EXPERIMENTAL STUDY AND MODELING OF THE ELECTROSPINNING PROCESS

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ABSTRACT
In this paper we report theoretical modeling of the electrospinning process which is substantiated by experimental study for comparison. Different types of polyethylene oxide nanofibres are spun in the presence and absence of poly allylamine hydrochloride (PAH) in the spinning solution. Two different paths of the fibre formation (jet modes), namely, straight and whipping jet paths are observed during this study. These jet paths are further analyzed to see their influence in the formation of uniform and bead free nanofibres. For the first time we report that the length of the straight jet path during the fibre formation plays a major role in the formation of uniform and bead free nanofibres in comparison to the whipping path. Nanofibres spun in the presence of PAH with higher concentration give rise to uniform fibres with longer straight jet path in comparison to the one spun without PAH. A theoretical model of the electrospinning process was developed by taking into account the straight and whipping paths of the fibre formation modes. The electric force acting on the charged polymer jet was calculated.

Keywords: electrospinning, jet path**,** modeling, nanofibres

1. INTRODUCTION
Electrospinning process is one of the simple and versatile methods of producing nanofibres with the help of electrostatic force. In this process, a high voltage source is used to create an electrically charged jet of polymer solution or melt out of a needle. Initially polymer solution is held by its surface tension. Once the solution is charged with an electric field, the mutual charges of repulsion of the surface charges cause a force directly opposite to the surface tension. As the intensity of the electric field is increased, the hemispherical surface of the fluid at the tip of the capillary tube elongates to form a conical shape known as Taylor cone (Taylor 1969, 1964). On increasing the electric field further, a critical value is attained at which the repulsive electrostatic force overcomes the surface tension of the spinning solution and the charged jet of the fluid is ejected from the tip of the Taylor cone. The discharged polymer solution jet undergoes an instability and elongation process due to the influence of electrostatic force, which allows the jet to become very long and thin. Meanwhile, fibres solidify as the polymer solvent evaporates and create an interlinked layer of fibres on the surface of a collector (Doshi and Reneker, 1995, Fong and Reneker, 2001). Many parameters like solution properties, processing and ambient conditions influence the transformation of polymer solutions into nanofibres during the electrospinning process. A number of good reviews on the effect of all these parameters on electrospinning process can be found in the literature (Huang et al., 2003, Subbiah et al., 2005, Ramakrishna et al., 2005, Patnaik and Pal, 2005, Patanaik et al., 2007).

Two different paths of fibre formation (jet modes), namely straight and whipping jet path, are generally observed during the formation of nanofibres. Although a great deal of research work has been reported on various conditions for spinning nanofibres, there is not much reported literature available on the basic mechanics of jet path during electrospinning. Till now it is not known how straight path length contributes to the formation of nanofibres and its subsequent effect on the whipping path.

One of the defects in the nanofibres is the presence of beads (Fong et al., 1999). For the potential application of nanofibres in various areas ranging from filtration to composites, it is always desirable to have fibres with uniform diameter and free from beads. The formation of beads is due to insufficient stretching of the charged jet during fibre formation as a result of low charge density of the polymer solution, apart from other parameters like solution properties and processing conditions. So obtaining smooth and uniform nanofibres is a challenging task. In order to overcome the above drawback, a charged species or polyelectrolyte is added to the spinning solution. Polyelectrolyte is a macromolecular species when added to water or any other solvent dissociates into highly charged polymeric molecule. Since these charges have a direct relation with the electric conductivity of the solution, the addition of a polyelectrolyte increases the charge density of the ejected jet, leading to an increase in the electric charges carried by the jet. It will be interesting to see the different modes of fibre formation (straight and whipping path) along with the profile of the Taylor cone when the concentration of the polyelectrolyte is varied during electrospinning.

Modeling of the electrospinning process will be helpful in understanding the factors that cannot be measured experimentally and so preclude in-depth understanding of the fibre formation modes. Also, the published literature in this field is scant (Reneker et al., 2000, Hohman et al., 2001), so new theoretical models need to be developed for understanding the mechanism of fibre formation modes. In view of this, modeling of the fibre formation mode was done by region growing algorithm and image analysis method of Matlab. Images from the each stage of fibre formation mode were taken into account and analyzed further. The electric force acting on the charged polymer jet is calculated by a localized approximation. A set of equations is used to calculate the jet path which takes into account the linear straight path and nonlinear path due to whipping resulting from electrostatic instability.

In view of the preceding discussion, polyethylene oxide (PEO) nanofibres were spun in the presence and absence of polyelectrolyte in the spinning solution. The concentration of the polyelectrolyte was varied during the experiment. Different fibre formation modes were captured by a high speed camera (Fujifilm model FinePix S7000). These images were analyzed further by image analysis techniques in order to see their influence in the formation of uniform and bead free nanofibres. The diameter and surface morphology of the nanofibres were determined by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Conductivity of the solutions was determined by a conductivity meter.

2. EXPERIMENTAL

PEO (molecular weight M_w = 3 x 10^5 g/mol), polyelectrolyte poly allylamine hydrochloride (PAH, M_w = 15 x 10^3 g/mol) was used for electrospinning. All chemicals and solvents were used without further purification, while all electrospinning experiments were carried out at room temperature. Based on our previous experience, 6 % (w/v) concentration of PEO solutions were prepared in HPLC grade water in absence and presence of PAH. In the present work 0.5 and 2 % of PAH by the weight of PEO were added to the aqueous solution of PEO. Unless otherwise stated from here onwards the expression of PAH concentration is in wt %. The electrospinning setup consisted of a Pasteur pipette (nozzle) with 1 mm diameter, an electrically grounded detachable flat metal screen that was adjustable to a desirable height and direction. A high voltage power supply was used to produce voltages ranging from 0-30kV. The distance between the nozzle and collector screen was maintained at 15 cm and the applied voltage of 13 kV was used during the electrospinning PEO nanofibres.

The structural morphology and diameter of the nanofibres were determined by SEM Cambridge/Leica Stereoscan 440 with a Tungsten filament after gold coating. Surface morphology of the nanofibres was measured by AFM Veeco dimension V. Conductivity of polymer solutions were determined by HACH Conductivity meter. Image analysis of the jet path and modeling was performed using Matlab.

3. RESULTS AND DISCUSSION

3.1 Influence of Variation in PAH Concentration

The influence of variation in PAH concentration on conductivity, jet path length and nanofibre diameters is indicated in Table 1. With the addition and increase in concentration of PAH, the conductivity of the spinning solution increases due to increase in the charge density of the solution. As a consequence of it, there is an increase in amount of electric charge carried by the jet and there is a continuous flow of charged solution towards the nozzle tip. This continuous flow of the charged solution towards the nozzle tip increases the shape and size of the Taylor cone. The Taylor cone for 2% concentration of PAH becomes larger in length and width in comparison to the 0% (without PAH) and 1% of PAH. The length (*l*) and width (*w*) of the Taylor cone obtained from image analysis are as follows: 0% - 0.5 mm, 0.5 mm; 1%- 1 mm, 1.5 mm, and 2%- 2 mm, 3 mm. A schematic representation of different profiles of the Taylor cone along with the straight path of the jet is shown in Figure 1.

Table 1 Influence of variation in PAH concentration on conductivity, jet path length, and nanofibre diameters

PAH concentration (wt%)	Conductivity (mS/cm)	Jet path length (cm)		Average fibre diameter (nm)
		Straight path	Whipping path	
0 (without PAH)	0.17^{-2}	1	14	220 (53)*
0.5	0.40^{-2}	2.4	12.6	180 (39)
2	0.95^{-2}	5	10	107 (21)

*Values in the parenthesis indicate the CV% in the measurement of nanofibres diameter.

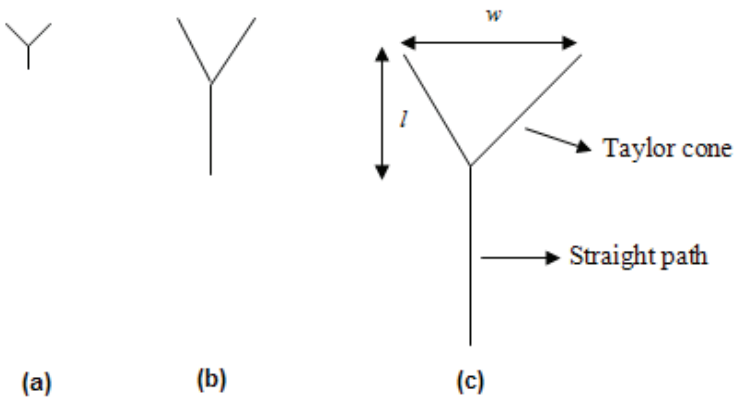

Figure 1 Schematic representation of different profile of the Taylor cone along with straight path for different concentration of PAH: (a) 0%, (b) 0.5%, and (c) 2%

Once electrostatic and Coulumbic forces overcome the surface tension of the liquid, the charged jet start flowing towards the grounded collector in a straight path followed by a whipping or bending path. Photographs of the jet path obtained from a high speed camera with exposure time of 25 ms for different concentration of PAH are shown in Figure 2. From this image we can only see the initial straight jet path of the nanofibres spun with 0 and 0.5 % of PAH. For nanofibres spun with 2% PAH, we can see the straight as well as the whipping path. These images are analyzed further by image analysis in order to have clear understanding of the role of different jet path length in the fibre formation. The images of the jet paths obtained from image analysis are shown in Figure 3. These images indicate that in all the cases, the path of the jet is a straight path followed by a whipping path, with varying lengths of both the paths influenced by the concentration of electrolyte used.

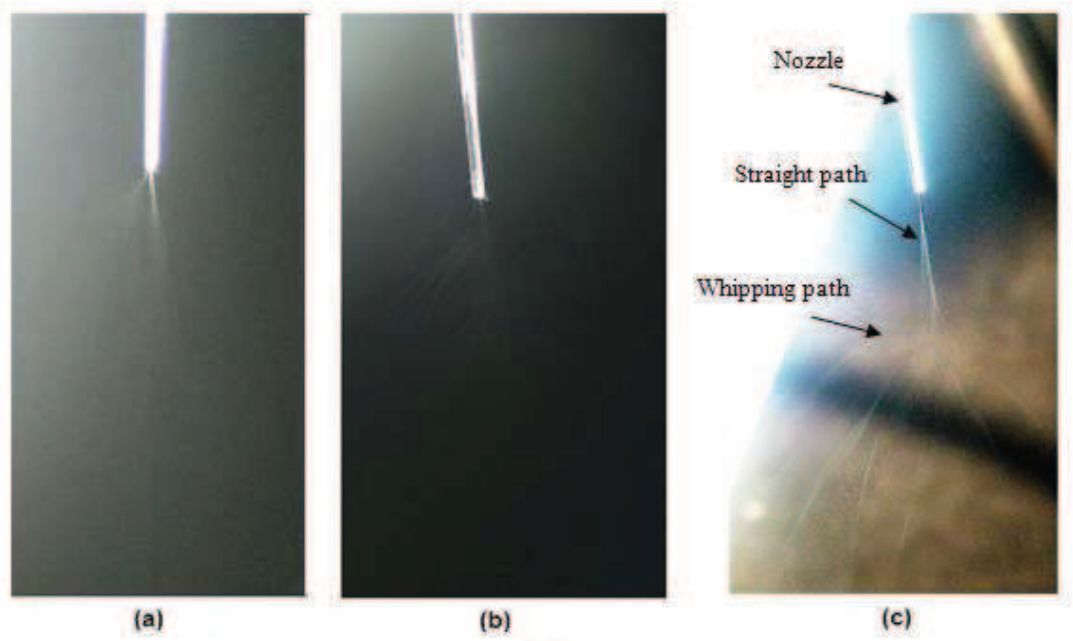

Figure 2 Photographs of the jet path obtained from a high speed camera with exposure time of 25 ms for different concentration of PAH: (a) 0%, (b) 0.5%, and (c) 2%

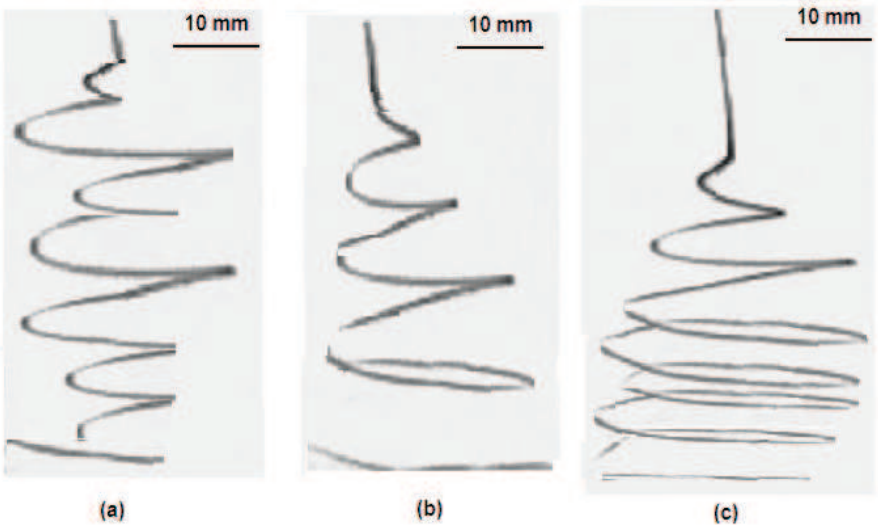

Figure 3 Images of the jet path obtained from image analysis for different concentration of PAH: (a) 0%, (b) 0.5%, and (c) 2%

Different values of jet path length obtained from image analysis are shown in Table 1. It can be observed that (Table 1 and Figure 3) with the increase in PAH concentration in the spinning solution, the length of the straight path increases with the corresponding decrease in the whipping path length. This can be attributed to the increase in charge density carried by a jet with the addition of PAH, which maintains the path of the jet beyond the Taylor cone zone. This provides some kind of additional stability to the jet path and keeps the path straight for the initial part. This jet stability is also influenced by the electric field force. This additional stability to the jet path controls its further stretching and thinning behavior which in turn influences formation of bead free and uniform nanofibres. It can be seen form Figure 3a, the path of the jet without adding PAH (0%) is dominant by non-uniform whipping path with a very small straight path length. Since the initial straight path is small (1 cm), there is no control or stabilizing effect over the fibre movement, so it follows a non-inform path with irregular stretching and thinning of the jet, resulting in the formation of nanofibres with round beads. The diameter of the nanofibres obtained from such path is indicated in Table 1 and SEM image is shown in Figure 4a. With the addition of 0.5% PAH to the spinning solution, there is an increase in straight path length and there is also increase in stabilizing effect over the initial jet path followed by the irregular whipping path (Figure 3b). This increase in stabilizing effect is not good enough to control the whipping path. As a result, still there is irregular stretching and thinning of the jet and the formation of nanofibres with spindle shaped beads (Figure 4b). The shape of the bead change from round to spindle shape with the addition of PAH is due to increased stretching resulting from the increase in charge density of the jet. With the further increase in PAH concentration (2%), there is a marked increase in straight path length and corresponding decrease in whipping path length (Figure 3c). This increase in straight path length improves the stabilizing effect over the jet path and the whipping becomes more precise and follows a regular helical path without much perturbation as evident in Figure 3c. There is an increase in the repulsive Coulombic force between the neighboring charged particles as the distance among them decreases and stretching and thinning of the charged jet become more regular. This resulted in the formation of bead free and even diameter nanofibres (Figure 4c). AFM image of the nanofibres spun with 2% of PAH also confirms the formation of the smooth surface nanofibres (Figure 4d). So the length

of the straight jet path during the fibre formation mode plays a major role in the formation of uniform fibres in comparison to the whipping path. Nanofibres spun in presence of PAH with higher concentration give rise to uniform fibres with longer straight jet path in comparison to the one spun without PAH.

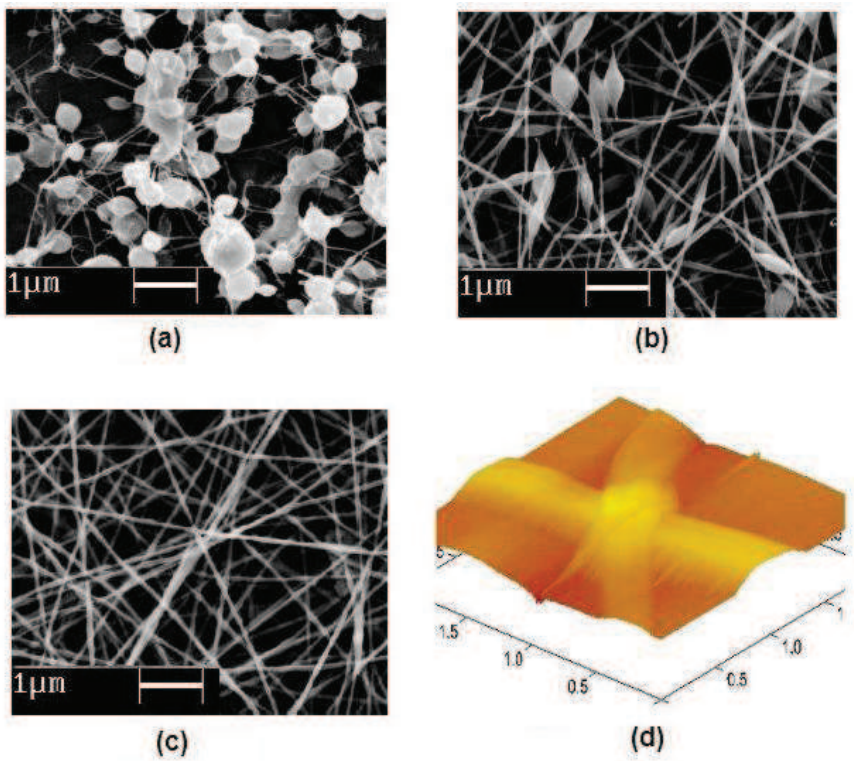

Figure 4 SEM images of the influence of variation in PAH concentration on formation of PEO nanofibres: (a) 0%, (b) 0.5%, (c) 2%, and (d) AFM image of nanofibres spun with 2% PAH

3.2 Modeling of the Electrospinning Process

The polymer solution used in the electrospinning process is a charged liquid. The following governing equations were used for modeling the charged liquid (Ramakrishna et al., 2005):

Conservation of mass, $\frac{\partial R^2}{\partial t} + \frac{\partial v R^2}{\partial z} = 0$

Conservation of momentum, $\frac{\partial v}{\partial t} + \frac{v \partial v}{\partial z} = -\frac{1}{\rho R^2}\frac{\partial p R^2}{\partial z}$

Conservation of charge, $I = \pi R^2 KE + 2\pi R v \sigma$

where, R; jet radius, t; time, v; jet velocity, z; downward vertical distance form the pendant droplet (straight path), ρ; liquid density, p; liquid pressure, I; total current in the jet, K; liquid conductivity, E; electric field, σ; surface charge density.

The following force balance equations based on Newton's Second Law was used for modeling the path of the charged liquid:

$\sum f = f_c + f_E + f_v + f_s$

where, f_c (Coulumbic force) = $\frac{e^2}{l^2}$, f_E (electric field or electrostatic force) = $-\frac{eV_0}{h}$, f_v (viscoelastic force) = $\left(\frac{\partial \sigma_v}{\partial t} = \frac{G}{l}\frac{\partial l}{\partial t} - \frac{G}{\mu}\sigma_v\right)$, f_s (surface tension) = $\alpha \pi R^2 k$

where e; charge, l; length of the straight path, V_0; applied voltage, h; distance between pendant drop and collector screen, σ_v; viscoelastic stress, G; elastic modulus, μ; viscosity, α; surface tension coefficient, k; jet curvature.

The forces which help jet initiation (electric field force and Coulumbic force) overcome the opposing forces (surface tension and viscoelastic force), the liquid droplet accelerates towards the grounded collector following initial straight path and the whipping path. The straight path of the jet is due to the influence of longitudinal stress caused by electrostatic force. After some distance from the straight path, the liquid jet undergoes stress relaxation and start following a whipping or looping path. At this point the repulsion between the charged elements begins to dominate the viscoelastic force of the liquid jet and initiating the perturbations and chaotic motion of the jet. This motion helps in further stretching and thinning of the liquid jet in resulting nanofibres. This whipping path can be described in following manner (Reneker et al., 2000).

If three point charges of equal magnitude are in a line, the centre charge B will be influenced by two forces of equal magnitude and in opposite direction and given by (Figure 5):

$F = kq_a q_b / r^2 = kq_c q_b / r^2$

where q_a, q_b, and q_c are charges of equal sign and magnitude, r is the distance between the charges and k is Coulombs constant. Due to this repulsion, q_b, will be moved out of the line to a position B' and the net force acting on it is given by:

$F_1 = 2F\cos\theta$

where θ is the angle between r and line perpendicular to jet axis. This force will lead to an inherent instability in the jet and causing whipping path of the jet.

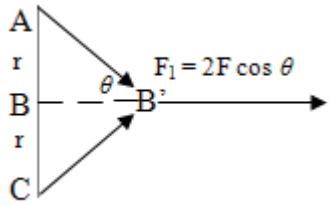

Figure 5 Forces on a charge element by the neighboring charges

The jet path model of nanofibres spun with 2% PAH is shown in Figure 6. Other modeled paths are not shown here as they also follow the similar profile of the images obtained from the image analysis. Exact prediction of the jet path would be difficult due to the factors like solvent evaporation and role of gravity which is not taken into account in present theoretical work. Nevertheless this path is quite similar to the one

obtained from the image analysis which is a good indication of a typical stability of the jet path at a higher concentration of PAH.

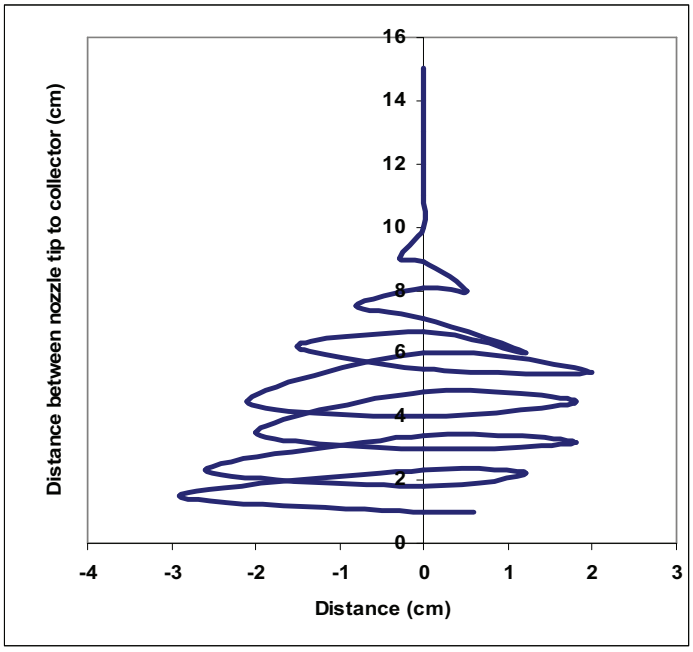

Figure 6 Modeled jet path of PEO nanofibres spun with 2% of PAH

4. CONCLUSIONS

Polyethylene oxide nanofibres were spun in the presence and absence of PAH in the spinning solution. Two different paths of fibre formation modes, namely straight and whipping jet paths are observed and analyzed further for their influence on the formation of uniform and bead free nanofibres. The length of the straight jet path during the fibre formation mode plays a major role in the formation of uniform and bead free fibres in comparison to the whipping path. Polyethylene oxide nanofibres spun in presence of PAH with higher concentration give rise to uniform fibres with longer straight jet path in comparison to the one spun without PAH. A theoretical modeling of the electrospinning process was developed by taking into account the different fibre formation modes and forces acting on the charged polymer solution. The modeled behavior appears realistic and consistent with the experimental observation. Further work in this field is in progress which will be reported in due course.

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