The Effect of Flow Rate on Morphology and Deposition Area of Electrospun Nylon 6 Nanofiber

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ABSTRACT

Electrospinning is a process that produces continuous polymer fibers with diameters of a nanometric scale. Nylon 6 in formic acid was electrospun to obtain the nanofibers. Fibers with different diameters were obtained using flow rates of 0.1, 0.5, 1 and 1.5 mL/hr, 20 wt% solution concentration, with an applied voltage of 20 kV and 15 cm spinning distance. Flow rate influenced the fiber diameter distribution, droplet size and its initiating shape at the capillary tip, the trajectory of the jet, maintenance of Taylor cone, areal density and nanofiber morphology. The morphology of the electrospun nanofibers was analyzed by using the scanning electron microscope (SEM). The effect of flow rate on the deposition area was also investigated for better control of the process. It was observed that a stabilized Taylor cone, small average droplet size, narrowest fiber diameter distribution, more stability in the originating jet, and uniform morphology of nanofiber is obtained at a flow rate of 0.5 mL/hr.

Keywords: Electrospinning; Nylon 6 nanofiber; Flow rate; Deposition area; Fiber diameter distribution; Average fiber diameter.

INTRODUCTION

Electrospinning is known as one of the most efficient, convenient methods to produce fibers of a nanometric scale. These nanometric fibers reveal several remarkable characteristics such as a large surface area to the volume ratio, high porosity, flexibility in surface functionality, and superior mechanical performance [1-2]. Nanofibers are utilized in a wide variety of applications such as filtration and multifunctional membranes [3-4], medical usages [5-9], and military systems [10] due to their outstanding properties. Recently, different polymers have been successfully electrospun into nanofibers from solutions or melts.

In the electrospinning process, the positive electrode which has a high voltage power supply is attached to a capillary tube, while the negative electrode is connected to a conductive collector. In this case, the polymeric fluid is drawn many times before reaching the collector due to the existence of the potential difference between the collector and the needle tip [11]. Throughout the process, the droplet shape at the end of the capillary tube is altered from a circular to a conical one, which is called a Taylor cone [12]. With increasing electric field, the polymeric jet originates from the Taylor cone and traveled in a direct route for few seconds, known as stable zone. After passing the stable zone, the discharged polymer solution jet undergoes bending and whipping instabilities, which make the jet draw many times before collecting on the target and producing fibers of a nanometric scale [13].

In order to produce uniform nanofibers, comprehensive investigations on the effective parameters such as viscosity, surface tension, distance between the tip and the collecting screen, applied voltage, flow rate, and solution temperature have been performed [14-22]. Flow rate is considered as one of the key parameters in controlling fiber diameter and its distribution, initiating droplet shape, the trajectory of jet, maintenance of Taylor cone and deposition area [23-27]. At high flow rates, larger droplets are formed, which increase the average fiber diameters and bead size. It is believed that at high flow rates there is a limitation with increasing the fiber diameter because the amount of charge and flow rates has not increased simultaneously [28-29]. On the other hand, lower flow rates are more desirable as the solvent will have sufficient time for evaporation. However, when the flow rate is high, a larger volume of solution is drawn from the needle tip, which needs a longer time to dry [30]. In this case, the residual solvent might induce the fibers to merge together and make webs instead of fibers.

Different modes of charged jet-originating from the Taylor cone-are strongly connected to the flow rate. Various degrees of instability lead to different modes of charged jet, and these are achieved by adjusting the flow rate. These modes affect the average droplet size and fiber diameter distribution. In an optimized flow rate, the Taylor cone is kept stable during the process, which results in the smallest average droplet size and narrowest fiber diameter distribution [22, 31].

In the present study, nonwoven mats of Nylon 6 nanofibers were prepared by the electrospinning process. An attempt was made to understand the effect of flow rate on morphological appearance, average fiber diameter and its distribution, deposition area, and initiating droplet shape. To our knowledge, so far there is no report investigating the influence of flow rate variations on deposition area.

EXPERIMENTAL

Materials and Methods

Nylon 6 fiber-grade chips (Molecular weight=1.86x104g/mol, melting point=220, density=1.12-1.15 g/cm^3 and relative viscosity=2.20-2.32) were purchased from Aliaf Co. (Iran) and dissolved in formic acid (Merck) as a solvent to yield 20 wt% solution. Prior to electrospinning the solution viscosity was measured at 24±1 using the Brookfield DV-III ultra rheometer (USA) equipped with a cone/plate accessory of spindle type RV03. The viscosity of the solution was 845.00±5cP. The morphology of the electrospun nanofibers was investigated by scanning electron microscopy (SEM-LEO440i, England), after coating the nanofiber samples with a thin gold layer to provide electrical conductivity. All statistical analyses were performed with the SPSS 13.0 statistical package. Data was regarded as significant when a P-value of 0.05 or less was obtained.

Electrospinning Set Up

The polymer solution was electrospun from a 50 ml plastic syringe with 20-gauge needle. After filling the syringe with a 20wt% polymer solution, a syringe pump (Top5300-Tokyo, Japan) was used to eject the solution to induce 20kV, a high voltage power supply (Gamma High Voltage Research, ES-60P, USA) was used. In this study, the positive electrode was subjected to the needle tip, and the opposing one was connected to the collector, which was placed 15 cm below the needle tip. The angle of the syringe was 45-degrees from a horizontal baseline. The collector was a cellulosic paper, which was placed on an aluminum sheet with the same dimension. Moreover, for investigating the effect of flow rate on the deposition area, black sheets with the same dimensions were used as collectors. All samples were electrospun for 15 minutes. The schematic illustration of the electrospinning set up is shown in *Figure 1*. In this study, flow rate was varied in the range of 0.1-1.5 mL/hr while other parameters were kept constant.

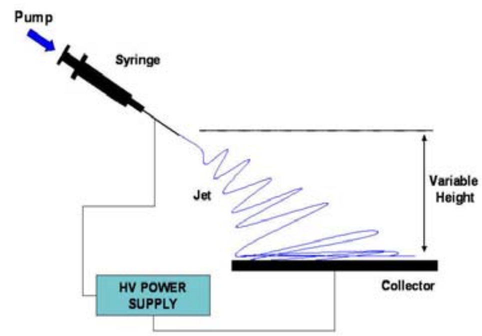

FIGURE 1. Schematic diagram of the electrospinning process.

RESULT AND DISCUSSION

The Effect of Flow Rate on Average Fiber Diameter

The average fiber diameters have been determined from the SEM images (magnification 60000X). At least 40 different fibers have been measured for each experimental condition. The statistical method for analysis of variation (ANOVA) was used to determine the effect of flow rate on average fiber diameter. One way analysis of variation proved that there is not any significant difference between the samples ($p>0.05$).

At lower flow rates, a small amount of solution was ejected from the capillary tips which lead to the formation of small droplet size. On the other hand, with increasing the flow rate, a greater amount of solution volume was ejected from the needle tip, which caused the jet of solution to be electrosprayed without any sufficient stretching. In fact, by increasing the flow rate at a constant voltage, the electric field strength was not capable of stretching the ejected solution due to the insufficient amounts of charged ions.

Depending on the conditions used throughout the electrospinning process, a variety of charged jets may form from the tip of the Taylor cone [31, 32]. According to the initial observations illustrated in *Figure 2*, the conical droplet changed into a very sharp shape due to the strength of electric field which overcame the surface tension (I). As time passed, there was a higher probability that the jet receded and initiated directly from inside the needle, where the edge of the liquid's surface met the needle wall with no externally visible droplet or cone formation. In other words, the Taylor cone completely disappeared in this case (II).

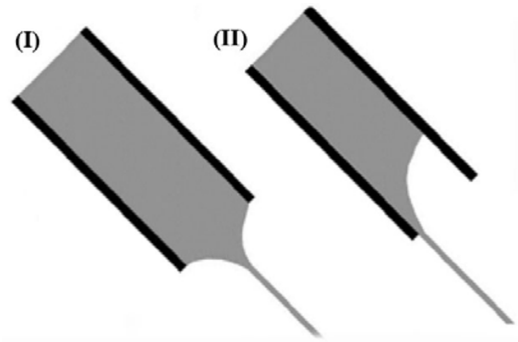

FIGURE 2. Schematic illustration of various charged jet modes in the electrospinning process with a flow rate of 0.1 mL/hr; (I) cone-jet and (II) receding jet.

At flow rate of 0.5 mL/hr, the feeding rate was proportional to the electrospinning speed. In this case, the electrospinning process was accomplished under a stable condition a lesser probability of instability and lesser falling droplets of the unspun polymer jet. In fact, at this flow rate, the Taylor cone maintained stability during the electrospinning process, which allowed sufficient time for evaporating the residual solvent and producing uniform fibers.

According to *Figure 3*, at high flow rates (1 mL/hr and 1.5 mL/hr) a large semi-spherical droplet was formed at the capillary tip (I (a), I (b)). At 1 mL/hr, after applying the electric field, the droplet was elongated and altered its shape (II (a)) while at 1.5 mL/hr, a great amount of polymeric fluid was aggregated at the capillary tip due to the high rate of feeding and weight effect (II (b)). Obviously, the effect of the gravitational force in 1.5 mL/hr was more noticeable compared to 1 mL/hr. In this case, the droplet was broken, and divided into one or more bigger segments without any extension. Finally, at these flow rates (1 mL/hr and 1.5 mL/hr), the electric field was unable to draw the whole polymeric jet and as a result unspun droplets were formed on the target (III (a) and III (b)), hence, an electrospray phenomenon was observed which affected the average droplet size and droplet size distribution.

There was also a qualitative agreement between the theoretical and experimental results. It was observed that, the number of unspun droplets at 0.5mL/hr, 1mL/hr and 1.5 mL/hr was 10, 40 and 33, respectively.

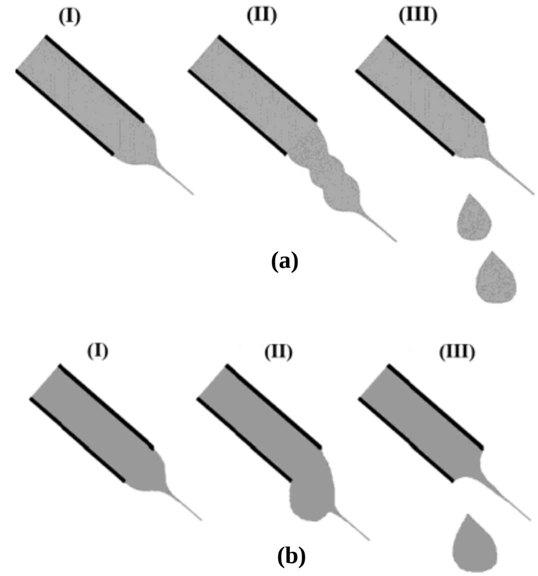

FIGURE 3. Schematic illustrations of various charged jet modes in the electrospinning process with flow rates of (a) 1 mL/hr and (b) 1.5 mL/hr.

The Effect of Flow Rate on Fiber Diameter Distribution

According to *Figure 4*, the distribution of fiber diameters was affected by flow rate variations. Obviously, when the flow rate was increased, fiber diameter distribution became wider.

In order to maintain a stabilized Taylor cone during the electrospinning process, it was necessary to adjust flow rate for a given voltage. In this research, a flow rate of 0.5 mL/hr was chosen as an optimum rate due to the formation of a stable Taylor cone, less instabilities and the narrowest fiber diameter distribution throughout the process. However, at flow rates below and above the threshold value, the Taylor cone became less stable, which produced wider distributions.

In order to produce continuous fiber it is necessary to form a stable Taylor cone. At 0.5 mL/hr, a uniform Taylor cone was observed during the electrospinning process, which led to produce uniform fibers with narrow distributions.

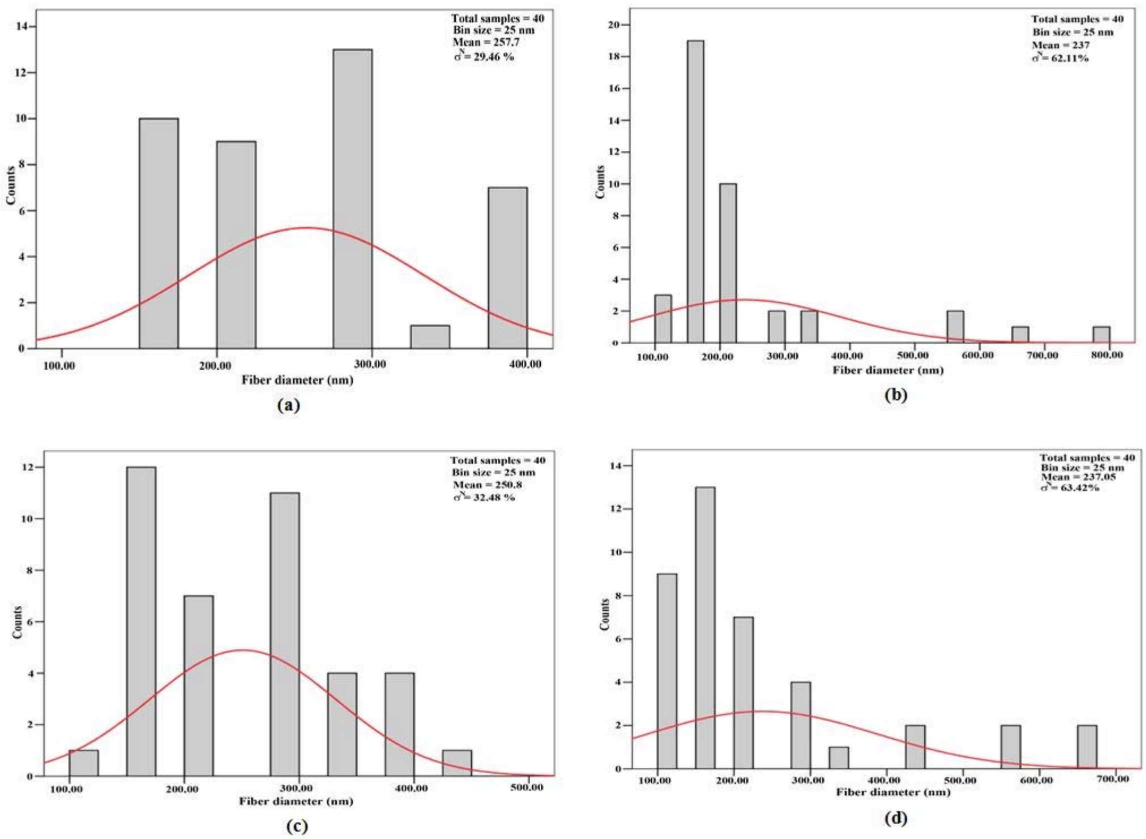

FIGURE 4. The effect of flow rate on the fiber diameter distribution at 20 wt%, 20 kv, and 15 cm according to SEM photographs.

At flow rates higher and lower than the threshold value, an asymmetric Taylor cone was formed which caused wider distributions. Under the optimum conditions, the jet was receded and originated from inside the needle and the Taylor cone disappeared completely. When it had entirely disappeared, strand breakages occurred. Indeed, at 0.1 mL/hr, shear stress between the polymeric fluid and the needle internal wall occurred. In fact, when the jet was receded, drawing forces were more concentrated on overcoming the shear stress and pulling out the available solution from the internal wall. As a result, a new Taylor cone was formed to resume the electrospinning process. On the other hand, a receding jet was always replaced by a new cone jet throughout the process, which produced electrospun fibers with a wide range of diameters.

An increase in flow rate increased the amount of material flowing through the tip, which in turn resulted in increased fiber diameter. At very high flow rates, the polymeric jet was unstable and tended to electrospray due to the effect of gravitational force. The formed Taylor cone was dropped off the end of the syringe tip, which resulted in wider distributions. Increasing the flow rate further also caused fibers to be collected without sufficient solvent evaporation, which led to the formation of flattened web-like structures.

Morphology of Electrospun Fiber

It was observed that the variation of applied flow rate significantly altered the shape of the initiating droplet and caused some changes in fiber morphology. The SEM image in *Figure 5(b)* revealed that by choosing appropriate flow rate, the formation of any defects such as blobs, splitting and branched fibers was limited and more uniform fibers were formed. As it is obvious, many defects were appeared in the morphology of the fibers by increasing the flow rate, mainly due to the greater droplet volume ratio and more unspun droplets. It was also possible to observe other defects such as branched or splitting fibers and blobs, as a result of less flight time and insufficient time for complete evaporation of the residual solvents in the deposited web. Therefore, the fiber uniformity

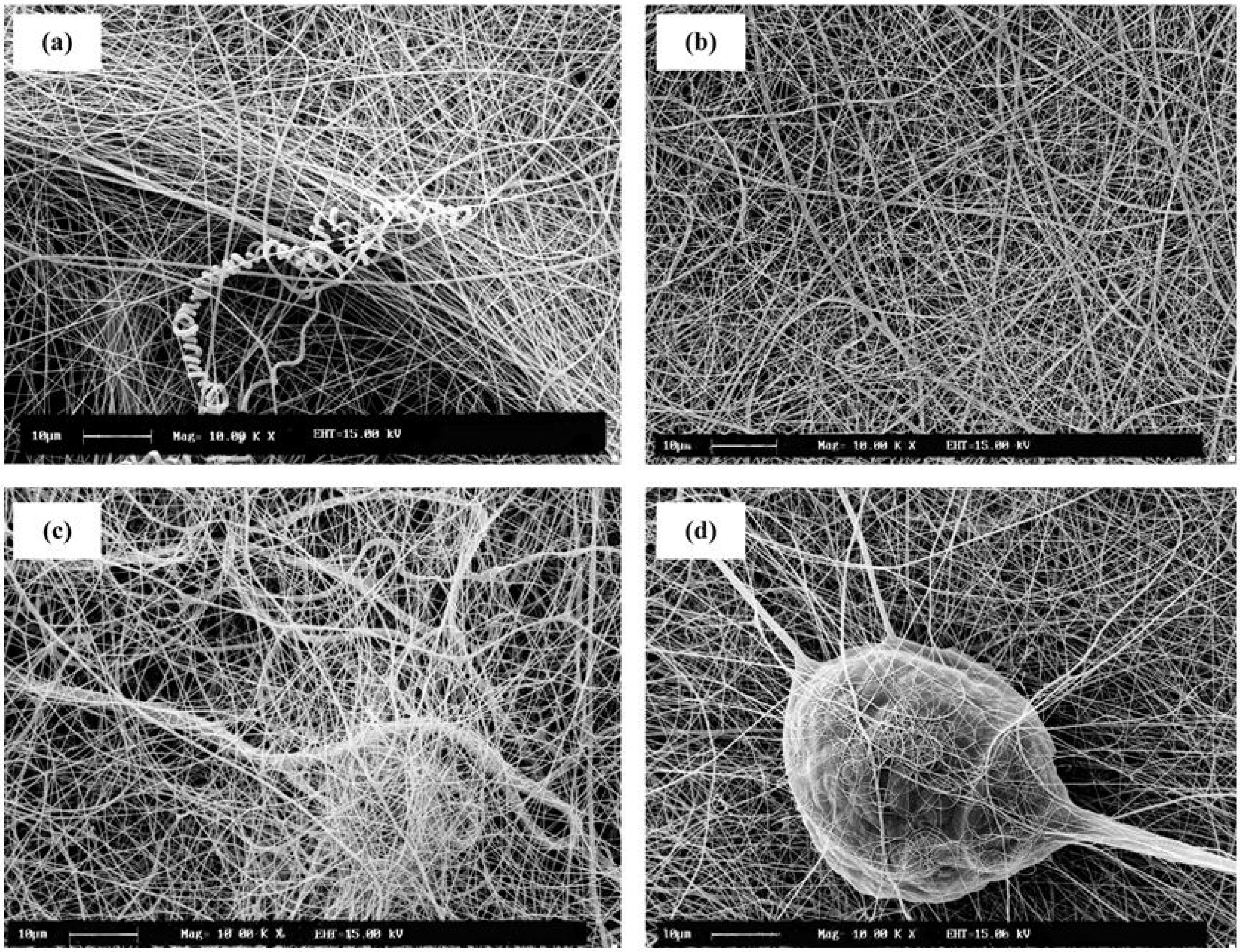

FIGURE 5. The SEM images of the electrospun nanofibers at various flow rates; (a) 0.1mL/hr, (b) 0.5 mL/hr, (c) 1 mL/hr, (d) 1.5 mL/hr.

was significantly affected by the flow rate. Moreover, it was found that the area density of the fibers decreases consistently increasing the solution flow rate.

The Effect of Flow Rate on Deposition Area

Many researchers have investigated various parameters affecting the deposition area of the electrospun nanofibers such as solution concentration, applied voltage, collection distance, and the type of the collector [33-35]. Undoubtedly, none of these existing reports were focused on the effect of the flow rate on deposition area of the Nylon 6 nanofibers. This parameter is investigated thoroughly in this paper since the control of deposition area is essential for nanofiber applications, and flow rate is considered as one of the affecting parameters on deposition area.

In the electrospinning process, after passing through the Taylor cone and stability zone polymeric fluid enters the unstable zone where the fiber is drawn through a spiral trajectory, before collecting on the screen. However, the controllability of nanofiber deposition is severely affected by instabilities caused by bends in the fiber [36].

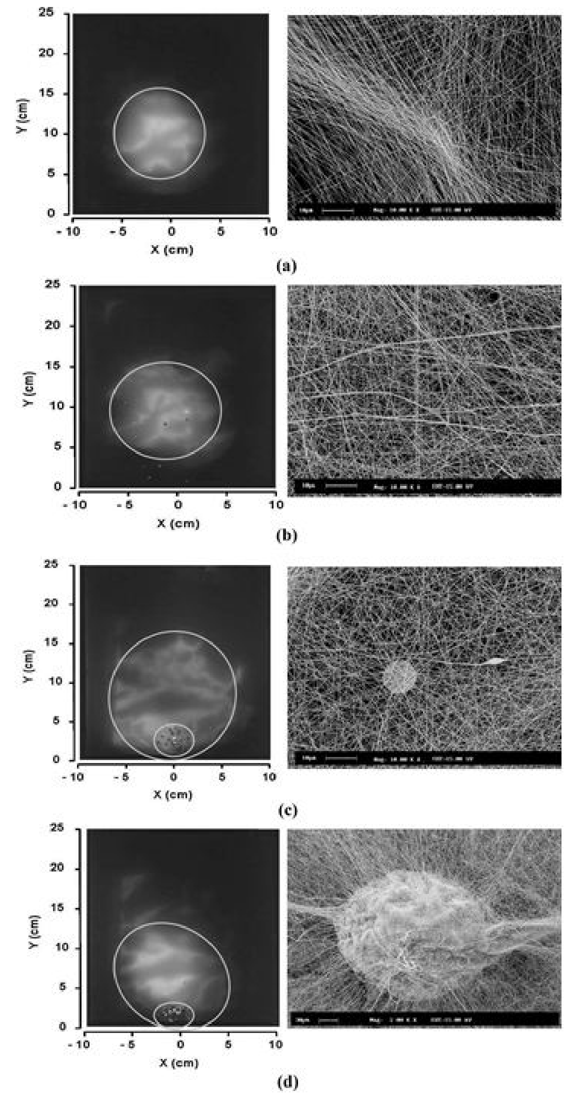

FIGURE 6. The effect of flow rate on deposition area based on SEM and scanning images of deposited nanofibers at various flow rates; (a) 0.1 mL/hr, (b) 0.5mL/hr, (c) 1.0 mL/hr, (d) 1.5mL/hr.

In *Figure 6*, the needle was exactly placed at the origin of the coordinates, at a 45-degree angle tilted downwards from the horizontal. The nanofiber webs produced in each experiment appeared as two separate half circles on black sheets which were the targets. According to previous research, it is believed that the formation of such a dual morphology may be influenced by the stationary fiber collector [37].

It was observed that the width of the deposited fibers increases with the flow rates up to 1 mL/hr, and then decreases. In 1 mL/hr, increasing instabilities resulted in the splitting of the primary jet into the multiple filaments, causing the wider deposition area.

As is illustrated in *Figure 6* and in the effects of gravity force and fluid momentum, the deposited fibers were shifted to the edge and base of the collecting screen. In fact, the fluid momentum decreased with increasing the spinning flow rate. Additionally, at 1.5 mL/hr the droplets appeared at closest to the edge of the collecting screen as a result of stronger gravitational force.

CONCLUSION

In this study, the effect of flow rate on the morphology of electrospun nylon 6 nanofibers was investigated. It was found that the droplet size and its initiating shape at the capillary tip, the trajectory of the jet and maintenance of Taylor cone, fiber diameter distribution and the morphology of the produced nanofibers were all influenced by the flow rate of the polymer solution.

At low flow rates, a small droplet size was formed at the capillary tip which made various types of charged jet. The charged jet reduced immediately due to the capability of electric field strength in drawing it during the electrospinning process. It was observed that at 0.5 mL/hr, the Taylor cone was more stable which resulted in the narrowest fiber diameter distribution. However, at high flow rates, a considerable amount of solution was electro sprayed. This was due to the influence of gravitational force and the electric field which was unable to draw a great volume of droplets. Increasing the flow rate caused fibers to be collected without sufficient solvent evaporation, which in turn led to the formation of some defects, such as branched, splitting fibers, blobs and flattened web-like structures.

At high flow rates, as a result of increasing the bending instabilities, and the occurrence of more splitting in the originating jet, the deposition area increased and larger areas were coated by deposited nanofibers.

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