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Design of Polyurethane Fibers: Relation between the Spinning Technique and the Resulting Fiber Topology

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ABSTRACT

Properties or characteristics of fibers are affected by their topology. In fact, these topology are found to have significant impacts in the functionalities of many applications. Hence, in this study, the relations between the spinning techniques and the topology of the resulting fibers are studied with the aim to provide a guideline for future reference where fibers with certain topology can be fabricated to suit specific applications. For this purpose, a polyurethane is chosen to be the raw material to fabricate the fibers due to its versatility to be applied in various fields. The surface morphology, structures and alignments of the fibers are studied. It is found that the polymer solution properties largely influence the mechanisms in the spinning process and can significantly affect the topology of the fibers. For instance, viscous solutions enable the spinning of coiled and smooth fibers, whereas conductive solutions encourage the splaying of the solution jet which results in the spinning of straight fibers.

INTRODUCTION

With the emergence of electrospinning technique, polymeric fibers are becoming more and more common.^{1,2} These electrospun fibers are found to have large surface area to volume ratio, better mechanical strength and highly porous, which are useful in many applications, such as water purification,³ polymer electrolyte,⁴ and biomedical field.⁵

The working principle of electrospinning involves the usage of high voltage to draw a solution jet from the orifice of a polymer solution containing reservoir. Initially, the polymer solution jet will form a Taylor cone at the orifice of the reservoir with the application of the high voltage. As the electrical potential difference increases, the viscosity and surface tension of the solution will be overcome. Then, a whipping instability of the jet will occur, causing it to travel in a vigorous spiral motion.⁶⁻⁹ Apart from whipping instability, the splaying or splitting of a single solution jet into multifilament can also happen.^{6,10} Both of these phenomena are found to help in reducing the diameters of the electrospun fibers to the submicron scale.

Parameters optimization in electrospinning is often studied in the literature in order to obtain the ideal straight fibers that have the smallest diameter with the absence of beads.¹¹⁻¹³ The presence of beads is frequently related to the poor mechanical properties of the fibers.^{14,15} Nevertheless, the beads on the fibers are found to be functional in drug release applications in human bodies.¹⁶⁻¹⁸ The drugs encapsulated in the beads of the fibers are found to have a sustained release which is favourable for cell differentiation in tissue engineering rather than a burst release. In addition, beads on fibers are also found to have interesting photonic

properties similar to dielectric microspheres.¹⁹ The luminescent effect is found in the beads of fibers due to the spatial distributions of the embedded chromophores.

There are studies conducted to control the beads formation on the fibers. The studies conducted by Fong et al.²⁰ and Liu et al.²¹ agree that the solution properties are playing important roles. Polymer solutions with high viscosity, high surface tension and low net charge density are prone to the formation of beads on the electrospun fibers. In a more recent study conducted by Krifa et al.,²² larger needle or spinneret size can also encourage the formation of beads on the spun fibers apart from the viscosity of the polymer solution. In the aspect of the spinning process, Bu et al.²³ used a mechano-electrospinning method where the fibers collector stage is moved in a linear path during the electrospinning process. It is found that the movement of the stage must be below certain threshold speed to enable the formation of beads.

Besides beads, the orientation of the fibers also plays an important role in their functionalities. As an example, cell seeding on highly aligned fibrous scaffolds is reported to be more effective than randomly oriented fibrous scaffolds.^{24,25} On the contrary, randomly oriented fibers are regularly applied in water purification.²⁶

This alignment of electrospun fibers is also commonly studied in the literature. Randomly oriented fibers can be easily fabricated using stationary collectors,^{11,12,27} whereas highly aligned fibers can be fabricated using high speed rotating collectors.²⁷⁻²⁹ Nonetheless, tedious parameters optimization may be needed to spin highly aligned fibers with high speed rotating collectors as the splaying and whipping instability of the solution jet during electrospinning will

hinder the alignment of the fibers as stated by Kiselev et al..³⁰ In order to remove the splaying and whipping instability of the solution jet, dry spinning can be used. It is reported that dry spinning is able to control and align the deposition of the fibers on to a collector. Arrays of properly aligned fibers is successfully fabricated by dry spinning.³¹⁻³³ Unlike electrospinning, dry spinning directly spins the fibers onto a collector without the usage of high voltage supply in drawing the fibers, and hence, splaying and whipping instability of the solution jet do not occur.

The required fiber structure is also dictated by the application. For instance, the randomly oriented fibers reported to be applicable in water purification are always straight in structure²⁶ while highly aligned fibers applicable in tissue engineering have wavy structures.^{34,35} More interestingly, helical or coiled structure of the fibers are found to be similar to many helical filaments found in organisms.³⁶ These helical biological filaments have inspired the fabrication of helical microfibers useful in crude oil cleanup.³⁷

In order to modify the structure of the fibres, normal straight electrospun fibers can be post treated with heat or solvent to make the fibres wavy according to a study conducted by Chao et al..³⁵ The wavy fibers can also be directly spun using a modified electrospinning technique, magnetic – field – assisted electrospinning technique in the study conducted by Liu et al..³⁴ The wavy fibers can be introduced by increasing the injection rate of the polymer solution. Another structure of the fibers, the coiled or helical fibers are said to be originated from the whipping instability of the solution jet in electrospinning.^{10,37}

Without prejudice, fibers with all kinds of structures, morphology and alignment are useful in one way or another as discussed in the aforementioned paragraphs. In fact, ideal fibers should

not be just confined to straight smooth fibers. An ideal fiber should be defect and orientation controllable as described by Raghavan et al..¹

In the literature, some of the common polymer fibers are spun from thermoplastics such as poly(methyl methacrylate),^{11,38,39} polyvinylidene fluoride,^{12,40} and polyethylene terephthalate^{41,42} due to their high mechanical strength. However, the elasticity of these fibers is low, typically having less than 50% maximum elastic strain. Apart from the mechanical strength, the elasticity of the fibers is also crucial to ensure their mechanical durability in harsh working environments. Hence, in this study, a polyurethane is used as the raw material in spinning the fibers as it is known to be a thermoplastic elastomer, possessing the elasticity of an elastomer with more than 100% maximum elastic strain and the strength of a thermoplastic.⁴³

In addition to the elastic mechanical behaviours, the polyurethane is also versatile with many interesting properties. Some of these properties are flame retardant ability,⁴⁴ biodegradability,⁴⁵ and self – healing capability.⁴⁶ This variety of properties can be tailored by changing the chemical composition of the polyurethane. It is also common that fillers are added to the polyurethane to add in certain property as a composite material. Examples of the fillers are zinc oxide nanoparticles for ultraviolet light blocking and antimicrobial properties,⁴⁷ carbon nanotubes for electromagnetic shielding,^{48,49} and carbon black for gas sensing.⁵⁰ Apart from adding fillers, blending of polyurethane with other polymers can also impart certain properties to the blends. For instance, polyurethane/poly(3,4 – ethylenedioxythiophene):poly(styrenesulfonate) blends are having high electrical conductivity⁵¹,

whereas poly(L-lactide)/thermoplastic polyurethane/poly(D-lactide) blends are having high heat resistance capability.⁵²

Despite of the suitability in the property of polyurethanes for various applications, the property alone is not sufficient or effective in certain applications. In fact, the structure or morphology of the polyurethane samples is essential as well as mentioned in the previous paragraphs. Following the structure, alignment and morphology needs of polyurethane, polyurethane fibers with different topology are investigated in this study. The fibers are spun using normal basic electrospinning and dry spinning set-ups without involving complex modifications as in the studies^{23,34} mentioned in the previous paragraphs. There are not post treatments to the fibers to alter their topology as well, unlike the studies mentioned in the previous paragraphs.³⁵ A number of polyurethane fibers topology are spun, different from most studies^{47,53-55} where the focus is only on certain topology, such as beads, diameter and alignment without detail study on the fibers structures. In short, this study is aimed to give readers guidelines to spin polyurethane fibers easily with specific topology without complex spinning set-ups and post treatments by understanding the relations between the spinning mechanisms and fibers topology.

EXPERIMENTAL

Materials

N,N-Dimethylformamide (DMF) and Tetrahydrofuran (THF) with purity more than 99% are mixed to dissolve MDI-polyester/polyether polyurethane (CAS Number: 68084-39-9) pellets into solutions. Three polymer solutions with different polymer concentrations and solvent ratios, denoted by Solution A, B and C are prepared as shown in Table 1. These polyurethane pellets and solvents are purchased from Sigma Aldrich and used directly without further processing.

After dissolving the polyurethane pellets, the viscosity and electrical conductivity of the solutions are measured using Brookfield DV-II + Pro EXTRA viscometer with S18 spinneret and Mettler Toledo SevenCompact Benchtop Meter respectively.

Spinning of Fibers

Two spinning techniques are used to fabricate the fibers in this study, which are the electrospinning and dry spinning. The two are detailed in the following sections.

Electrospinning

The basic setup of electrospinning is presented in Figure 1 (a, b). It consists of three main components, a high voltage supply, a syringe pump and a collector. In this study, syringes with 27 gauge size needles are used to contain the polymer solution while the syringe pump is used to control the solution injection rate. A 10 kV of electrical potential difference is applied between the tip of the syringe needle and the collector. The fibers are drawn from the syringe

to the collector by the strong electrical force. Two types of collectors are used, a stationary and rotating collector as shown in Figure 1 (a) and (b) respectively. For the rotating collector, a high rotating speed of ± 1000 rpm is applied to increase the alignment of the fibers.²⁷⁻²⁹ The processing parameters of the electrospinning techniques are as shown in Table 2.

Dry Spinning

Dry spinning is a less complicated technique in the fabrication of fibers as compared to electrospinning. It uses mechanical force to draw fibers out of the solution to the collector.^{33,56}

The setup of dry spinning in this study only comprises of a syringe pump and a rotating collector as shown in Figure 1 (c). Similar to the electrospinning, syringes with 27 gauge size needles are used to contain the polymer solution while a syringe pump is used to control the solution injection rate.

In order to start the dry spinning process, a fiber is drawn manually from the syringe to the rotating collector. Then, the rotating collector takes up the spinning of the fibers by mechanical drawing force. The polyurethane solution must be viscous and volatile enough, so that a fiber can be continuous drawn from the solution in the syringe. In this case, Solution C is used to be dry spun. The rotational speed used in this dry spinning is very low, ± 100 rpm as compared to the ± 1000 rpm of rotational speed used in electrospinning. This is to ensure that the rotational force is not too strong to break the continuous drawn fibers. If the continuous fibers break, manual drawing of the fibers has to be repeated. A weak voltage is also applied between the tip of the syringe needle and collector during the spinning process in order to study the effect of the electrical force on the dry spun samples. However, it is important to note that the applied

voltage is not strong enough to initiate the electrospinning process. The processing parameters are listed in the Table 3.

Surface Characterizations

Phenom ProX desktop scanning electron microscope (SEM) is used to observe the surface of the fibrous samples. Then, the OrientationJ Distribution processing method in OrientationJ plugin of ImageJ 1.48v software is used to evaluate the orientation of the fibers in the micrographs under the magnification of 1000 ×. In this fibers orientation analysis, assumptions are made, such that the fibers orientation is in plane and the orientation at the top layer is considered to represent the average fibers orientation of the whole sample.¹² As for the diameters measurement of the fibers, measuring tools in the ImageJ 1.48v software is used. The diameters of 100 fibers in the micrographs under 5000 × magnification are measured.

RESULTS AND DISCUSSION

Properties of the Polymer Solutions

The viscosities and electrical conductivities of the polyurethane solutions with different concentrations and solvent ratios are as shown in Table 4.

With reference to Table 1, the viscosity of the polyurethane solution is highly dependent on the concentration of the solution. An obvious increase in the viscosity of the polyurethane solution from 1.50 to 8.16 Pa.s is measured when the solution concentration increases just from 10 to 15 wt %. The solvent used in the solution does not affect much in the viscosity. Solution B and C with the same concentration are having similar viscosity, 8.16 and 8.20 Pa.s respectively despite having different solvent ratios.

Although having not much effects in the viscosity of the solution, the solvent ratio seems to affect the electrical conductivity of the solution. Solution C has lower electrical conductivity than Solution B as the THF in Solution C is having lower electrical conductivity than DMF. Besides solvent ratio, the electrical conductivity of the polymer solution seems to be affected by the polymer concentration as well. Solution B with higher polymer concentration, 15% are having lower electrical conductivity than Solution A with lower polymer concentration, 10% despite having the same solvent ratio.

Surface Analysis of Electrospun Fibers

Figure 2 shows the representative SEM micrographs of 5 electrospun samples. All these electrospun samples are in the form of mat or film made up of assemblies of fibers. The main characteristics of the samples can be summarized in Table 5.

Orientation of Fibers

Figure 3 shows the orientation distribution curves of the electrospun fibers. PU1, PU2 and PU4 fabricated using stationary collector have very small or no peak in the orientation distribution curves, indicating the random orientation of the fibers similar to the study of Wong et al..¹²

An obvious peak can be observed in the orientation distribution curves of PU3 and PU5 at around 0° angle, which corresponds to the horizontal direction of the micrographs indicated by the blue arrow in Figure 2 (c, e). The fibers are partially oriented in the horizontal direction as shown in Figure 2 (c, e). This is due to the usage of high speed rotating collector in electrospinning²⁷⁻²⁹. The strong rotational force is able to drive the fibers to align in the circumferential direction of the rotation indicated by the blue arrow as shown in Figure 2 (c, e).

The peak in the orientation distribution curve of PU3 is much sharper than PU5 although both samples are fabricated using the rotational speed of ± 1000 rpm. This is due to the wavy structure of the fibers in PU5 which will be discussed further in the later session. In this fibers orientation analysis by ImageJ software, a straight fiber is considered to be oriented in one direction whereas a wavy fiber is considered to be oriented in more than one direction.

Therefore, the peak in the curve of PU5 is not as sharp as PU3 although the overall orientation is similar.

Beads on Fibers

If a fiber does not have a uniform diameter along its axis, beads can be observed as shown in the micrograph of PU1 in Figure 2 (a). The beads appear to be swollen segments along the axes of fibers. These beads can reduce the cohesions or interactions between fibers in the sample¹⁴ and act as stress concentrations during mechanical loadings,¹⁵ resulting in poorer mechanical properties.

Low viscosity of the Solution A may be the causation of the beads on the fibers. It is found that solution with low viscosity encourages the formation of the beads.^{20,22,55,57} This is due to the insufficient viscoelastic force to overcome the surface tension of the solution jet from the syringe, favouring the formation of larger beads. Thus, by using polyurethane Solution B and C with much higher viscosities, the electrospun fibers do not possess beads.

Structure of Fibers

Regarding the structures of fibers, 3 types of structures can be observed: straight, coiled and wavy fibers.

Straight Fibers

The straight fibers in PU1 could be originated from the splaying of the polymer solution jet, where multifilament are split out from a single solution jet.^{6,7} This splaying of the solution jet is likely to be attributed to the DMF solvent in Solution A as stated in Table 1. It is found that DMF

can increase the electrical conductivity of a polymer solution along with the reduction of surface tension, thus encourages the splaying of the solution jet.⁵⁸ The split out fibers are in a straight manner and deposited on the stationary collector as illustrated in Figure 4. On the contrary, the straight fibers in PU3 is not originated from the splaying effect mentioned. Instead, it is due to the usage of rotating collector. Without considering the type of collector, PU2 and PU3 have the same solution and processing parameters. Hence, the fibers in PU3 should have the same coiled structures as in PU2. However, the rotating collector stretches the supposedly coiled fibers in PU3 into straight fibers.^{30,37,59}

Coiled Fibers

Most electrospun fibers are straight^{7,12,14,15,27-29,57,60} and only small traces of coiled fibers can be found in some studies.^{11,59,61} It is unique to have all coiled fibers in PU4 and high portion of coiled fibers in PU2.

According to a study conducted by Bagchi et al.,¹⁰ this coiled fibers originate from the whipping instability of the polymer solution jet. Whipping instability causes the fibers to travel in a spiral path and deposit as coiled fibers on the collector³⁷ as illustrated in Figure 5. The polymer solution jet travels in a straight path before the chaotic motion of whipping instability starts. In the cases of PU2 and PU4, it is hypothesized that the degree of whipping instability is low, where the straight path is long with very small diameter of spiral motion before reaching the collector. This may be due to the highly viscous Solution B and C as high viscosity solution is found to decrease the degree of chaotic motion in whipping instability.⁶²

As shown in Figure 6, these coiled fibers tend to stack up to form tower like structures in PU4. The diameter of the spiral motion of polymer jet could be as small as 24.6 μm as evidenced by the diameter of the hollow section of the tower like structure. However, this structure is only observed in certain areas of the sample. It is most likely caused by the disruption of orderly organisation of the fibers due to the repulsions between fibers⁶³ since electrospun fibers are found to have residual charges.^{64,65} As the stacking of coiled fibers increases, the packing of fibers becomes denser and the accumulation of residual charges increases. To a certain extent, the electrical repulsive force is strong enough to repel the incoming fibers. Thus, stacking is no longer possible. Then, fibers start to scatter all around the surface of collector away from the tower like structures as clear gaps are observed between the tower like structures and scattered fibers.

Wavy Fibers

Wavy fibers are found in PU5 similar to a study conducted by Kiselev et al.³⁰ but not in PU3 despite that both samples are actually fabricated using a rotating collector with ± 1000 rpm. However, PU3 is spun using Solution B whereas PU5 is spun using Solution C as stated in Table 1. In Solution B, polyurethane is dissolved in DMF only but polyurethane is dissolved in a mixture of DMF and THF in Solution C. It is known that THF is more volatile than DMF.^{53,66} Hence, Solution C is more volatile than Solution B. The solution jet of Solution C may dry and solidify into fibers earlier than Solution B. As a result, the fibers spun from Solution C may experience greater stretching forces by the rotating collector. Thus, greater contraction maybe

experienced by the fibers in PU5 when they are removed from the collector, which manifested into the wavy fiber structure.³⁴

Diameter of Fibers

Based on the micrographs in Figure 2, an obvious non-uniformity in the fiber diameters of PU2 and PU3 can be observed in Figure 2 (b, c) respectively.

Two fibers in PU3 which have apparent difference in diameters are measured. The diameters are 1.461 and 0.866 μm respectively as shown in Figure 2 (c). The reason for this observation is unaccountable.

Observations in Figure 2 (b), however, show that coiled fibers have relatively larger diameters than the straight fibers in PU2. Thus, further analysis on the fiber diameters are carried out. 100 diameter measurements are taken from coiled fibers and straight fibers respectively. Coiled fibers have an average diameter of $2.897 \pm 0.16 \mu\text{m}$, whereas straight fibers have an average diameter of $0.933 \pm 0.048 \mu\text{m}$. The separate diameter measurements of coiled and straight fibers could not be done on PU3 since the rotating collector stretched the coiled fibers into straight fibers.

As mentioned in the previous session, coiled fibers are due to the whipping instability of polymer solution jet while straight fibers are due to the splaying of polymer solution jet. Both fibers structures present in PU2 indicate that both whipping instability and splaying of polymer solution occurred during the fabrication of this sample. With reference to the diameter measurements of coiled fibers and straight fibers, it can be inferred that the splaying of

polymer solution jet can fabricate smaller diameter fibers than the whipping instability of polymer solution jet.

In the literature, high electrical conductivity polymer solutions help in reducing the fiber diameter^{53,67} and this reduction in diameter may be due to the splaying of polymer solution jet⁵⁸ as mentioned in the previous paragraph. The electrical conductivity of the polyurethane solution is in the order of Solution A, B to C from the highest to lowest magnitude as shown in Table 1. By using Solution A with the highest electrical conductivity, the fabricated fibers in PU1 are all straight due to splaying of solution jet. Solution B has the intermediate electrical conductivity and therefore, the fabricated fibers in PU2 are partially coiled and straight due to both phenomena. Lastly, Solution C with the lowest electrical conductivity is used to fabricate coiled fibers in PU4 due to the whipping instability of the solution jet.

The average diameters of all the electrospun fibers are tabulated in Table 5. In this study, two concentrations of polyurethane solution, 10 and 15 wt % are used for electrospinning. Many studies have reported that electrospun fibers with lower concentration of polymer solution have smaller diameters.^{7,11,12,54} PU1 is the only sample electrospun from 10 wt% polyurethane solution and it has smaller average diameter than all the samples, except for PU5. This is because PU5 is fabricated using a high speed rotating collector of ± 1000 rpm despite being spun from 15 wt % polyurethane solution. The high rotational speed can stretch the fibers further and therefore, decreases the diameters of the fibers.^{68,69} Electrospun fibers using rotating collector in PU3 shows 44.4% of reduction in average diameter as compared to the electrospun fibers in PU2 using stationary collector although the other processing and solution

parameters are the same. Similar reduction in average diameter of fibers can also be observed between PU5 and PU4, where the reduction is 50.1%.

Dry Spinning

The idea of Kiselev et al.³⁰ is adapted in this study. It is proposed that the polymer solution jet should travel in a straight path to reach the rotating collector, so that the fibers fabricated would align following the rotation.

Parameters optimization on the electrospinning set up in this study is conducted to drive the polymer solution jet to travel in a linear manner before depositing onto the rotating collector. Consequently, the splaying in electrospinning is successfully eliminated and the whipping instability is reduced to a minimum extent through the parameter optimization. However, only partial alignment can be observed in PU3 and PU5 as shown in Figure 3.

Due to the difficulties to completely eliminate the whipping instability in electrospinning due to the high voltage application, a dry spinning technique is opted to fabricate highly aligned polyurethane fibers in this study. The polymer solution jet is able to travel in the straight manner to reach the rotating collector without the application of high voltage as illustrated in Figure 7. Nonetheless, the dry spun fibers are in bundles, unlike the electrospun fibers, are in mats.

Surface Analysis of Dry Spun Fibers

The micrographs of all the dry spun samples are as shown in Figure 8. All the samples have the similar topology. The observed fibers are without beads, highly aligned, and uniform in diameters. Although these fibers are dry spun, the three characteristics mentioned are ideal for electrospun fibers as described by Raghavan et al..¹

Orientation of Fibers

The orientation distribution curves of all the dry spun samples are plotted in Figure 9 (a). All the distribution curves show a sharp peak, in line with the observations on the SEM micrographs in Figure 8. The blue arrows correspond to the direction of the 0° angle.

Orientation distribution curves of PU2, PU3 and PU7, corresponding to not aligned, partial aligned and highly aligned fibers are plotted in Figure 9 (b) for comparison purpose. The orientation distribution curve of PU7 is a representative of all the dry spun fibers as the orientation distributions are similar as shown in Figure 9 (a). It is obvious that dry spun fibers have the sharpest peak and thus, the fibers are highly aligned as compared to the electrospun fibers in this study.

Diameter of Fibers

The average diameters of the dry spun fibers range from 2.620 to 2.799 μm are much larger as compared to the electrospun fibers, which range from 0.618 to 1.915 μm . Nevertheless, the diameters of these dry spun fibers still fall into the range of the diameters fabricated through electrospinning which is ranged from nanometre to micrometer.³⁶

In spite of the application of 0 to 5 kV voltage during the dry spinning process respectively, the diameters of the fibers do not change much as shown in Figure 10. It is common that the diameter of fibers changes with the change in the applied voltage during electrospinning.^{1,11,66} Apparently, the applied voltages in this dry spinning are too low to have significant effects on the diameter of the fibers.

CONCLUSIONS

In this study, polyurethane fibers with different topology are fabricated through electrospinning and dry spinning techniques.

By adjusting the solution parameters in electrospinning, the polymer solution jet from the syringe can be controlled before the deposition of fibers on the stationary collector. Solutions with high viscosity and low electrical conductivity are able to induce the whipping instability of the solution jet to form coiled fibers, while solution with low viscosity and high electrical conductivity are able to induce the splaying of the solution jet to form straight fibers.

As for the fibers orientation, randomly oriented electrospun fibers are deposited on the stationary collector, whereas highly aligned fibers are deposited on the high speed rotating collector. Despite being able to align the fibres, the high speed rotating collector can impose excessive stretching on the fibers, evidenced by the fibers with wavy structure due to contraction. Thus, dry spinning is a more suitable technique to be used. Results show that the dry spun fibers are straight and highly aligned although having larger diameters.

In the case of fibers diameter, fibers electrospun with higher concentration of polymer solution are without beads but having larger diameters. Further reduction of the fibers diameters can be achieved by depositing the fibers on a rotating collector to elongate the solution jet further during the spinning process.

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CAPTIONS OF FIGURES

Figure 1. Electrospinning of fibers with (a) splaying^{6,7} and (b) whipping instability^{6,10}; (c) Dry spinning assisted by weak electrical field.³³

Figure 2. SEM micrographs of (a) PU1, (b) PU2, (c) PU3, (d) PU4 and (e) PU5.

Figure 3. Orientation distribution curves of fibers in electrospun samples.

Figure 4. Illustration of deposition of straight and randomly oriented fibers on the stationary collector due to the splaying of the solution jet.

Figure 5. Illustration of deposition of coiled fibers on the stationary collector due to the whipping instability of the solution jet.

Figure 6. Tower like structures in PU4.

Figure 7. Illustration of deposition of straight and aligned fibers on the rotating collector as the solution jet is travelling in a straight manner.

Figure 8. SEM micrographs of (a) PU6, (b) PU7, (c) PU8 and (d) PU9.

Figure 9. Orientation distribution curves of (a) dry spun samples; (b) PU2, PU3 and PU7.

Figure 10. Variation of the fiber diameter with the applied voltage.

CAPTIONS OF TABLES

Table 1. Polymer solution parameters.

Table 2. Processing parameters of electrospinning.

Table 3. Processing parameters of dry spinning.

Table 4. Viscosities and electrical conductivities of the polymer solutions.

Table 5. Surface morphology, structure and alignment of the fibers.

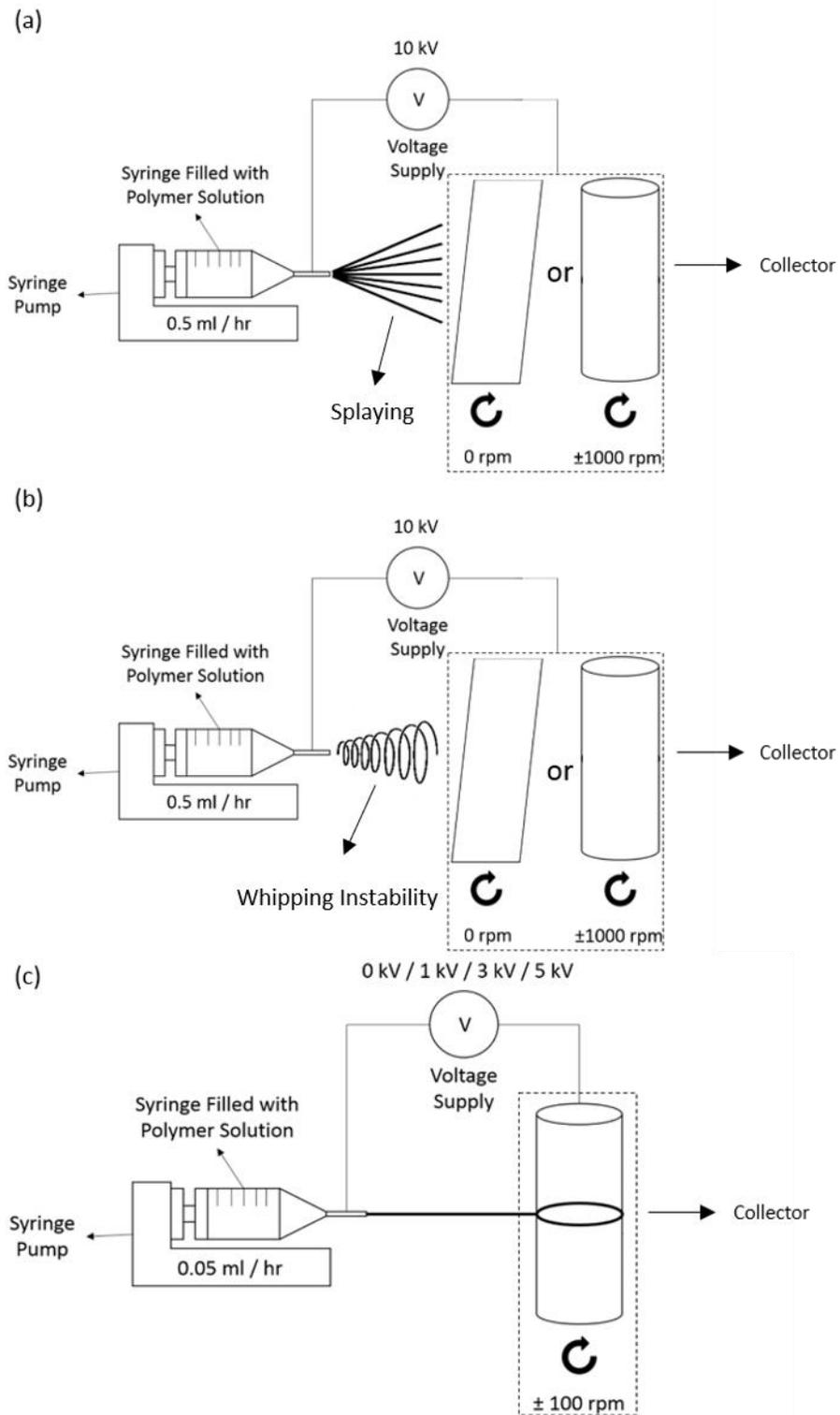


Figure 1. Electrospinning of fibers with (a) splaying^{6,7} and (b) whipping instability^{6,10}; (c) Dry spinning assisted by weak electrical field.³³

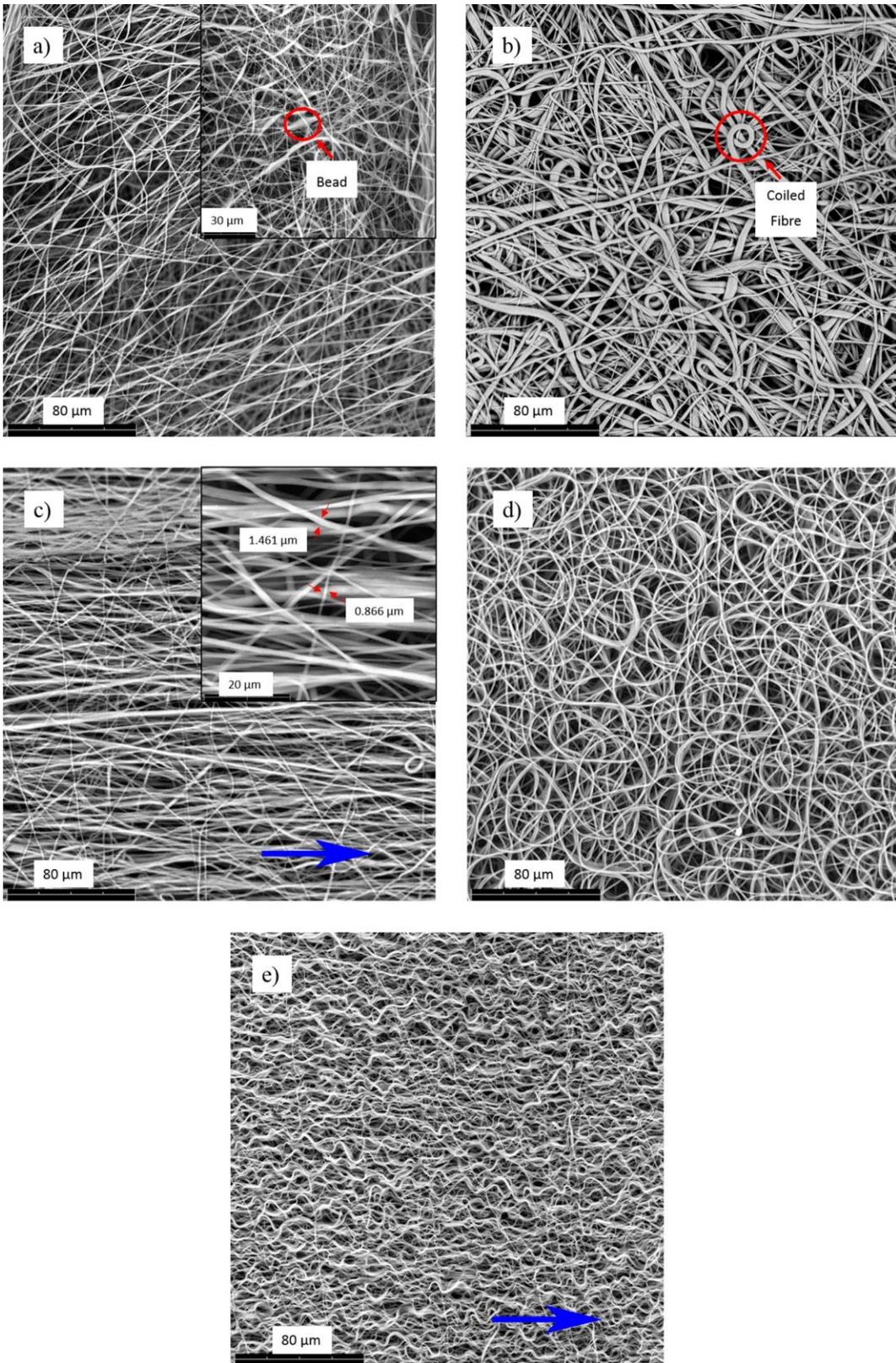


Figure 2. SEM micrographs of (a) PU1, (b) PU2, (c) PU3, (d) PU4 and (e) PU5.

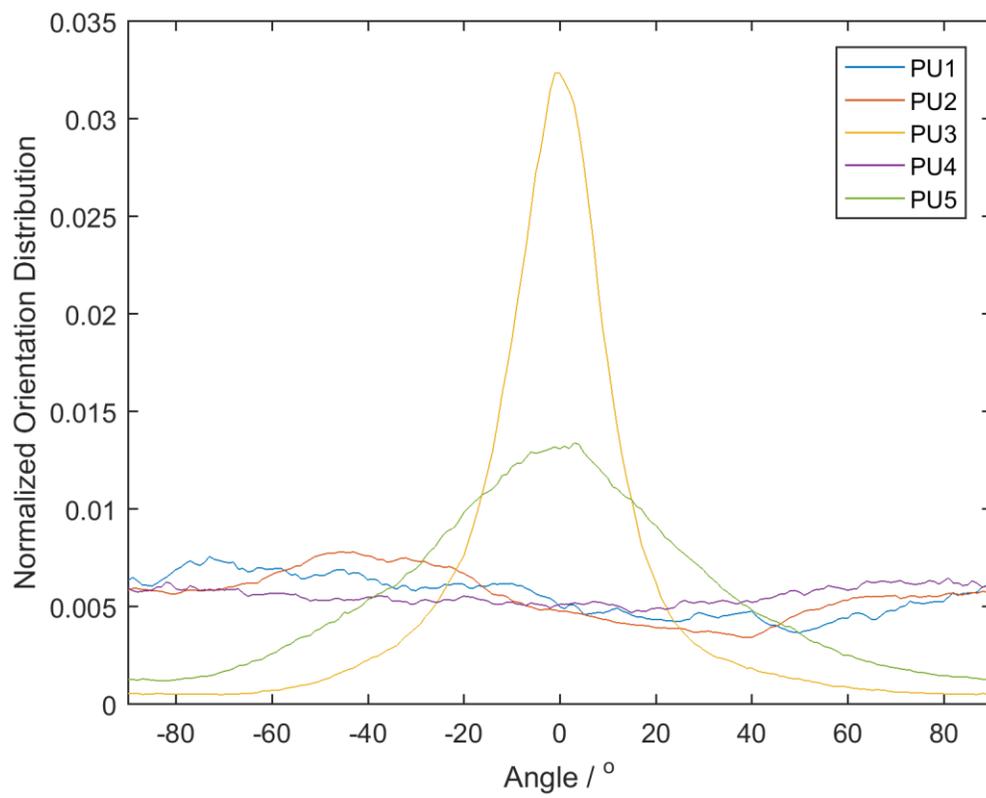


Figure 3. Orientation distribution curves of fibers in electrospun samples.

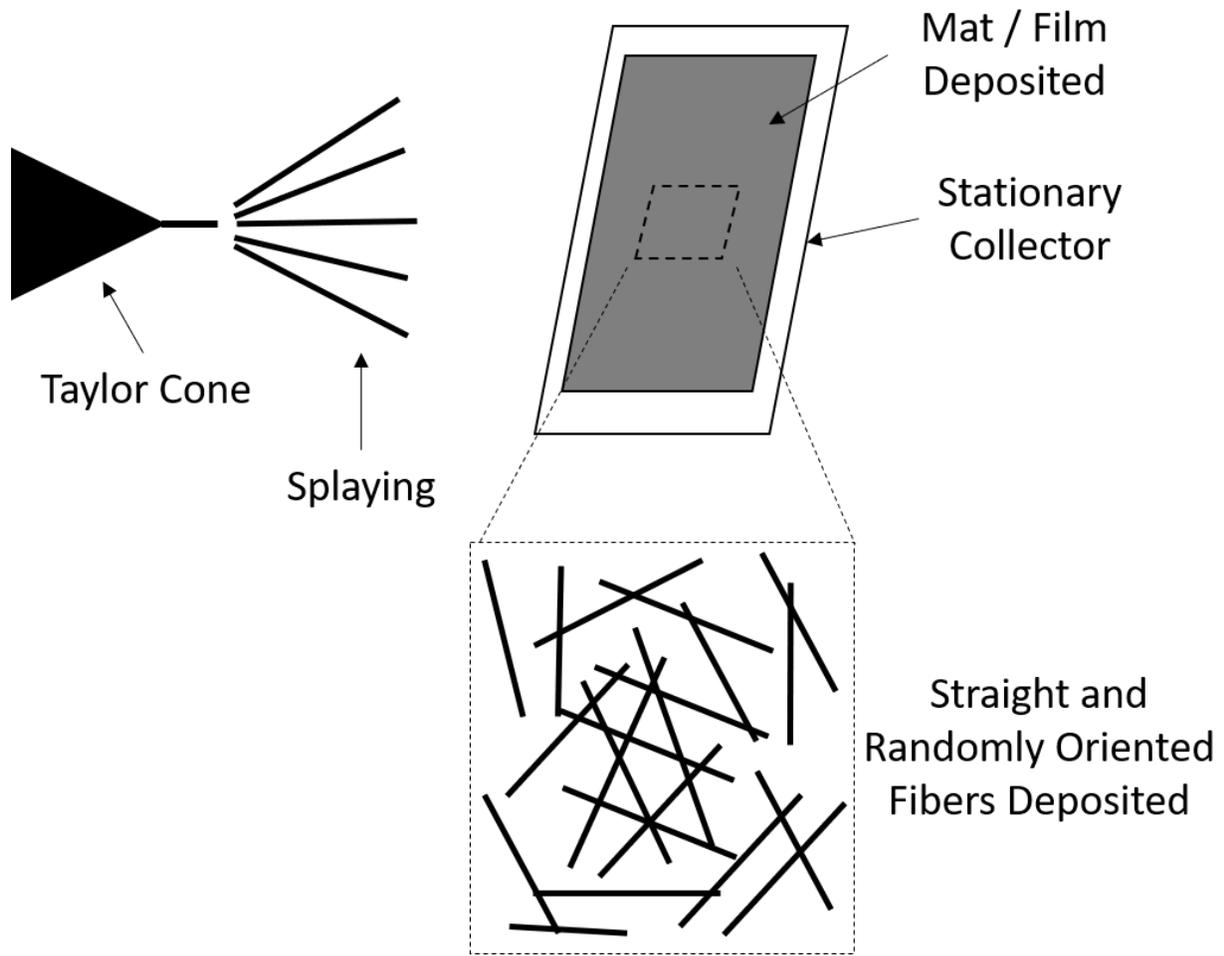


Figure 4. Illustration of deposition of straight and randomly oriented fibers on the stationary collector due to the splaying of the solution jet.

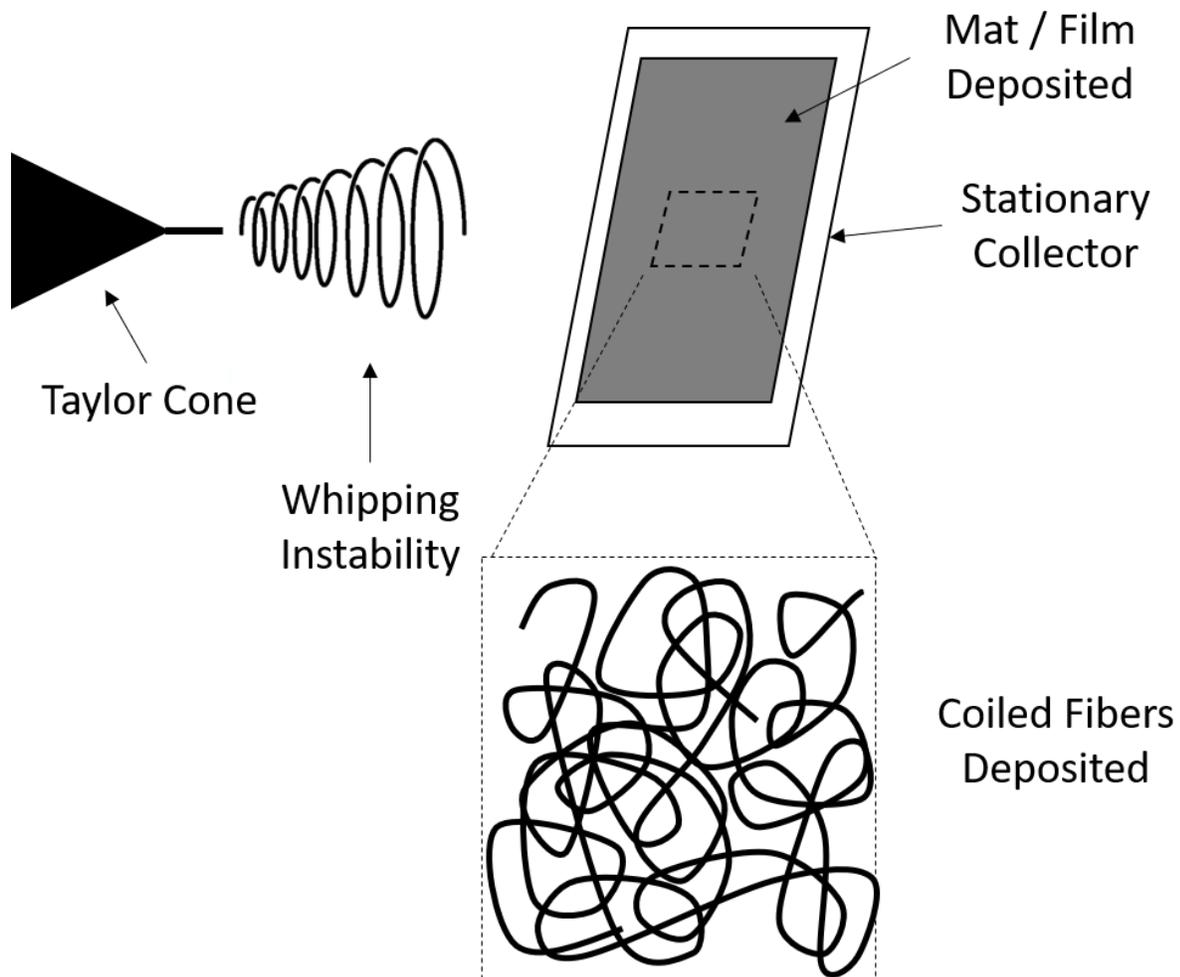


Figure 5. Illustration of deposition of coiled fibers on the stationary collector due to the whipping instability of the solution jet.

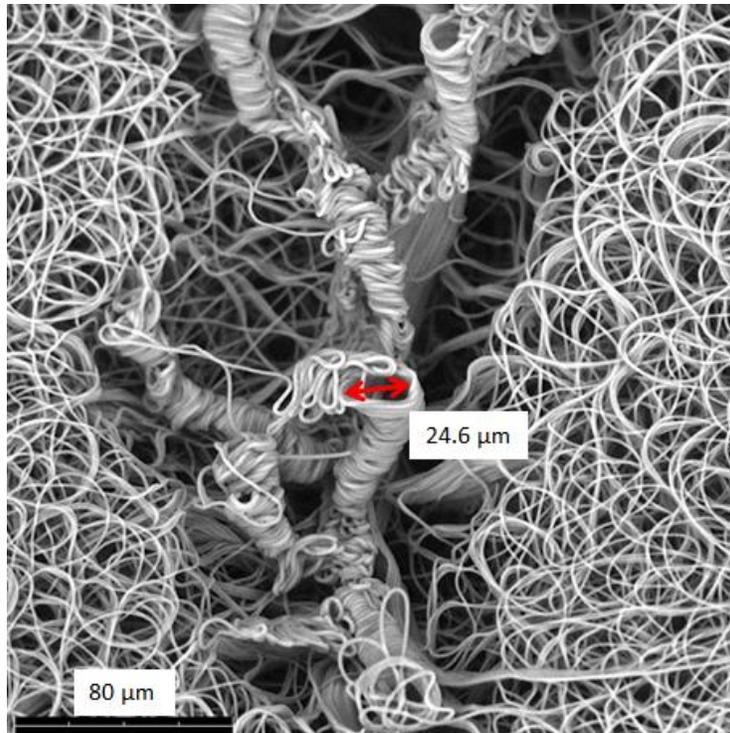


Figure 6. Tower like structures in PU4.

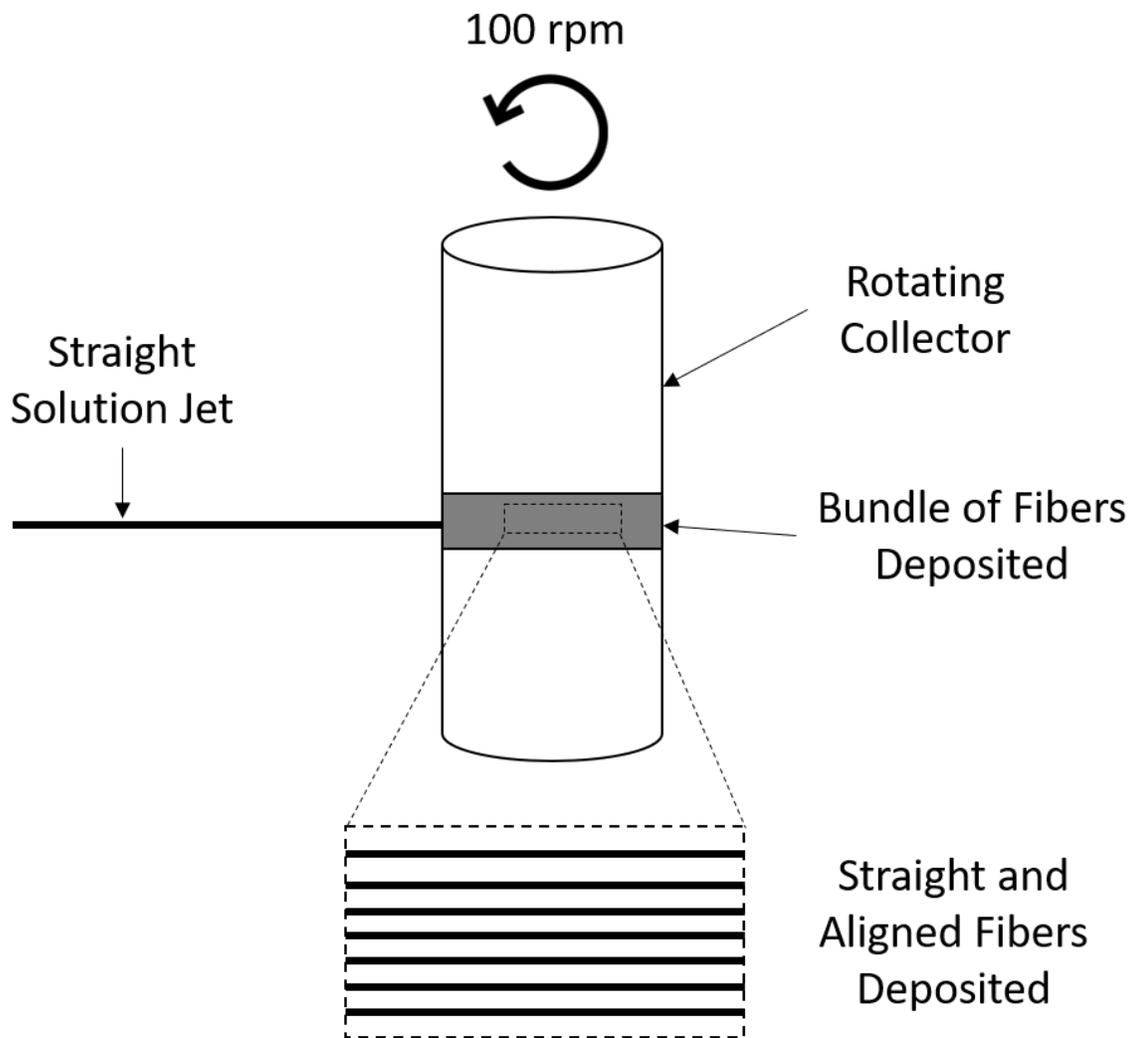


Figure 7. Illustration of deposition of straight and aligned fibers on the rotating collector as the solution jet is travelling in a straight manner.

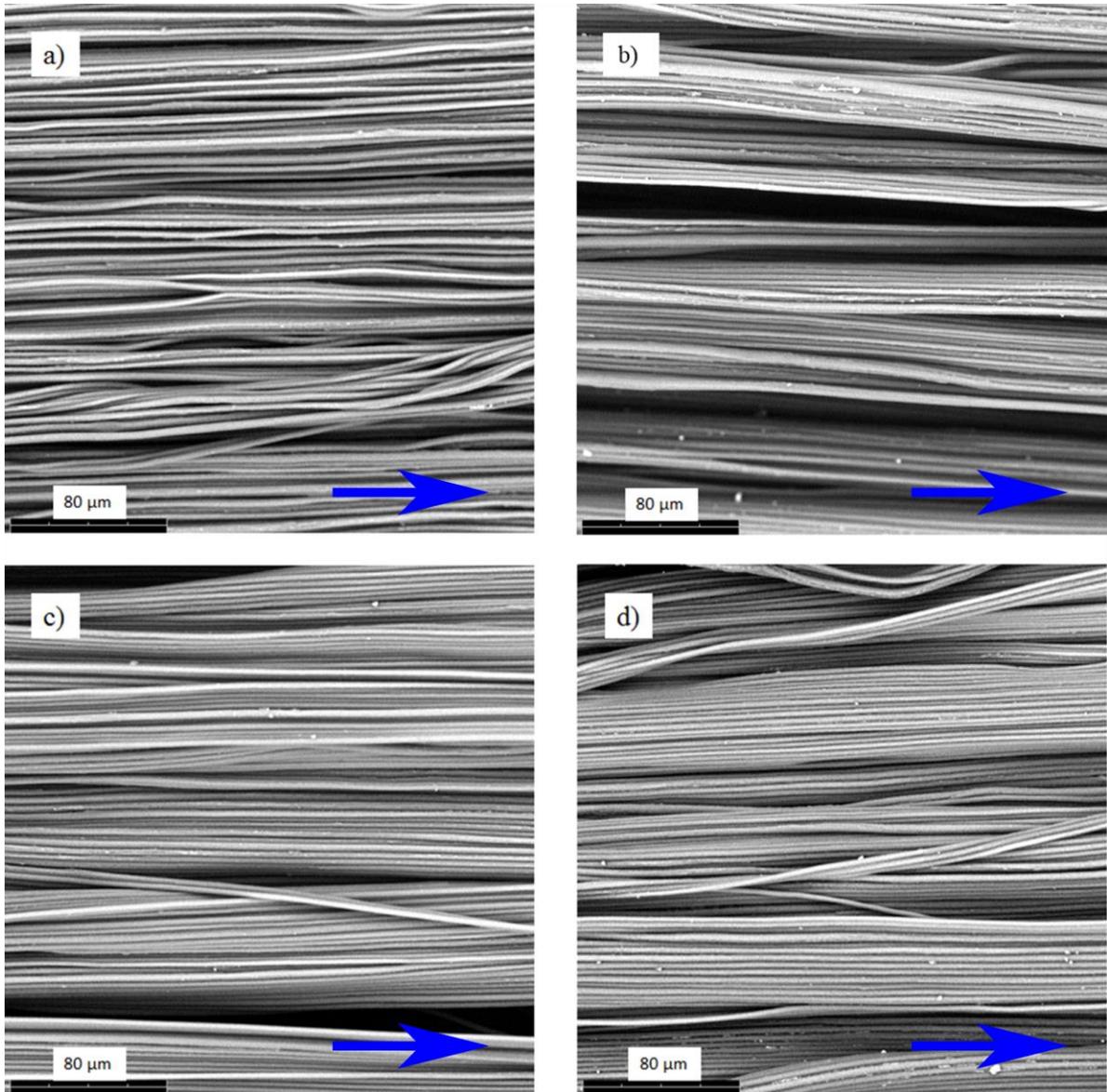


Figure 8. SEM micrographs of (a) PU6, (b) PU7, (c) PU8 and (d) PU9.

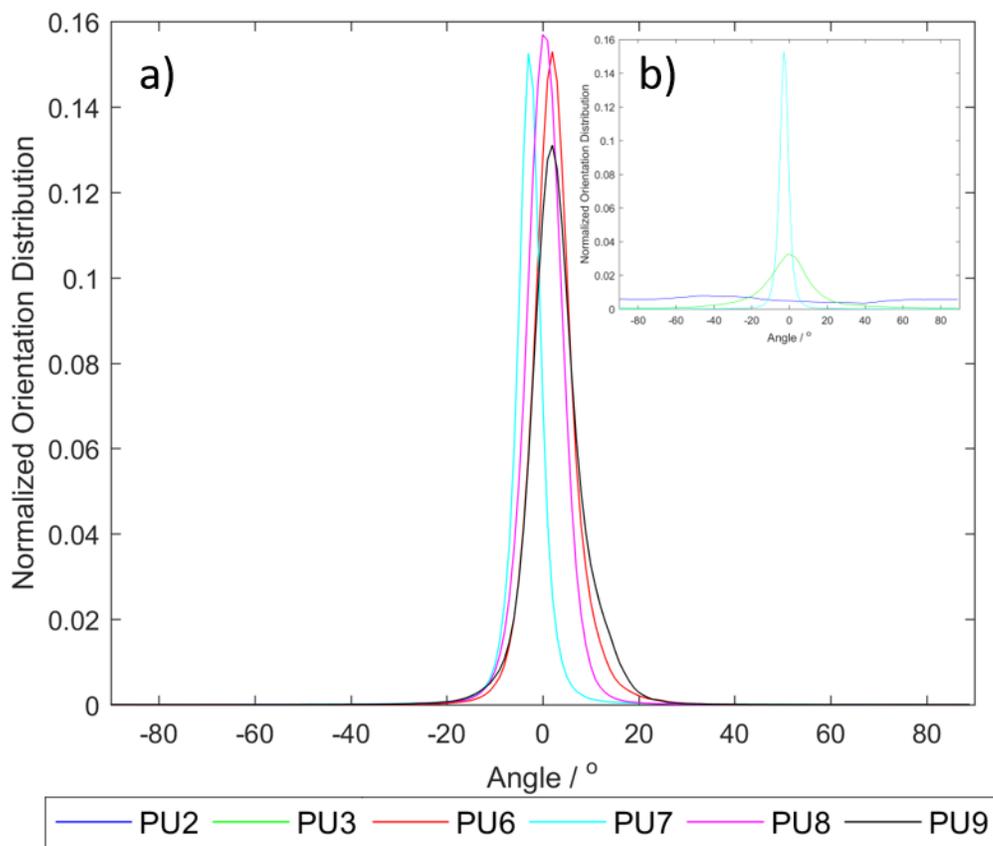


Figure 9. Orientation distribution curves of (a) dry spun samples; (b) PU2, PU3 and PU7.

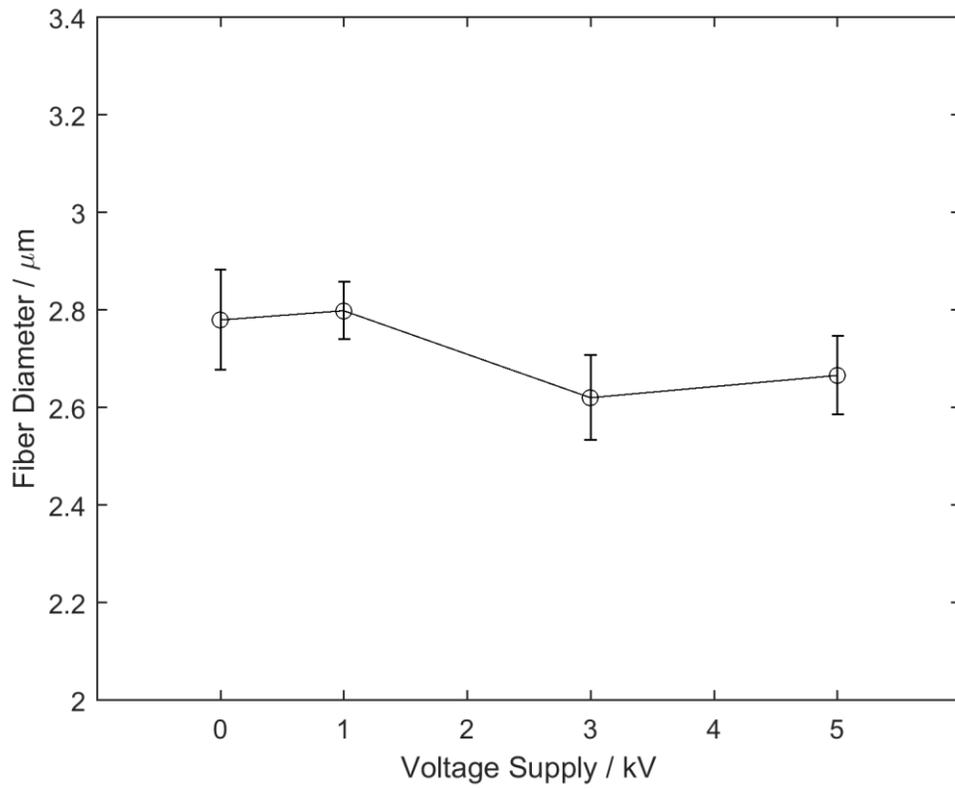


Figure 10. Variation of the fiber diameter with the applied voltage.

Table 1. Polymer solution parameters.

Solution	Solvent Ratio (DMF:THF)	Polymer Concentration (wt %)
A	1:0	10
B	1:0	15
C	1:1	15

Table 2. Processing parameters of electrospinning.

Sample	Solution	Applied Voltage (kV)	Tip to Collector Distance (cm)	Rotational Speed (rpm)	Solution Injection Rate (mlhr⁻¹)
PU1	A	10	15	0	0.5
PU2	B	10	15	0	0.5
PU3	B	10	15	± 1000	0.5
PU4	C	10	15	0	0.5
PU5	C	10	15	± 1000	0.5

Table 3. Processing parameters of dry spinning.

Sample	Solution	Applied Voltage (kV)	Tip to Collector Distance (cm)	Rotational Speed (rpm)	Solution Injection Rate (mlhr⁻¹)
PU6	C	0	15	± 100	0.05
PU7	C	1	15	± 100	0.05
PU8	C	3	15	± 100	0.05
PU9	C	5	15	± 100	0.05

Table 4. Viscosities and electrical conductivities of the polymer solutions.

Solution	Solvent Ratio (DMF:THF)	Polymer Concentration (wt %)	Viscosity (Pa.s)	Electrical Conductivity (μScm^{-1})
DMF	-	-	0.71	4.650
THF	-	-	0.37	0.029
THF and DMF	1:1	-	0.50	1.481
A	1:0	10	1.50	1.822
B	1:0	15	8.16	1.550
C	1:1	15	8.20	1.380

Table 5. Surface morphology, structure and alignment of the fibers.

Sample	Alignment of Fibers	Beads on Fibers	Structure of Fiber	Diameter of Fibers (μm)
PU1	Random	Present	Straight	0.712 ± 0.026
PU2	Random	Absent	Partially Straight and Partially Coiled	1.915 ± 0.162
PU3	Partially	Absent	Straight	1.064 ± 0.080
PU4	Random	Absent	Coiled	1.238 ± 0.014
PU5	Partially	Absent	Wavy	0.618 ± 0.019