Experimental Nanobiotechnology

Prof. P. Gopinath

Department of Biosciences and Bioengineering,

Indian Institute of Technology Roorkee

Lecture 13: Fabrication of Nanofibers Using Electrospinning

Hello everyone, today we are going to learn fabrication of nanofibers using electrospinning. In today's lecture, we are going to learn what is nanofiber, what are the applications of nanofibers, and how to fabricate nanofibers using electrospinning. We are also going to learn about the various parameters involved in the electrospinning process. At the end of this lecture, by practical demonstration, we'll also learn this electrospinning technique in detail.

Let us see what is nanofiber. A nanofiber is a continuous fiber which has diameter in the range of nanometer. To give a broad idea about the scale difference, when we compare this human hair, which is 80,000 nanometers, we can see how small nanofibers are. We can also understand the scale difference by comparing an animal cell to a nanofiber.

You can see here the size of the cell is in the range of 10 to 20 micrometers when compared to the nanofiber, which is 100 nanometers. So, what are the unique properties of nanofibers? Nanofibers are very small in size, which gives them unique physical and chemical properties.

So that allows the nanofibers for various applications. Nanofibers also have a huge surface area compared to their volume. And these nanofibers come under 1D material, that is one-dimensional materials. It means they have two dimensions at nanoscale and the remaining one dimension is larger than 100 nanometers. The nanofibers have wide applications.

Out of that, I will talk about some of the important applications. The first application is tissue engineering. The nanofibers which mimic like your ECM, that is extracellular matrix. So they can act as a scaffold for tissue engineering applications. And we can also use these nanofibers loaded with anti-cancer drugs or any therapeutic material

which will be very useful for controlled drug release. And we can also use these nanofibers for air and water filtration. We can also use them for wound dressing applications. When you are using a biopolymer like silk, it can be useful for wound dressing applications. It can prevent scar formation and also provides antibacterial shielding.

Nanofibers can also be useful for sensing application. It can be useful for chemical sensor or gas sensor. And due to its higher efficiency in fluid absorption, it can be useful for haemostatic devices. And we can also use the nanofibers in food industry for making edible packaging and biodegradable packaging. We can also use it for other applications such as energy storage device or cosmetic application.

We can make the face mask or we can use it for skin healing therapy. We can use nanofiber based products. How to make these nanofibers? There are three methods to make the nanofibers. The first one is self-assembly.

The second one is phase separation. And third one is electrospinning. So out of these three techniques, the electrospinning is a simple and widely accepted method for making the nanofibers. Before I talk about electrospinning, let me briefly explain about melt spinning.

So let us see how to make nanofibers by the melt spinning technique. Some nanofibers can be made by melting polymers. And spinning them through very small holes. As the fiber spins out, it stretches smaller and smaller. So, let us see a simple example to understand this concept.

Most of you might have seen cotton candy. The principle is similar to cotton candy. How do we make cotton candy? The vendor adds sugar crystals here, and the sugar will melt and the polymer solution will be spun out through tiny holes.

As the fiber spins, it is pulled thinner and thinner, and what you get is cotton candy. The principle of melt spinning is similar to this. I hope you understood the concept of melt spinning. Let us move on to the technique called electrospinning.

How electrospinning can be useful for making the very smaller size fibers that is nanofibers. Electrospinning is a electrohydrodynamic technique in which a liquid droplet is electrified to create a jet. which is then stretched and elongated to form small fibers. This is a horizontal electrospinning setup where your spinneret and collector, these are kept in horizontal. Let us see the electrospinning technique in detail.

Here, the syringe is loaded with the polymer and when you apply the high voltage power supply to the spinneret, what happens is an electrostatic potential is applied between the spinneret and collector. And the polymer is slowly pumped out through the spinneret and the droplet is held by its own surface tension at the spinneret tip until it gets electrostatically charged. After threshold accumulation of the charges, the polymer fluid assumes a conical shape

and thin stream of fiber elutes from the droplet. This conical shape is called as Taylor cone. It is named after the scientist. This is a vertical electrospinning setup. You can see the collector and spinneret is kept in vertical.

The electrospinning technique has more advantages when compared to other methods. It is a simple technique, and we can combine the polymers at the monomer level, fibrous level, and scaffold level. For example, we can also make core-shell nanofibers. In the core, we can load one type of anti-cancer drug. And in the shell, we can load another type of anti-cancer drug.

We can make core-shell nanofibers using the coaxial electrospinning setup. We can also use different kinds of electrospinning setups for various applications. We can control the fiber diameter by simply adjusting the concentration, viscosity, and other parameters. Let us see what the various parameters involved in this electrospinning process are. The parameters can be divided into three types.

The first one is solution parameters. Under the solution parameters, the concentration of the solution, conductivity, viscosity, solvent, volatility, surface tension, and molecular weight. Under the process parameters, the distance between the tip and collector, voltage, flow rate, and the collector type. The collector type is a stationary collector.

And we can also use this kind of rotating drum collector if you want to get the aligned fibers. This I will discuss later in detail. And the third parameter is the environmental conditions where the humidity, temperature, pressure and the local atmospheric flow will play a very important role. Let us see the parameters one by one in detail.

The first one is polymers. There are three types of polymers used in electrospinning. They are classified based on the source. It can be a synthetic polymer. As the name implies, these are man-made polymers designed to meet the application requirements.

Some examples are PCL, that is polycaprolactone, or PVA, that is polyvinyl alcohol, or PEO, that is polyethylene oxide. These are inexpensive, so it is easy to fine-tune these polymers for their various mechanical properties and the degradation rates can also be modified by simply mixing with different combinations of the polymers. And the next one is the natural polymers.

Under the natural polymers: gelatin, collagen, So, these are obtained from natural sources. These are very useful for tissue engineering as well as for various biomedical applications. The third one is semi-synthetic polymers, which are a combination of natural polymers but chemically modified. For example, we can treat cellulose with acetic acid.

It becomes cellulose acetate. We can use these semi-synthetic polymers for various applications. So, these are some of the applications I tabulated for easy understanding. The natural polymers, semi-synthetic polymers, and also synthetic polymers. The applications are denoted as DD, which stands for drug delivery application,

E denotes energy, F for filtration, FE for food packaging, MD for medical devices, and T for tissue engineering applications. So, we can select the right polymer according to your final application. The next important parameter is applied voltage. Applied voltage is one of the important parameters in the fabrication of electrospun nanofibers.

In the electrospinning process, a voltage is applied to the needle, allowing charges to collect and overcome the surface tension of the polymer. When an appropriate voltage approaches the surface energy, the droplet shape becomes deformed and forms a Taylor cone-like structure. In this picture, you can see the droplet shape is deformed and forms a cone-like structure.

This cone-like structure is called a Taylor cone. And from here, you get the nanofiber. It releases the nanofiber. The critical value of applied voltage changes depending on the polymer solution.

If you apply high voltage to the polymer solution, it will stretch and form thinner and smaller nanofibers. But if you apply very high voltage beyond the surface energy, that leads to beads or broken fibers. You may get beads on the fibers or broken fibers when using high voltage. The next important parameter is viscosity and concentration. The polymer concentration is directly proportional to its viscosity.

The optimum concentration for different polymers varies according to the type of polymer and the solvent used. And if you are using the polymer at low viscosity, it leads to bead production. When you are making the fibers, you get the bead formation, and when you adjust the viscosity and if you are having the highly viscous solution you get the fibers with greater dimensions.

You may get thick fibers, or sometimes it may block the spinneret, and you do not get any fibers. So the spinnability of the polymer solution is determined by its concentration and viscosity. So let us see the role of viscosity in detail with some examples. If you have very low viscosity, there will be more bead formation. You can see there are a lot of beads on the nanofibers, and when you adjust that viscosity

you can see the number of beads has gone down when compared to the previous, and when you are using the optimal viscosity you get the proper nanofibers without any bead formation. The next important parameter is conductivity. When you are using a polymer solution with high conductivity, it will have a high charge-carrying capacity and higher tensile force.

When you are using the conductive polymer, you get the proper thin nanofibers. And if you are using the less conductive polymer or non-conductive polymer, you don't get proper nanofibers. The next important parameter is flow rate. A crucial flow rate allows the fabrication of consistent electrospin nanofibers without the formation of beads. Lower flow rates are preferred to provide the solution adequate time to polarize.

With increased flow rates, the nanofiber would have a shorter drying period resulting in an accumulation of fibers with beads and sometimes increase in flow rate with a decrease in voltage or decrease in rotational speed for drum collector will increase the diameter of the fibers and this Taylor cone shape may get smaller when the flow rate decreases when you are using the optimal flow rate you get this kind of proper Taylor cone

with respect to the increase in the flow rate what happen is you get this receded jet or you can get this semi-spherical droplet or you get the aggregated fluid and if the flow rate is very high Along with the cone jet, you may get the unspun droplets which will fall on your fibers and it will create the beads on the nanofibers. Let us understand the role of flow rate with some examples.

When you use a high flow rate, you can see more bead formation, and when you adjust the flow rate, you get fewer beads. At the optimum flow rate, there is no bead formation. What you get are very good nanofibers. And when you reduce the flow rate further, what happens is you will get splashing in the fibers. It may look like normal nanofibers, but there will be splashing in the nanofibers.

The next important parameter is environmental conditions. Environmental conditions also play an important role. For example, temperature, relative humidity also plays a very important role in the final product, which is the nanofibers. For example, when you use low humidity, it causes the solvent to dry

and increases the pace of evaporation. At high humidity, you get thicker fiber diameters. You can see here that at high temperatures, the polymer gets degraded, and when you use these optimum environmental conditions, you get proper nanofibers. In the case of moisture, the fiber structure gets deformed. The next important parameter is working distance. What is working distance? The distance between the tip and the collector is called the working distance.

In the electrospinning process, a minimum distance is required to allow for solvent evaporation before the fiber reaches the collector. If you keep the optimum distance between the spinneret and collector, you get the nanofiber. If you keep the collector close to the spinneret, you get thick fibers or bead formation. And if you keep the collector further away, you get broken fibers. Let us understand the working distance with some examples.

If you use the minimum distance, you get heterogeneous fibers. If you use the optimum distance, you get homogeneous fibers. If the distance increases, the field strength starts to weaken. And if the distance is too great, it leads to broken fibers. As I mentioned earlier, we get broken fibers if the distance is too great.

The next important parameter is the collector type. So, depending on the collector, the final product will also vary. For example, if you use a stationary collector, you get random or misaligned fibers. And if you use a rotating drum collector, you get aligned nanofibers. You have to select the right collector depending on your final application.

So, let us see the summary of various parameters. The first one is molecular weight. If you are using the high molecular weight, it will reduce the number of beads and if the solution concentration is very high, it will increase the fiber diameter and if the surface tension is higher, it leads to instability of jets and if you are using the increase in conductivity that leads to the decline in fiber diameter

if you are using the low viscous polymer you get the bead formation and if you are using the high viscous it will increase the fiber diameter let us see the summary of process parameters and applied parameters in the process parameter the first one is tip to collector distance there will be a formation of beads when you are keeping the distance very small or very large we have to use the optimum distance to make the uniform size nanofibers.

And if you are keeping the flow rate low, you get the smaller fibers and if you are keeping the flow rate high, there will be a bead formation. And based on the voltage, if you are using the optimum voltage, you get the proper nanofibers. The fiber diameter will decrease with respect to increasing the voltage. Under the applied parameters, the first one is humidity.

If the humidity is high, there will be a formation of circular pores in the nanofibers. And if the temperature is higher, it leads to degradation or rupture of fibers. So, let us see some of the common issues in the electrospinning process and how to overcome those challenges to get proper nanofibers.

The first one is the jet formation problem. If there is no jet formation, it may be due to low voltage; increase the voltage to overcome surface tension or it may be due to high viscosity; reduce the viscosity for better flow. It may be due to tip buildup; clear the blockage at the needle tip. Or it may be due to the volatile solvent.

You can use a less volatile solvent. Or it may be due to the high flow rate. You have to adjust the flow rate to avoid the bottleneck, and we also have to adjust the humidity levels. The next one is if you are getting droplet formation; it may be due to the high flow rate. The increased flow rate results in the accumulation of fibers with beads.

So we have to adjust the flow rate. The droplet formation may be due to low viscosity. Increase the viscosity for better fiber formation. And it may also be due to high voltage. So we have to adjust the voltage to prevent overstretching.

Or it may be due to the tip buildup. Clear the minor blockages and adjust the humidity. Some of the other issues related to the electrospinning process are beading of fibers or uneven diameters. So how to overcome these beading of fibers? If you are using a drum collector, we have to increase the speed for better alignment, and we can also

Check the drum stability. Make sure that you are using a stable drum setup and also ensure there is no airflow disturbance. Maintain a consistent temperature so that you can avoid bead formation and obtain proper fibers. If you are getting uneven diameters, you can adjust the needle position and

The distance between the collector and the spinneret. We can also adjust the voltage for optimal stretching. And we have to adjust the flow rate for consistent fiber formation. We also have to check the temperature for ideal viscosity as well as the evaporation rate. By doing this, we can get fibers of uniform size and avoid fibers of different diameters.

Let us see what the contact angle is and how to measure it. When we place a small droplet of water on a solid surface, the tangential outline of the droplet on the solid forms the contact angle. If the contact angle is less than 90 degrees, that means your material is hydrophilic in nature. If it is between 90 to 120, that means your material is hydrophobic in nature. If it is more than 150, your material is superhydrophobic in nature.

By this simple contact angle measurement, we can determine whether our material is hydrophilic or hydrophobic in nature. I hope you understood the theory as well as the basic principle of the electrospinning technique. Let us go to the lab and learn this electrospinning technique in more detail. In this experiment, we will learn how to fabricate nanofibers using an electrospinning instrument. To proceed with the experiment, the materials required are polyvinyl alcohol (PVA) as the polymer.

Ultrapure water, a beaker with a magnetic bead, glutaraldehyde as a crosslinking solution, a syringe, and a desiccator. We need to prepare a 10 percent polymer solution. So, we begin by weighing 5 grams of PVA. Next, measure 50 mL of ultrapure water. Place the beaker with the magnetic stir bar on the stirrer.

Add some ultrapure water to the beaker and turn on the stirrer. Set it to 37 degrees Celsius and 400 rpm. Gradually add the PVA powder into the beaker. Cover it with aluminum foil and continue stirring. After a while, add the remaining water.

Let the solution stir until the polymer is completely dissolved. Once the polymer is dissolved, carefully pour the solution into the syringe. Make sure there is no air gap in the syringe. This is the electrospinning machine where we will fabricate the nanofibers. Make sure that you are standing on this thick rubber mat when operating the instrument.

Start by turning on the machine. Here is the temperature controller, which can be adjusted according to the polymer we are using. These are the different settings for the electrospinning machine. On the left side, we have pump 1. On the right side, pump 2.

Next, you can see the diameter. It denotes the diameter of the backside syringe. This is the value for the flow rate, which denotes mL per minute. These are the on and off settings. These are the forward or reverse settings for the syringe pump.

Pressing forward rotates the syringe pump in an anti-clockwise direction. While reverse rotates it in the opposite direction. The syringe translation settings can be adjusted. We will set 60 for the forward direction and 30 for the reverse direction. First, we will press home and then start, and you can see the syringe moving 60 mm forward.

that is left and 30 mm in reverse that is right. Next the plate translation settings. We will set 30 mm forward and 60 mm in reverse. Pressing home and start will move the plate 30 mm downward and 60 mm upward. The collector is a stationary part but you can connect this drum to the setup to act as a rotating collector

which will rotate in one direction. We can adjust the distance between the needle and the syringe. If you press forward it will move in the forward direction and if you press reverse it will move in the reverse direction. Next in running time, we are going to set for 10 hours. Finally, we have the high voltage setup.

Be cautious during this step. The red light indicates that the voltage is on. Adjust the voltage based on the polymer and the distance. Now, we will begin the electrospinning process. Open the door.

First, use the grounding rod to ground all components. Next, place the syringe with the spinneret in the holder. Then, place the collector. Adjust the distance between the syringe and the collector. Once the distance is set, move the syringe pump forward to ensure that the polymer comes out of the syringe.

Use tissue paper to collect any excess polymer. Finally, attach the high-voltage wire to the tip of the needle. And connect the ground wire to the collector. Close the door, turn on the pump, and initiate the process. We can now observe the formation of the Taylor cone and the deposition of nanofibers on the collector.

This is the final output of the fabricated nanofibers from the electrospinning machine. Now, we will peel the nanofibers from the collector using forceps and then cut them into pieces according to our requirements. Here, you can observe the side view of the nanofibers to examine their thickness. Now, we will perform the crosslinking step.

We will crosslink the nanofibers using a 2.5 percent glutaraldehyde solution. Pour the glutaraldehyde solution into a Petri dish and place it at the bottom of the desiccator. Place the nanofiber mat in the desiccator. Heat it at 37 degrees Celsius for 15 minutes in a hot air oven. After that, flip the fibers.

Once it is done, place the fiber in another desiccator and leave it overnight for the evaporation of glutaraldehyde. After crosslinking, store the nanofibers in a Petri dish, covering them with parafilm as they are highly sensitive. The image in this slide illustrates the surface morphology of the fabricated nanofibers. The diameter of the nanofibers is observed to be in the nanometer range, with an average size of approximately 170 nanometers,

and this image represents the histogram plot of the nanofibers' diameter. Next, we will perform a contact angle measurement on the fabricated nanofibers. First, open the camera for imaging. Position the syringe above the designated measurement area and gradually press it to form a single well-formed droplet.

Carefully remove the droplet using the tissue paper to wipe the area clean. Place the nanofibers in the measurement area. The surface of the nanofiber should be smooth and plain. Press the syringe so that the water droplet falls onto the nanofibers. Record a video to observe the contact angle.

So in this lab session, we have learned the fabrication of nanofibers using an electrospinning setup and contact angle measurement. We have previously observed the contact angle for fabricated nanofibers using the PVA polymer. In this image, we can see the contact angle of nanofibers synthesized from the hydrophobic polymer, which is PCL. Also, it is to be noted that PVA is not a stable polymer, so it can be added

with some other polymer as a blend to make it stable. As a summary, in today's lecture, we learned about nanofibers and their various applications. We also learned how to fabricate nanofibers using electrospinning and the various parameters involved in the electrospinning process. Through practical demonstration, we also learned how to fabricate nanofibers using electrospinning.

I thank you all for your kind attention. I will see you in another interesting lecture.