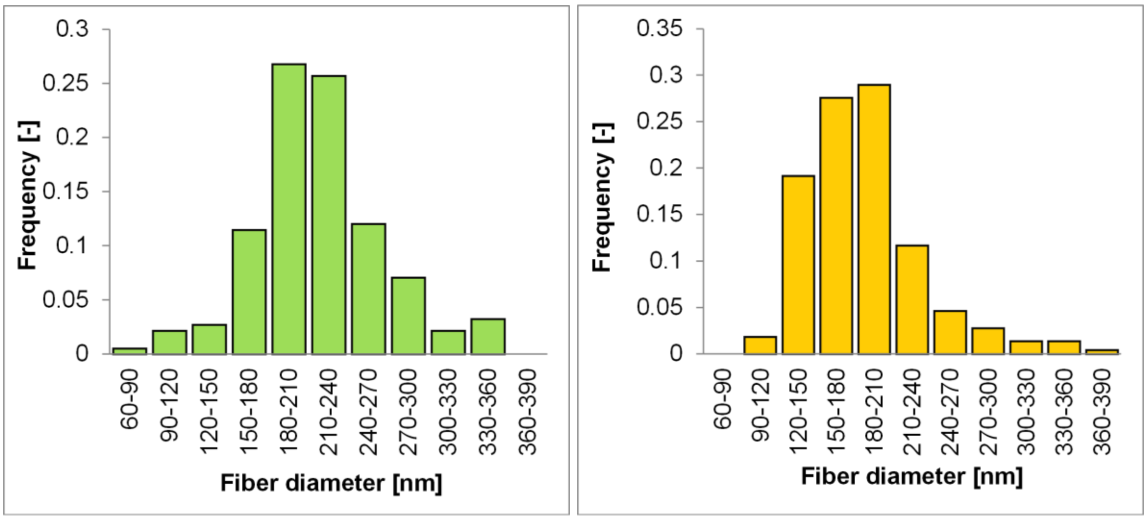


Figure 6. SEM images of the nanofibers made by the novel setup in A:10,000x and B) 20,000x magnifications

With the classical electrospinning setup (single capillary) the average diameter of the processed fibers was 214 ± 68 nm, while the fibers of the new method were only 187 ± 65 nm in diameter that is a 15% change. The change of diameters can possibly be originated from the ventilation and rotation that could possibly help in the drawing of the fibers. The rotation speed was approximately 200 rpm in our studies. To analyze the effect of the rotation speed itself further tests are necessary.

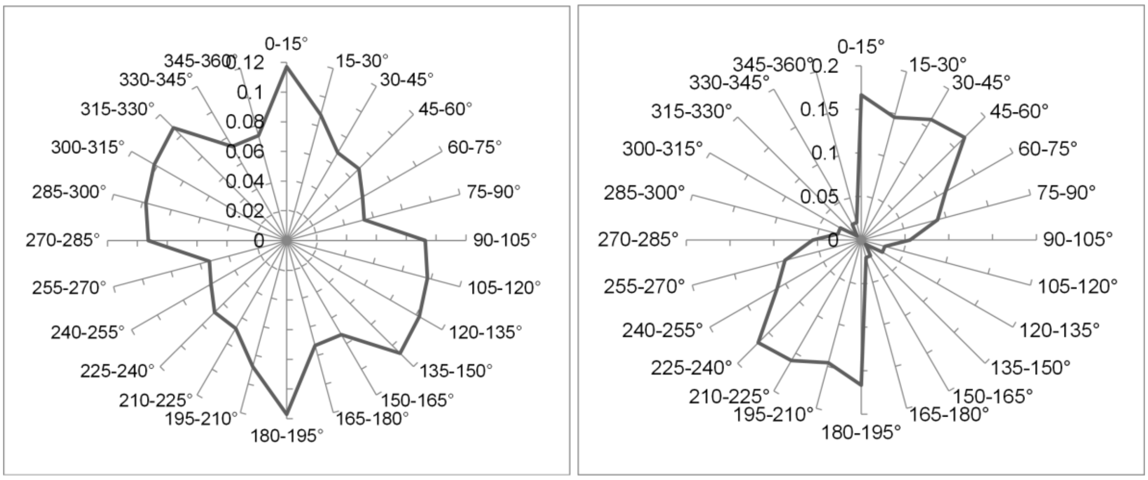
The fiber diameter distributions are depicted in Figure 7. The vast majority of fibers are in the 180-240 nm diameter range for the classical, single capillary setup, while those are rather in the 150-210 nm for the novel setup.



a) b)

Figure 7. Fiber diameter distribution of the a) single capillary, b) novel setup

The fiber orientations were also determined to confirm the orientation (and possible drawing) effect of the ventilation that was used during the sample preparation. Figure 8. shows the fiber planar orientation diagrams.



a) b)

Figure 8. Fiber orientation diagrams of the a) single capillary, b) novel setup

It can be seen that using ventilation results in a moderate orientation of the fibers. The fibers of the single capillary setup are less oriented (supposed to be homogeneously distributed) but that is not for the novel setup. The ventilation of the electrospinning space led to moderate orientation of the structure.

5 CONCLUSIONS

Our research group has elaborated a needleless electrospinning technology that operates with a rotating circular electrode. The rotating electrode includes a thin circular gap where the solution is continuously supplied. The Taylor-cones are formed from the liquid meniscus at equal distances. The fiber geometry was analyzed by SEM and it was found that the fiber diameter distributions produced by the novel method is quite similar to that of the single capillary setup. At the same time the productivity rate could be raised from 1 ml/h up to 45 ml/h without overflowing of the solution.

Further experiments are necessary to understand the role of the rotation. It is believed that the vibration facilitates Taylor-cone formation and the acceleration also helps in the initiation of the jets.

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