Chapter

Electrohydrodynamic Processes and Their Affecting Parameters

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Abstract

Electrohydrodynamic processes such as electrospinning and electrospraying are simple, flexible, and cost-effective. Both processes use electrically charged jet of polymer solution for the fabrication of micro- or nanofibers and micro- or nanoparticle. Both of these electrodynamic techniques have been receiving increasing attention not only in the scientific community but also in industry. These fibers and particles offer several morphological and functional features that are suitable for tissue engineering in biomedical applications. The main apparatus used for both of these processes is almost the same. Both need electric voltage to induce charge on the droplet, which at optimized electric field leads to micro- or nanofibers and micro- or nanoparticles. Rayleigh in 1882, for the first time, theoretically estimated the maximum amount of charge that a liquid droplet could carry to change in a jet. This theory is now known as the “Rayleigh limit.” He predicted that a droplet on reaching Rayleigh limit would move as fine jets of liquid. More than 100 years later, Rayleigh limit theory was confirmed experimentally. Beside electric field there are other operating and solution parameters that need to be optimized before we obtain a desire product.

Keywords: electrohydrodynamic processes, cost effective, micro and nanofibers, micro and nanoparticles

1. Electrospinning

Since the late twentieth century, electrospinning, a technology used for the fabrication of nanofibers, has been receiving increasing attention not only in the scientific community but also in industry. With this technique fibrous material was conveniently prepared with fascinating properties such as ultrafine diameters in the range of 10–500 nanometer (nm), high permeability, porosity, surface area per unit mass, and small inter-fibrous pore size [1–3]. It is, therefore, considered to be a vital scientific and commercial venture with global economic benefits. This technology traced its legacy back to 1902 [4, 5] and 1934 [6], when the very first patents entitled “Apparatus for Electrical Dispersion of Fluids” and “Process and Apparatus for Preparing Artificial Over and Done Threads from Electrically Dispersed Fluids” were registered. Since then, this process was largely ignored until the 1990s. However, with the recent revelations by researchers who are associated with the field of nanotechnology mainly nanofibers,
investigations into the preparation of nanofibers using the aforementioned technique picked up momentum [7].

In the literature, various techniques are reported for the fabrication of nano-materials. These include drawing-processing, template-assisted synthesis, self-assembly, solvent casting, phase separation, and electrospinning [8–10]. With advancement of research in nanotechnology, particularly associated with nanoparticles, nanostructures, and more explicitly with the preparation of scaffolds, electrospinning emerged as a highly developed and frequently used technique/process. This process is favored over other techniques such as solvent casting and phase separation, since nanofibers have high surface area to volume ratio and inter-/intra-fibrous pores. In addition to the previously mentioned properties, it has the advantages of being easy to use and have a low processing cost. The growing literature on electrospinning has helped this technique to pave the way for advancements in areas like environmental protection, bioengineering, electronics, and catalysis [11–13]. The capability of this technique to produce nanomaterials from numerous raw materials ranging from simple natural polymers to complex materials such as composites has attracted a large number of researchers. For example, scientists have reported a wide range of applications of electrospun nanofibers in the protection of the environment, most importantly in water and air filtration. Subramanian et al. [14] and Feng et al. [15] emphasized the importance of using electrospun nanofibers for the removal of contaminants from water, focusing on the application of electrospun nanofibers in nanofiltration.

Furthermore, polymers with a piezoelectric effect (i.e., polyvinylidene fluoride) can be subjected to an electrospinning technique for the fabrication of nanofiber scaffolds with a piezoelectric effect. Apart from the use of nanofibers in scaffolds with piezoelectric effect, they can also be used for producing high-surface-area nanosensors. Huang et al. suggested that scaffolds of the copolymer poly(lactide-co-glycolide) (PLGA) could be used as sensing tools in both chemical and biological fields [16]. Investigators have also highlighted that sensors prepared of nanofibers might demonstrate improved sensing capabilities for chemicals such as 2,4-dinitrotulene DNT, mercury (Hg), and ferric (Fe^{3+}) ions as compared to orthodox thin film.
Furthermore, fluorescent polymer electrospun nanofiber optical sensors also showed high sensitivity [17]. Ultrafine electrospun nanofiber scaffolds can also be applied in the preparation of nanotubes, which are of prime importance in various industries [18]. To prepare nanotubes, electrospun nanofibers are coated with the raw material of the nanotubes, and upon the evaporation of a solvent via solvent evaporation or the thermal degradation of the polymers, the nanotubes are synthesized. Bognitzki et al. adopted a physical and chemical vapor deposition technique using poly (L-lactide) (PLLA) nanofibers as a template and synthesized polymer composite nanotubes comprised of poly(p-xylene)/aluminum metal with a thickness of 0.1–1 mm [19]. Hou et al. prepared nanotubes with an even smaller diameter by adopting the same technique using poly(L-lactide) (PLA) and poly(tetramethylene adipamide) (PA) as templates [16, 20].

Electrospun nanofibers have also played a pivotal role in the area of biomaterials. The importance of electrospun nanofibers in the biomedical field can be determined from the fact that numerous articles are being published every
year on a regular basis in high-quality journals, highlighting their significance in biomedical engineering. Nanofiber scaffolds were also functionalized with desired triggering groups. These triggering groups performed a significant role in providing conducive atmosphere to the cells, which resulted in their enhanced

Figure 4.
Country-wise Scopus data of electrospinning. The data is taken on February 09, 2019.

Figure 5.
Nanofiber market to 2025—Global analysis and forecasts by material (polymer nanofiber, carbon nanofiber, ceramic nanofiber, composite nanofiber, and glass nanofiber) and application (energy, medical life science and pharmaceutical, and chemical and environmental and defense and security, consumer, electronics, https://www.theinsightpartners.com/reports/nanofiber-market). Polymer nanofiber market, research report—Forecast to 2023 https://www.marketresearchfuture.com/reports/polymer-nanofiber-market-4416.
Electrohydrodynamic Processes and Their Affecting Parameters
DOI: http://dx.doi.org/10.5772/intechopen.89929

anchoring, proliferation, and differentiation. For example, collagen fibril has been known to enhance the interaction between cells and scaffolds. Similarly, electrospun nanofiber scaffolds are also used as a drug delivery carrier for carrying drugs to their target sites [21, 22].

Nanofibers, until now, have been produced using electrospinning from nearly 100 diverse polymers of natural and synthetic origins. All polymers have been electrospun via solvent and melt spinning. Even with the persistent use of this technique, the understanding of the basics still need to be acquired. Figures 1–5 show the research interest in the area of electrospinning and the market interest in the electrospun product. More than 200 universities and research institutes worldwide (some with high publications are shown in Figure 3) are still studying a variety of the electrospinning processes, their various aspects, and the nanofibers produced. The market of electrospun product is expected to increase mostly in filtration and medical fields by 2025 (Figure 5).

2. Electrospinning and its mechanism

Much research has been done on the electrospinning technique. Based on the literature, the fundamental setup used for electrospinning (Figure 6a) consists of mainly four parts: a glass syringe (holding solution), needle (metallic), applied voltage, and collector (metallic, with a variable morphology). The process commences, when electric charges, produced on the needle due to the applied voltage, transfer into the polymer solution via the metallic needle [22]. These charges cause instability within the polymer droplet. The repulsion of charges generates a force opposite to surface tension. These forces cause the polymer solution to move in the direction of the electric field (Figure 6b). An increase in the electric field forces the spherical droplet to distort and adopt a conical shape. At this phase, fine nanofibers (nano to micro in diameters) appear from the conical droplet called Taylor cone, which are whippingly collected on the collector and kept at an optimized distance. A steady charge jet could only form, when the polymer solution possesses adequate cohesive force. This whipping of the fibers permits the polymer chains to stretch.

![Figure 6. Schematic depicting (a) electrospinning setup, and (b) phenomenon of electrospinning.](image-url)
and slide past each other in the solution, which leads to the fabrication of fibers with diameters as mentioned above [23, 24].

3. Effects of parameters on electrospinning

There are various factors that affect the electrospinning process. These factors are classified as electrospinning parameters and solution parameters. The electrospinning parameters include the applied electric field, distance between the needle and collector, flow rate, and needle diameter. The solution parameters include the solvent, polymer concentration, and viscosity. All of these parameters directly affect the generation of smooth and bead-free electrospun fibers. Therefore, to gain a better understanding of the electrospinning technique and fabrication of polymeric nanofibers, it is essential to thoroughly understand the effects of all of these governing parameters. Detailed information highlighting the role of electrospinning and the effects of the solution parameters on the morphology of electrospun polymeric nanofibers are summarized below.

3.1 Effect of changes in applied voltage

Generally, it is a known fact that the flow of current from a high-voltage power supply into a solution via a metallic needle will cause a spherical droplet to deform into a Taylor cone and form ultrafine nanofibers at a critical voltage (Figure 7a–f). This critical value of applied voltage varies for different polymers systems. The creation of nanofibers with smaller diameter as the applied voltage is increased could be ascribed to the stretching of the polymer solution and charge repulsion in the polymer jet [25]. An increased applied voltage further than the critical value

![Diagram](image-url)

**Figure 7.** The images showing the droplet deformation and eventual fiber ejection with an increase in electric field on droplet and effect of charges on polymeric solutions [28].
while keeping the flow rate constant will lead to the creation of beads or beaded nanofibers. The creation of beads or beaded nanofibers with an increased applied voltage is ascribed to the decrease in size of the Taylor cone and increase in the jet velocity. Deitzel et al. reported bead formation with an increase in the applied voltage using poly(ethylene oxide) (PEO)/water. Similar results were also reported by Meechaisue et al. and Zong et al. [26]. Furthermore, the diameter of the nanofibers was also reported to increase with an increase in the applied voltage. This increase in the diameter was attributed to an increase in the jet length with the applied voltage (Figure 7) [27].

4. Effect of solution flow rate

The movement of solution through the tip of the needle controls the morphology of the nanofibers. Uniform beadless nanofibers could be fabricated via a critical flow rate. The flow rate varies for different polymers systems. An increase in the flow rate further than the critical value results in the creation of beads. For instance, the increase in flow rate of polystyrene (PS) to 0.10 mL/min led to bead creation. However, when the flow rate was reduced to 0.07 ml/min, bead-free, narrow-diameter electrospun fibers were formed. Because an increase and the decrease in the flow rate affect the nanofiber diameter, a minimum flow rate is preferred to maintain a balance between the leaving polymeric solution and replacement of that solution with a new one during jet formation [29, 30]. This will also permit the formation of a steady cone jet and sometimes a receded jet: a jet that appears from the inside of the needle with no apparent droplet or cone. Receded jets are not steady jets, and during the process, these jets are unceasingly substituted by cone jets. This phenomenon results in the formation of nanofibers with wide range diameters (Figure 8a–h) [31]. Numerous research groups have studied the effect of the flow rate on the morphology and diameter of nanofibers. For instance, Zong et al. revealed that smaller diameter nanofibers can be prepared using a low flow rate, whereas a high flow rate will not only yield high-diameter nanofibers, but the bead formed will also have a high diameter [32]. Megelski et al. showed an increase in the pore size and fiber diameter of PS nanofibers by increasing the flow rate of the polymeric solution. They also concluded that fibers with beads were formed at a high flow rate as a result of the incomplete drying of the nanofibers jet during its flight between the needle tip and metallic collector [29]. In addition to bead formation, in some cases, at an elevated flow rate, ribbonlike defects [29] and unspun droplets (Figure 8e) have also been reported in the literature [31]. The creation of beads and ribbonlike structures with an increased flow rate was mainly ascribed to the low stretching of the solution in the flight between the needle tip and metallic collector and the non-evaporation of the solvent. Similar effect could also be ascribed to an increase in diameter of the nanofibers with an increase in the flow rate [29]. The presence of the unspun droplets is attributed to the influence of the gravitational force [31]. Another important factor that may cause defects in the nanofiber structure is the surface charge density. Any change in the surface charge density may also affect the morphology of the nanofibers. For example, Theron et al. found that flow rate and electric current are directly linked to each other. His group investigated the effects of the flow rate and surface charge density using PEO, polyacrylic acid (PAA), polyvinyl alcohol (PVA), polyurethane (PU), and polycaprolactone (PCL). They noted that, in the case of PEO, an increase in the flow rate increased the electric current and decreased the surface charge density at the same time. A decreased surface charge density permits the merger of nanofibers in their flight to the collector. This merger of nanofibers helps in the creation of garlands [33, 34].
4.1 Effects of polymer concentration and solution viscosity

Electrospinning counts on the uniaxial stretching of a charged jet. The stretching of the charged jet is considerably affected if the solution concentration is changed. For instance, when the concentration is low, the applied electric field and surface tension force the entangled polymer chains to rupture into fragments before reaching the collector [23, 35]. These fragments then lead to the creation of beads or beaded nanofibers. Increased concentration of the solution, however, leads to an increase in the viscosity, which subsequently increases the chain entanglement. These entanglements then overcome the surface tension and eventually result in uniform and beadless nanofibers. Moreover, increasing the concentration further than a critical value impedes the flow of the solution through the needle tip. In simple words, viscous solution partially blocks and dries at the needle tip. This eventually leads to defective and beaded nanofibers [23]. The morphologies of the beads depict an interesting shape change from a round droplet-like shape (with low-viscosity solutions) to a stretched droplet or ellipse to smooth fibers (with sufficient viscosity) as the solution viscosity changes (Figure 9a–h). This effect of the concentration/viscosity on the morphology of the nanofibers was also reported by Doshi et al. Working with PEO, they concluded that the optimum viscosity for the generation of electrospun nanofibers is 800–4000 cp [7]. In addition to the work of Doshi et al., an experiment on a polyacrylonitrile (PAN) polymer solution showed that smooth electrospun nanofibers could be prepared when the viscosity of the solution was kept at 1.7–215 cp. Hence, it can be concluded that in addition to the
electrospinning parameters, the determination of the critical value of the concentration/viscosity is also essential to obtain beadless nanofibers [27].

4.2 Role of solvent in electrospinning

The selection of solvent is one of the key factors for the fabrication of smooth and beadless electrospun nanofibers. Usually two things need to be kept in mind before selecting the solvent. First, the preferred solvents for electrospinning process have polymers that are completely soluble. Second, the solvent should have a moderate boiling point. Its boiling point gives an idea about the volatility of a solvent. Mostly volatile solvents are desired as their high evaporation rates boost the fabrication of nanofibers. However, very highly volatile solvents are commonly avoided since their high evaporation rate forces the drying of jet at the needle tip. This drying blocks the needle tip and thus hampers the electrospinning process. Likewise, low-volatile solvents are also avoided since their low evaporation inhibits their drying in the flight. The deposition of solvent-containing nanofibers on the collector will cause the formation of beaded nanofibers [25, 38]. Numerous research groups have studied the effects of the solvent and solvent system on the morphology of nanofibers (Figure 10a–f) [39] and concluded that similar to the applied voltage, solvent also affects the polymer system [40]. Moreover, solvents also play a vibrant role in the fabrication of highly porous nanofibers. This may happen when a polymer is dissolved in two solvents, where one act as solvents and the other as a non-solvent. The difference in the evaporation rates of the solvent and non-solvent causes phase separation, which results in the creation of pores in nanofibers (Figure 10f) [25]. Similar results were also reported by Zhang et al. [41]. Megelski et al. prepared porous nanofibers by varying the ratio of tetrahydrofuran (THF)
and dimethylformamide (DMF) [29]. The conductivity and dipole moment of the solvent are also very vital. Jarusuwannapoom et al. from the test of 18 solvents concluded only five solvents (ethyl acetate, DMF, THF, methyl ethyl ketone, and 1,2-dichloroethane) were feasible to be used in the electrospinning of PS, since these solvents displayed relatively superior conductivity and dipole moment [42].

4.3 Effects of capillary and collector distance

The distance between the metallic needle tip and collector plays an essential role in determining the morphology of electrospun nanofibers. Similar to the applied electric field, viscosity, and flow rate, the distance between the metallic needle tip and collector also varies with the polymer system. The nanofiber morphology could be easily affected by the distance because it depends on the deposition time, evaporation rate, and whipping or instability interval [44]. Hence, a critical distance needs to be maintained to prepare smooth and uniform electrospun nanofibers, and any changes on either side of the critical distance will affect the morphology of the nanofibers [45]. Numerous research groups have studied the effect of the distance between the needle tip and collector and concluded that defective and large-diameter nanofibers are formed when this distance is kept small, whereas the diameter of the nanofibers decreased as the distance was increased [27, 44, 46]. However, there are cases where no effect on the morphology of the nanofibers was observed with a change in the distance between the metallic needle and collector [47].

Figure 10.
SEM images of 5% PCL solutions dissolved in different solvents: (a) glacial acetic acid, (b) 90% acetic acid, (c) methylene chloride/DMF = 4/1, (d) glacial formic acid, (e) and formic acid/acetone, along with (f) SEM images of PVB nanofibers prepared from 10 wt% THF/DMSO (9/1 v/v) [39, 43].
5. Electrospray

Electrospray is a technique that uses electricity to disperse a liquid and produce fine aerosol. High voltage is applied to a liquid supply usually a glass or metallic capillary. The liquid on reaching to the tip of the capillary tube (in ideal conditions) forms a Taylor cone, which produces a liquid jet through its top. Varicose waves (twisted and lengthened waves) on the surface of the jet lead to the creation of small and highly charged liquid droplets, which due to Coulomb repulsion are radially dispersed. Electrospray deposition technique is very famous among chemical and medical researchers. This system has several advantages (such as high drug-loading efficiency and self-dispersion) over conventional methods.

5.1 Evolution history of electrospray

In the late sixteenth century, Gilbert [48] described the behavior of magnetic and electrostatic phenomena. He noticed that, in the presence of a charged piece of amber, a drop of water deformed into a cone. This effect was clearly related to electrospray and considered to be the first such observation. Gilbert did not record/elaborate the observation. In 1750, a French clergyman and physicist Jean-Antoine (Abbé) Nollet noticed that water flowing from a vessel aerosolized when the vessel was electrified and placed near electrical ground. He also observed that if a person is electrified due to a connection to a high-voltage generator, he would not bleed normally if he were to cut himself. The blood would only spray from the wound [49]. In 1882, Rayleigh theoretically estimated the maximum amount of charge a liquid droplet could carry [50]. This theory is now known as the “Rayleigh limit.” He predicted that a droplet on reaching Rayleigh limit would move as fine jets of liquid. More than 100 years later, Rayleigh limit theory was confirmed experimentally [51]. In 1914, Zeleny studied the behavior of fluid droplets at the end of glass capillaries. The work was later published [52]. The report presented experimental evidence for several electrospray-operating regimes (dripping, burst, pulsating, and cone jet). A few years later, the first time-lapse images of the dynamic liquid meniscus were captured [53]. Between 1964 and 1969, Taylor produced the theoretical groundwork of electrospraying [54–56]. Taylor demonstrated a cone formation by the fluid droplet when an electric field was applied. This characteristic droplet shape is named as the Taylor cone. He further worked with Melcher to develop the “leaky dielectric model" for conducting fluids [57].

6. Mechanism of electrospray

Electrospraying is a technique (Figure 11) used for liquid atomization that achieves the stretching and breakup of polymeric solution via electrical forces to obtain micro- or nanoscale particles. Many forces control and direct the electro-spraying process; the most important are (i) gravity of polymeric solution, (ii) electrostatic force generated (from external electric field) between nozzle and collector, (iii) repulsion force (Coulomb forces) among adjacent charged carriers on the surface of jet, (iv) viscoelastic force of polymeric solution, (v) interfacial surface tension between air and liquid, and (vi) frictional force between the charged jet and the surrounding air. Among these forces, electrostatic, repulsion, viscoelastic forces, and surface tension affect the stretching and atomization of the droplets during the electrospraying process. When a solution flows out of the nozzle (needle), the charge distribution and carried charge quantity on the surface
of the solution will change in varying degrees, according to its electrical conductivity and dielectric constant, because of the polarization effect coming from the external electric field. At the same time, initially, the uncharged liquid becomes charged jet and is further stretched toward the direction of electrostatic attraction. However, compared to gravity and electrostatic force that accelerates the movement and stretching of polymeric solution from the nozzle to the collector, the surface tension and viscoelastic ones prevent this movement and elongation because of their opposite behavior on the electrosprayed solution. When these forces reach a balance at a certain range, the droplets at the tip of the nozzle are stretched from the spherical surface into conical surface. In 1964, Taylor proposed, for a perfectly conducting liquid, a first explanation of the conical shape formation, corresponding to a hydrostatic balance between electrostatic forces and surface tension. The presence of the conical surface at the tip of the nozzle during electrospraying is also called Taylor cone. According to Rayleigh’s theory, when the charge quantity distributed on the surface of droplets reaches the value between 50 and 80% of the Rayleigh limit, the breakup and fission of charged droplets occur due to Coulomb repulsions among charged droplets [58]. A classical electrospray setup is considered, with the glass capillary tube situated at a distance (d) from a grounded counter-electrode. The liquid being sprayed is characterized by its viscosity (μ), surface tension (γ), conductivity (κ), and relative permittivity (εr).

6.1 Effect of small electric fields on liquid menisci

The liquid meniscus adopts a semispherical shape at the needle tip under the influence of surface tension. Application of the voltage (V) will bring into effect the electric field [60]:

$$E = \frac{2V}{r \ln(4d/r)}$$
where \( r \) is the liquid radius of curvature. The electric field causes the polarization of the liquid into negative and positive charges. At low voltage, the liquid assumes an equilibrium geometry with a small radius of curvature.

### 6.2 Taylor cone

A Taylor cone is formed at the applied electric field above the threshold value. Theoretically, the shape of the cone depends on two assumptions: first the cone has equipotential surface, and second the cone is in steady-state equilibrium [54]. To meet both of these conditions, the electric field must have \( R^{1/2} \) dependence and azimuthal symmetry to counter the surface tension. The answer to this problem is given as below:

\[
V = V_0 + AR^{1/2}P_{1/2}(\cos \theta_0)
\]

where \( (V=V_o) \) equipotential surface occurs at a value of \( (\theta_o) \) (regardless of R) leading to an equipotential cone. The angle necessary for \( (V=V_o) \) for all R is a zero of the Legendre polynomial of order 1/2, \( P_{1/2}(\cos \theta_o) \). There is only one zero between 0 and \( \Pi \) at 130.7099°, which is the complement of the Taylor’s now famous 49.3° angle.

### 6.3 Singularity development

The top of the conical meniscus cannot turn into substantially small. A singularity develops when the hydrodynamic relaxation time \( \tau_H = \frac{rH}{\eta} \) becomes larger than the charge relaxation time \( \tau_C = \frac{\epsilon_C e}{\kappa} \) [61]. The undefined symbols stand for characteristic length \( r \) and vacuum permittivity \( \epsilon_0 \). Due to intrinsic varicose unsteadiness, the charged jet that ejection from the cone ruptures into small charged droplets, which are dispersed radially by the space charge.

### 6.4 Closing the electrical circuit

The charged liquid ejects through the cone top and is collected as charged droplets on the collector which act as electrode. To balance the loss charge, the

\[\text{Figure 12.}\]

Scopus data showing year-wise publication in the area of electrospraying. The data is taken on February 09, 2019.
negative charge (which is in excess) is neutralized electrochemically at the nozzle tip. A disproportion between the amount of charge produced electrochemically and that of the lost at the cone top could result in numerous electrospray regimes. For a stable electrosprays, the potential at interface (metal/liquid) self-regulates to produce the equal amount of charges that are lost through the cone tip \[62\].

Various institution and disciplines around the world are working on electrospray technique to prepare nano- and microparticles for a number of applications ranging from food to biomedical. **Figures 12–15** show the research interest in the area of electrospraying. However, even with the widespread use of the electrospraying technique, the understanding of this method is still very limited.

**Figure 13.**
*Country-wise Scopus data of electrospraying. The data is taken on February 09, 2019.*

**Figure 14.**
*Showing Scopus data subject wise where electrospraying has been used. The data is taken on February 09, 2019.*
7. Effects of parameters on electrospraying

Similar to electrospinning, there are various factors that affect the electrospraying process. These factors are classified as operating and solution parameters. The operating parameters include (i) applied voltage, (ii) working distance, (iii) liquid flow rate, and (iv) nozzle type. The solution parameters include (i) electrical conductivity, (ii) surface tension, (iii) viscosity, (iv) vapor pressure, and (v) dielectric constant. All these parameters directly affect the formation of the Taylor cone, which leads to the production of particles having a low mean diameter and narrow particle size distribution. Therefore, to gain a better understanding of the electrospraying technique and achieve low mean diameter and narrow particle size distribution, it is essential to thoroughly understand the effects of all of these governing parameters [58].

7.1 Applied voltage

Applied voltage is one of the essential parameters, which needs to be optimized to get low diameter and narrow particle distribution. Voltage applied between the nozzle and collector not only influences the stretching of the jet but also the formation of the Taylor cone at the end of the nozzle. Increase in the applied voltage increases the electrostatic forces that are acting on the surface of the charged droplets. This causes the spray mode to gradually take its route from dripping to multi-jet and then to a stable cone jet (Figure 16 and Table 1). When the electrostatic forces acting on the surface of the spray droplets are not sufficiently strong to overcome surface and viscoelastic tensions (low applied voltage causes drop-to-drop mode), film formation occurs on the collector. In the dripping area, electrified liquid form drops at the capillary end till the gravitational and electrical forces overcome their surface tension. The droplets emerge at the end of the capillary at low frequency and maintain spherical morphologies due to gravitational force and surface tension. As the voltage is increased, the shape of the ejected droplet is affected by its wetting properties, which allows the formation of particles with high average diameter and wide size distribution. At higher voltages, the jet mode changes to stable conical jet mode (Figure 17). At this point the electrostatic forces...
are strong enough to overcome surface and viscoelastic tension, which leads to a balance between different forces and fabrication of low mean diameter particles of narrow size distribution [63, 64].
7.2 Flow rate

The flow rate of the electrospray solution is also an essential factor in the formation of the Taylor cone. The optimization of this parameter depends on two intrinsic characteristics of the solutions: (i) vapor pressure of the solvent (ii) and electrical conductivity of the solutions. A stable Taylor cone prefers low flow rates because the uncharged drop at the tip of the nozzle needs sufficient time polarization. This polarization generates charges on the droplet surface, which in turn promote Taylor cone formation. At higher flows, the decrease in the polarization/partial polarization of the droplets result in continuous dripping of droplets due to gravity. Having said this, for different materials the flow rate to form a stable jet varies. The use of a solvent with a high-saturation vapor pressure needs a higher flow rate to avoid nozzle blocking, when the solvent evaporates. A lower flow rate is recommended for solutions prepared from solvents having low saturated vapor pressure. This is done to ensure complete removal (evaporation) of the solvent during solidification process. Another factor that might affect the optimization of flow rate is the conductivity of the solutions. It is a known fact that conductivity of a solution influences the droplet polarization time. This means, it will also influence the adjustment of an adequate flow rate. Since low conductivity solution will need more time to polarize and generate charges on the droplet, hence in such case low flow rate is recommended. Reverse is the case with high-conductivity solutions [66].

7.3 Working distance

The working distance between the metallic nozzle tip and collector also plays an essential role in determining the formation of a table Taylor cone. Similar to the applied electric field, viscosity, and flow rate, the distance between the metallic needle tip and collector also varies for different polymer systems. Smeets et al. achieved the formation of a stable Taylor cone using a larger tip-to-collector distance and low flow rate. The working distance between the tip and the collector is controlled to achieve a critical electric field (at constant applied field) and ensure the formation of the Taylor cone. At shorter distance, the electric field is higher. This leads to the formation of small particles. However, this is only possible when the
solvent is more volatile; otherwise swelled particles are collected on the collector. Long working distance may cause lower yield. This is attributed mainly to the loss of material to the surrounding due to the turbulent droplet flight. Having said this, long working distance is needed when denser polymer particles are required. The particles do not swell on the collectors because of the availability of sufficient time for the droplet’s solvent to evaporate in the flight from nozzle tip to the collector. For low conductive solution with more volatility, nozzle to collector distance is smaller and vice versa for the high-conductivity and low-volatility solution [64].

7.4 Electrical conductivity

In the process of electrospraying, a solution is stretched and converted into a jet at the tip of the nozzle due to the electrostatic force, when an electric field is applied between the nozzle tip and collector. A balance between gravity, electrostatic force, Coulomb repulsions, viscoelastic and frictional forces, and surface tension leads to the formation of a Taylor cone at the tip of the nozzle (Figures 11 and 17). The strength of the electrostatic force and Coulomb repulsions that are acting on the electrosprayed droplets depends on the amount of polarization charge on the droplets, which in turn depends on the strength of the applied electric field. These electrostatic attractions counteract the surface tension and viscoelastic forces, which then leads to the formation of Taylor cone. When the electrical conductivity of the solution is too high, this high conductivity causes increased Coulomb repulsions among charged droplets and breakup of the charged droplets. This phenomenon leads to the modification of the balance between gravity, electrostatic force, Coulomb repulsions, viscoelastic and frictional forces, and surface tension and a change from a stable cone jet to an unstable jet. Similarly, a too low electrical conductivity causes decreased electrostatic attractions on the droplets, which leads to the same unbalance among the abovementioned forces and results neither in the Taylor cone formation at the nozzle tip nor the formation of particle. Hence, a critical conductivity of the solution is needed, which results in the formation of a stable Taylor cone. Jaworek and Xie et al. suggested that an electrohydrodynamic process is carried out under cone-jet mode, when the electrical conductivity of the solution is in the range of $10^{-11}$ to $10^{-1}$ S/m [67].

7.5 Surface tension and viscosity

As discussed earlier, unbalance between the forces affects the formation of a Taylor cone at the tip of the nozzle during the electrospraying. One of these forces is surface tension. Cloupeau and Smith suggested that the surface tension value of the solution used in electrospraying must not exceed 50 mN/m, though some studies reported more value for glycerine (63 mN/m) and water (72.8 mN/m) [68–71]. A high surface tension of a solution will result in a corona discharge at the tip of the nozzle, which will cause a stable cone jet to change into an irregular spraying and an asymmetrical mode. Similar to surface tension, viscosity of the solutions also affects the formation of a stable Taylor cone. Since the direction of the viscoelastic force is opposite to the direction of the gravity and electrostatic attraction, when the viscosity of the solution is low, the combined viscoelastic force and surface tension are sufficiently strong to counteract the gravity and electrostatic attraction forces. This leads to dripping instead of cone jet. A high-viscosity solution does not allow the formation of a stable Taylor cone due to the drying of the polymeric particles, which block the tip of the capillary and therefore restricting the formation of a stable Taylor cone. Thus, in order to achieve a stable cone jet during electrospraying process, a critical range of viscosity is needed. This range will be different for different for polymeric systems. For some the range may be from 1.5 to 5500 mPa·s [52, 53].
7.6 Vapor pressure and dielectric constant

Boiling point of the solution in electrospraying also affects the formation of Taylor cone. Since the evaporation of solvent and the formation of Taylor cone at the tip of the nozzle occur simultaneously in jetting, thus a too low boiling point (high vapor pressure) changes the shape of the stable cone jet into an unstable one. Furthermore, a low boiling point of solution will result in the drying of the polymeric particles at the tip of the nozzle and will block the tip and stop the process. The effect of the dielectric constant on the cone-jet formation is similar to the electrical conductivity. A very high and too low dielectric constant is not favorable to obtain a stable cone jet during electrospraying process (e.g., polycaprolactone (PCL)). Some research published on the electrospinning of PS correlated to the dipole moment and the dielectric constant of the solutions. To date, very few articles have studied the effect of dielectric constant on the outcomes of electrospaying; much work is needed to completely understand its effects [42, 72].

8. Conclusion

Electrospinning is a technique used for the fabrication of nanofibers, whereas electrospray is a technique used for the preparation of micro- or nanoscale size, mono-dispersed particles. Both of these electrodynamic techniques have been receiving increasing attention not only in the scientific community but also in the food, environmental, and biomedical industries. The main apparatus used for both of these processes is almost the same. Both need electric voltage to induce charges on the droplet, which at optimized electric filed leads to micro- or nanofibers and micro- or nanoparticles. Rayleigh in 1882, for the first time, theoretically estimated the maximum amount of charge a liquid droplet could carry to change in a jet. This theory is now known as the “Rayleigh limit.” His predicted that a droplet on reaching Rayleigh limit would move as fine jets of liquid. More than 100 years later, Rayleigh limit theory was confirmed experimentally. Beside electric filed there are other operating and solution parameters that need to be optimized before we obtain our desired products. The particle and fiber formation mechanisms and principles of electrospraying and electrospinning are still complicated, and more studies are needed understand both of these processes.
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