

Concept of Minimum Electrospinning Voltage in Electrospinning of Polyacrylonitrile *N,N*-Dimethylformamide System

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ABSTRACT: Polyacrylonitrile solutions in *N,N*-dimethylformamide (DMF) were electrospun into nanofibers by charging the polymer fluid in an electric field. Controlled experiments were performed using a needle type spinneret to investigate the effect of various electrospinning parameters on the percentage conversion of polymeric fluid into fibers and on fiber diameter obtained. It was found that when the polymeric fluid was continuously fed at a constant rate, application of a minimum electrospinning voltage (MEV) was necessary to “completely” convert the ejected fluid into nanojets to form nanofibers. Also, that the maximum amount of splitting or elongation that a polymeric fluid could undergo was primarily dependent on number of entanglements per chain in the fluid. This resulted in obtaining nanofibers with a particular diameter

irrespective of the values of important electrospinning variables such as applied voltage, flow rates, and distance between the electrodes. On the other hand, MEV, necessary to obtain full conversion into nanofibers, was found to be strongly dependent on the spinning parameters and was unique for a given set of parameters. The significance of the MEV was evident from the fact that the square of the MEV, which is a measure of the electrical energy utilized by the system, was found to be directly proportional to the rate of formation of fiber surface area during the electrospinning process. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 856–866, 2011

Key words: minimum electrospinning voltage; rate of surface formation; electrospinning efficiency

INTRODUCTION

Electrospinning is a process of fiber formation with the aid of electrostatic forces on a polymeric fluid. It is normally carried out in a set-up where the polymeric fluid, mostly in the form of a polymer solution, is slowly pumped out of a needle type spinneret. When the polymer solution is pushed, it accumulates at the exit of the needle. The needle is charged by conduction using a high-voltage source. A grounded or oppositely charged counter electrode, called the collector is placed at a distance from the needle. The charged polymeric fluid experiences force to move along the electrostatic field. The electrostatic force acting on the droplet, forces one or more Taylor cones from the droplet, which discharges the polymeric fluid from the droplet. The acceleration of the charged polymeric fluid in the direction of the electric field elongates and splits the fluid. As the spinning jets move toward the collector they solidify and deposit as a web of fine nanofibers. The process of electrospinning, being a

simple process, has emerged as a preferred technique for making nanofibers for various upcoming applications, in the field of filtration, biomaterial, catalysis, superabsorbent materials etc.¹

The process of electrospinning is dependent on solution property of the dope, the process variables, and the ambient parameters. The effect of direct and derived parameters that affects electrospinning have been widely studied and reported.^{2–9} There seems to be a general agreement that increase in polymer solution concentration increases fiber diameter. However, there exist a number of inconsistencies in the reported results. Wang et al.³ and Du⁴ reported that the fiber diameter increases with flow rate while others notably Ramakrishna² reported that there is no effect of flow rate on fiber diameter; still Heikkilä⁵ reported decrease of fiber diameter with increase in spinning pressure signifying increased flow rates. Similarly, although several authors showed that there is no effect of applied voltage^{2,6} or electric field³ on nanofiber diameter, others showed that diameter varies with the voltage,⁵ either increases^{4,7} or decreases^{8,9} The viscosity of the polymer solution has been correlated with the nanofiber diameter.¹⁰ The multifaceted effect of the material, machine, and operating parameters on the properties of the nanowebs of nanofibers has been modeled to predict the nanofiber properties.¹¹

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The electric current has been considered as a resulting variable in the electrospinning process.¹² The electric current is the amount of charge carried by the polymer solution is thus dependent on flow rate of the solution. Fallahi et al.¹³ reported that a steady state where the flow rate of the polymer is exactly balanced with the voltage applied could be determined from the current measurement. However, in these studies, the actual measured current was found to fluctuate with time and only the average values of current could be considered. Hence, the jet current could not be utilized to obtain any relations with properties of spun web in the electrospinning.

Wang et al.¹⁰ reported that the fiber diameter increases linearly with viscosity of the solution. The role of chain entanglement on fiber formation has been investigated.¹⁴ Prediction for fiber formation versus the defect generation (like bead formation) has been examined with reference to the number of entanglements per chain. For moderately concentrated solution in a good solvent where there is presence of overlapping of macromolecular chains, the entanglement number in solution $(n_e)_{\text{soln}}$, which is defined as the ratio of polymer molecular weight (M_w) to its solution entanglement molecular weight (M_e), is related to the polymer volume fraction (Φ_p) has been used to relate to the defect formation:

$$(n_e)_{\text{soln}} = (\Phi_p \times M_w) / M_e \quad (1)$$

As one entanglement necessarily involve two chains

$$\begin{aligned} &\text{The number of entanglements per chain} \\ &= (n_e)_{\text{soln}} - 1 \end{aligned} \quad (2)$$

The minimum entanglements per chain required for defect free fiber formation is reported to be 2.5.¹⁴

The process of electrospinning, being dependent on a large number of interrelated parameters, is difficult to study by varying one parameter while maintaining all the others as constant. Moreover, there is a general lack of agreement on standard parameters like temperature, humidity, needle to collector distance and electrospinning voltage. Many researchers preferred electric field over voltage as a parameter which had been calculated by dividing the applied voltage with the distance of separation between needle and collector. However, the electric field strength is vastly nonuniform for the needle-plate geometry and should not be simplified to parallel plate capacitor system. The field strength at the needle tip is highest and can be calculated to be varying within the electrospinning zone. However, the voltage applied on the electrodes is fixed according to the power supplied from the high-voltage

source. Therefore, in this study, voltage has been considered as a parameter and not the electric field. All experiments were conducted by charging the needle either directly by conduction or indirectly by induction. Electrospinning may be considered as a process to convert electrical energy into mechanical work done on the polymer dope. However, there has not been any insight in the literature about how to determine the efficiency of the electrospinning process. This work has been undertaken with a view to systematically perform a parameter study, to understand the effect of charging by conduction and induction, and to investigate the factors that controls the diameter of the nanofibers.

EXPERIMENTAL

Materials

Fiber grade commercial acrylic terpolymer, with M_w of 75,000, procured from Pasupati Acrylon, India was used for the experiments. The terpolymer had about 8% methyl acrylate and 1% 2-acrylamido 2-propane sulfonate as comonomers in addition to acrylonitrile. Laboratory grade reagent N,N -dimethylformamide (DMF) was used as a solvent.

Electrospinning

The terpolymer was dissolved in DMF to obtain homogeneous spinning dope of concentrations in the range of 6–14% (w/w). The electrospinning was carried out using an infusion syringe pump KDS 100 from KD Scientific with a flat tip needle (internal diameter = 0.6 mm) as the spinning head and 40 kV dual polarity high-voltage power supply, Model: DES40PN from Gamma HV. The syringe pump was used to control the flow rate, whereas the high-voltage supply was used to charge the needle and the collector, as needed. A 30-cm diameter circular steel plate of 1 mm thickness was used as collector, which was connected to the high-voltage supply. The dope was pushed out of the syringe at a fixed rate in the range from 0.1 mL/h to 5 mL/h for different experiments. The schematic experimental set-up is shown in Figure 1(a). The polymer droplet was charged by conduction by connecting the needle with the high-voltage supply. It was also charged by induction by connecting the collector with the high voltage of opposite polarity. In the experiments, polymer dope droplet was thus charged by a combination of conductive and inductive charging.

The distance from the tip of the needle to the collector was varied from 5 cm to 30 cm. The temperature and relative humidity was maintained at 25°C, 50% RH for all experiments.

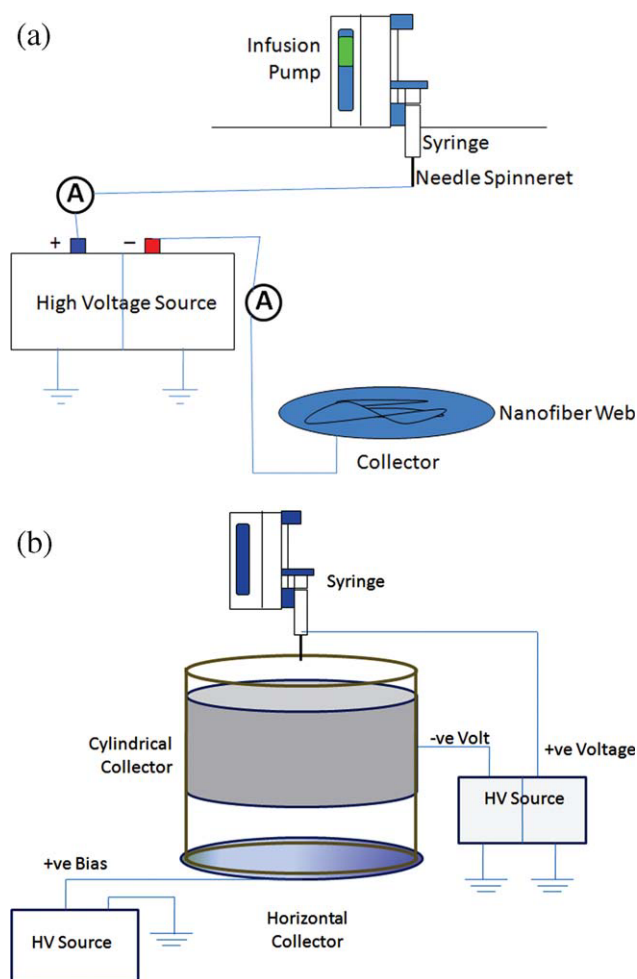


Figure 1 (a) Experimental set-up of electrospinning. (b) Experimental set-up for characterization of electrospinning voltage [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

Estimation of minimum electrospinning voltage

To study the effect of voltage necessary for electrospinning, a set-up as shown in Figure 1(b) was designed. The polymer was charged by conduction by connecting the needle to a positive high-voltage source. It was varied in the range from 0 to 40 kV. The nanofibers were collected by the cylindrical collector placed around the needle at a distance of 14 cm referred to as the wall. The collector was connected with a constant negative voltage source and maintained at 6 kV. The polymer solution droplets, which were not converted into nanofibers, were allowed to fall on the aluminum foil placed vertically beneath the needle, connected to another high-voltage source maintained at a positive bias voltage of 0.4 kV. The nanofibers and the droplets were separately dried in vacuum oven at 150°C for 2 h at a vacuum of 50 Torr and weighed to estimate the percent conversion of extruded polymer solution into nanofibers.

Measurement of electrospinning current

The current was measured by placing two ammeters, one in series with the needle and another with the collector. This is shown in Figure 1(a). The ammeter would provide an estimate of average current flowing through the circuit. Measurements were made with and without polymer solutions flowing through the needle with varying distance in the range of 10 cm to 30 cm.

Fiber characterization

The diameter of the nanofibers was measured using nanowebs samples collected for two minutes under fixed experimental conditions. The nanowebs were dried under vacuum for 2 h and coated with silver before taken for observation under scanning electron microscopy (SEM), Model: Steroscan 360 from Cambridge Instruments UK. The SEM micrographs were then analyzed for diameter using software Image J from Research Service Branch, National Institute of Health, USA. Fifty fibers were randomly chosen from each quadrant of the SEM image and their diameters were determined. The mean and standard deviation of the 200 readings were calculated for each sample.

Estimation of rate of surface area formation

The surface area of undried fibers formed per unit time was derived from the measured mean diameter of the dried nanofibers from the SEM images. The surface area of the undried fibers was calculated using the following assumptions:

- The fiber cross section was considered circular.
- The extruded dope could split or elongate to the maximum extent before drying.
- The volume contraction of the electrospun fibers during drying of nanojets due to solvent evaporation was considered isotropic (i.e., proportional along the diameter and length of the fiber).

The surface of the undried fibers created per second (S), can be expressed similar to a relation reported for microfiber spinning¹⁵

$$S = (c^{1/3} \times 10f)/9.d \quad (3)$$

where f is the feed rate of the polymer solution in ml/h, c is the polymer concentration; d is the mean fiber diameter in nm after drying. The initial surface area of the extruded polymer dope, being a very small value compared with the final surface of nanojets, was neglected.

RESULTS AND DISCUSSION

Effect of needle voltage on behavior of spinning

During electrospinning a variety of situations are encountered on the collector: (a) Drips and droplets of polymer, (b) combination of nanofibers and droplets, (c) all fibers. These change with changing spinning parameters. To investigate the effect of applied needle voltage (NV) on behavior of electrospinning, a special spinning set-up was designed as shown in Figure 1(b). The droplets were separated from the electrospun fibers as discussed in "Estimation of minimum electrospinning voltage" section. As the mass to charge ratio of the electrospun fibers was low, they were attracted to the oppositely charged cylindrical collector, whereas the polymer droplets having higher mass to charge ratio, which could not be attracted by the cylindrical collector, were instead collected below on the horizontal collector due to the gravitational pull. To prevent the nanofibers from being deposited on the horizontal electrode, it was connected to a slightly positive voltage (the same as that of the needle). This resulted in a complete separation of the nanofibers from the droplets.

From the dried mass of nanofiber collected from the cylindrical electrode and that of droplets collected from the horizontal electrode the percent conversion of the polymer into nanofibers, based on the total extruded polymer, from the needle, was calculated. The effect of increasing NV on the percentage conversion is shown in Figure 2 for four different PAN solution concentrations at a flow rate of 2 mL/h. As the NV was increased, the conversion percentage of the PAN dope into nanofibers increased steadily until it reached a maximum conversion value. The percent conversion of the 10 wt % and 12 wt % PAN solution into nanofibers steadily increased and reached complete conversion into nanofibers at a NV of 20 kV and 16 kV, respectively. This NV where the polymer solution was completely converted into nanofibers, was termed as the "minimum electrospinning voltage" (MEV). On further increase of the NV, the percent conversion did not change. For solutions containing less than 10 wt % PAN the conversion increased steadily and was observed to be stabilized at a maximum value but did not reach 100% conversion into nanofibers. In such cases, the voltage at which the maximum conversion was achieved was termed as MEV for the given system.

The SEM images of the nanofibers collected on the cylindrical walls are shown in Figure 3. From the SEM images, the nanofibers diameters were determined and are shown in Figure 4. From Figure 4, it can be seen that there is no significant change in fiber diameter with change in the NV (as can be seen from the standard deviation error bars). It was

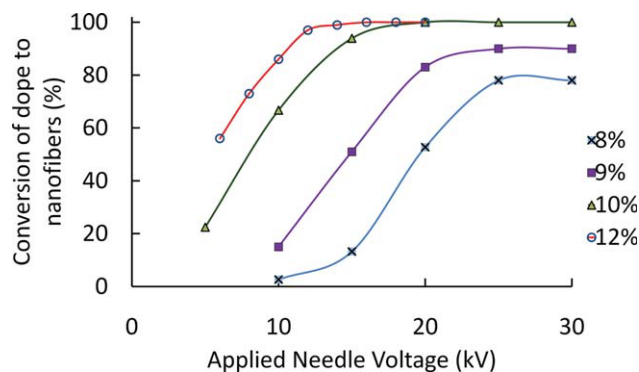


Figure 2 Effect of needle voltage on conversion of dope to nanofiber at a flow rate of 2 ml/h [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

interesting to note that when the voltage was below MEV, the part of the polymer which was converted into the nanofibers gave the same fixed diameter while the remaining unconverted polymer was collected as large droplets. This was the case for all four PAN solutions. These results were in contrast to our expectation that the entire polymer solution may get uniformly split/elongated to a lesser extent to give a higher diameter under application of a lower voltage than MEV. This implies that at spinning voltages below MEV, the charge generated due to the applied voltage is utilized in extending/splitting only a part of the extruded polymer solution, however, to the maximum extent. The remaining solution drips for the lack of available charge. It is only when MEV is applied that sufficient charge is generated to convert the entire polymer solution. From this result, it can be inferred that the NV is not the determining factor for the fiber diameter. Fiber diameter appears to be fixed for a given polymer dope possibly because of the entanglement density or elasticity of the polymer system. This has been discussed later in detail. The effect of increasing the voltage was only to increase the conversion of the extruded polymer dope into nanofibers.

To determine MEV in a normal set-up consisting of one needle and horizontal collector [as shown in Fig. 1(a)], the experiments were repeated keeping the same parameters. The NV was increased in steps and behavior of electrospinning at the needle was observed for short duration. When the voltages were low, the suspended droplet grew in size at the needle tip and dripped in chunks of polymer fluid along with electrospun fibers. This behavior was captured by high speed photography and is shown in Figure 5. As the voltage was increased, the dripping reduced and eventually stopped at a particular voltage. Interestingly, this voltage was found to be close to that observed as MEV in the earlier set-up

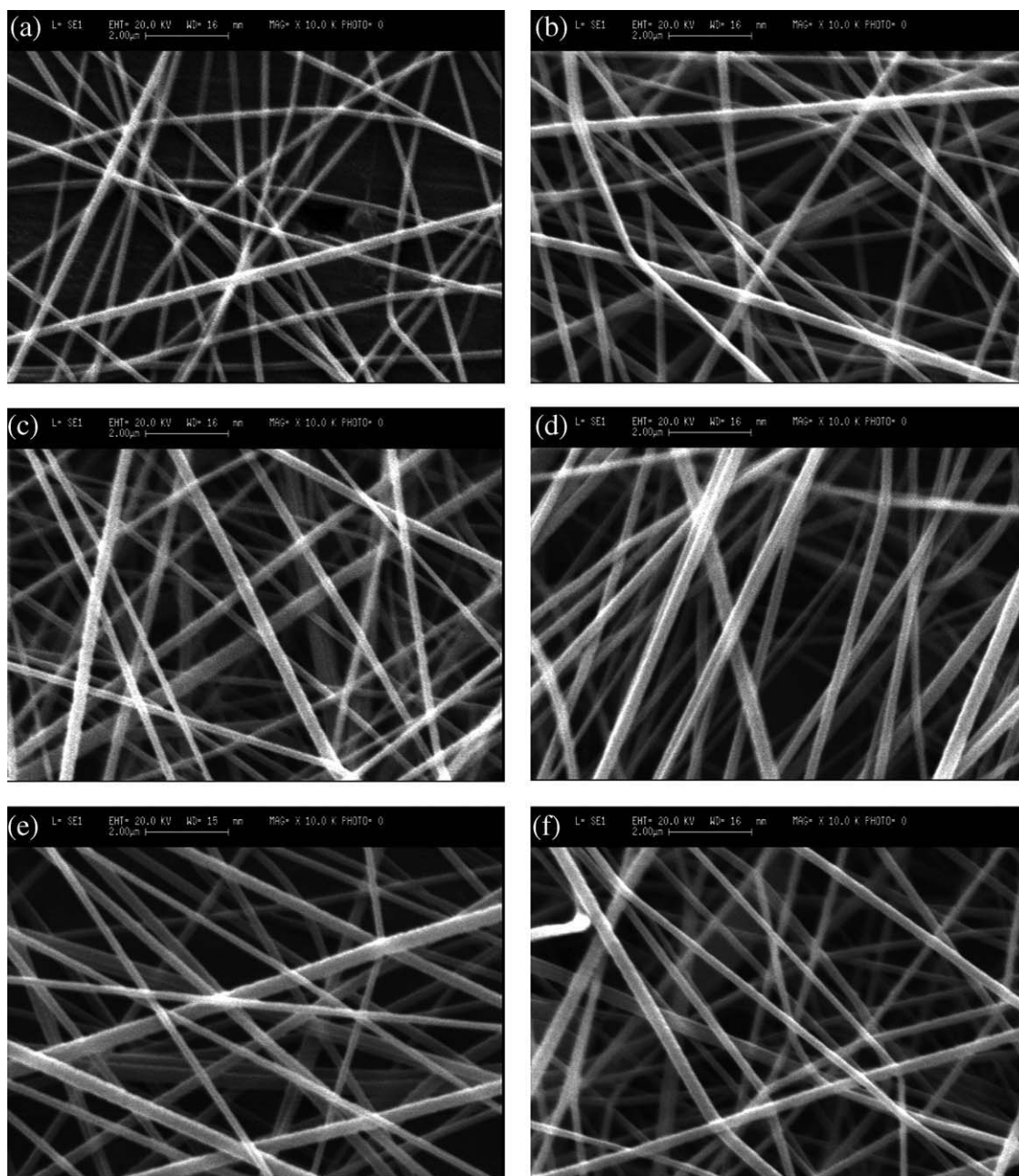


Figure 3 Micrographs of nanoweb obtained by electrospinning 12 wt % PAN in DMF at needle voltage of (a) 5kV, (b) 10 kV, (c) 15 kV, (d) 20 kV, (e) 25 kV, and (f) 30 kV.

described above. The droplet at this voltage could remain suspended at the needle tip for a long duration (i.e., for hours) while electrospinning continued. This situation corresponds to macroscopic view of the deposited nanofiber web on the collector that did not have any droplets. When the voltage was further increased (i.e., above MEV), the electrospinning process became discontinuous. Electrospinning took place whenever a small pool of polymer fluid accumulated at the needle tip and stopped when it got exhausted. The periodicity of the cycle depended on the value of the applied voltage. This behavior on spinning voltage was reproducible for polymer

concentration of 10 wt % and above and could be used to determine the MEV. However, for concentration below 10 wt %, dripping did not stop, therefore, NV corresponding to MEV could not be determined by visual observation. Since the MEV appeared to be an important parameter, subsequent experiments were conducted only for concentration higher than 10 wt % PAN solution using normal set-up shown in Figure 1(a) where MEV could be visually observed.

From the above experimental results, it is evident that for carrying out electrospinning, a MEV was necessary to completely split the polymer dope into

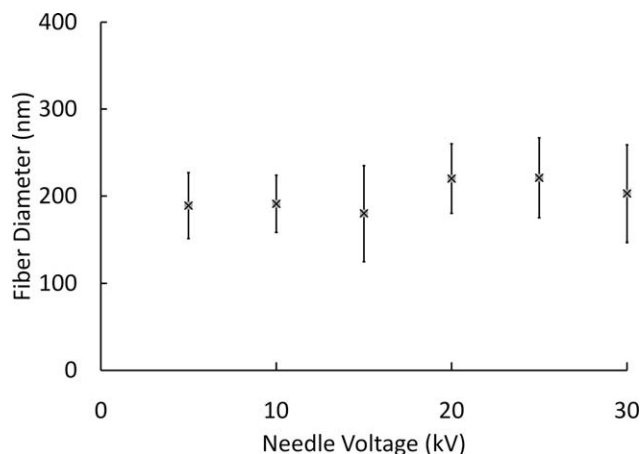


Figure 4 Effect of needle voltage on nanofiber diameter with 2 ml/h flow rate and 12% PAN concentration.

nanofibers. Electrospinning at higher voltage than MEV did not cause any defect formation or change in the nanofiber diameter. Hence this voltage may be considered as an important parameter in defining electrospinning of a dope.

Effect of collector voltage

The polymer droplet may be charged either by conduction, induction or combination thereof. The MEV could therefore be arrived by applying either the collector voltage (CV) or the NV or both. However, charging of polymer fluid by conduction is expected to be more efficient than the induction. To understand the relative contribution of the CV and the NV in maintaining MEV condition, voltage was varied for a given CV to arrive at the minimum voltage necessary for electrospinning with MEV condition. It was observed that by increasing the CV, the NV could be decreased suitably to maintain the MEV condition. There exists a strong correlation between the CV and NV to maintain MEV.

The relationship between NV and CV to maintain the MEV condition in spinning of PAN solutions at varying concentration and flow rates is shown in

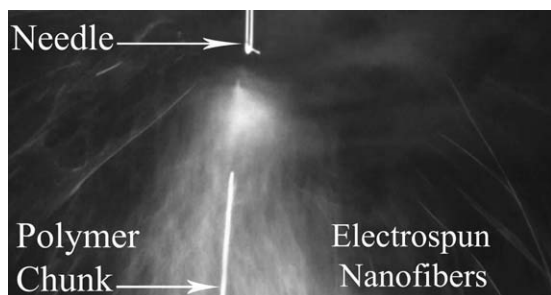


Figure 5 High speed photograph of electrospinning showing electrospinning along with excess polymer solution ejected from the needle.

Figure 6(a,b). At both concentration of 10 wt % and 14 wt % and flow rates from 0.1 mL/h to 5 mL/h, the required NV to maintain MEV condition decreases with increase in CV. The slope of the iso-gradient trendlines was found to be -0.4 for every series of experiments. From the slope of the trendlines in Figure 6(a,b), it can be inferred that the ratio of CV to NV is 2.5. This implies that CV should be kept at 2.5 times of the NV to generate the same force on the polymer solution as the NV. In other words, the effective contribution of CV is only 0.4 toward MEV. The ratio remains constant irrespective of the flow rates or concentrations of the polymer. For a distance of 20 cm, the relationship between NV and CV required to maintain MEV conditions of electrospinning can be expressed as:

$$\text{MEV} = \text{NV} + 0.4 \text{ CV} \quad (4)$$

However, this relationship changes when the needle to collector distance is changed. Hence, it can be considered as a geometric constant of the electrospinning set-up. The effect of needle to collector distance on the effective contribution of the CV toward MEV is being further investigated. The stronger

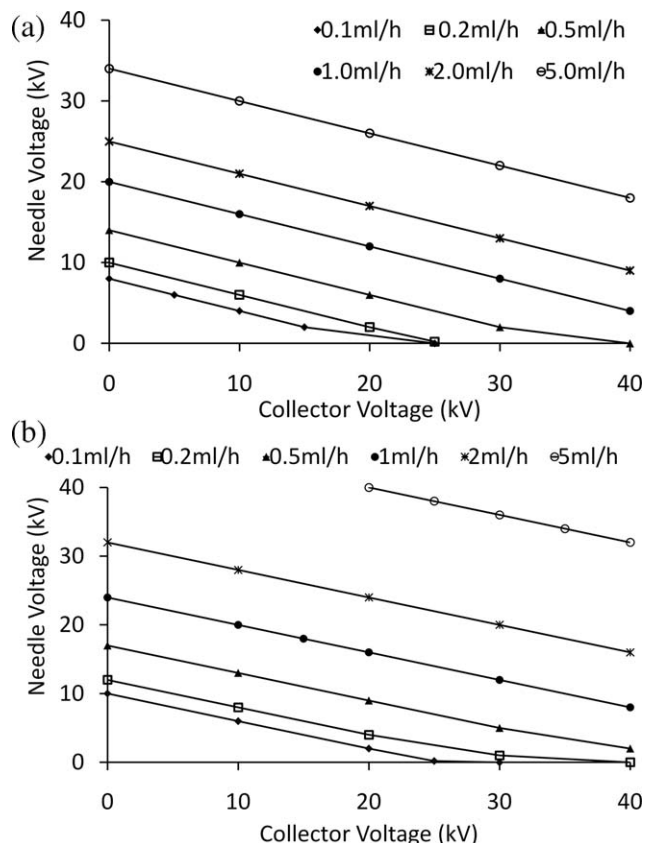


Figure 6 Dependence of needle and collector voltage at MEV for (a) 14% PAN concentration. (b) 10% PAN concentration.

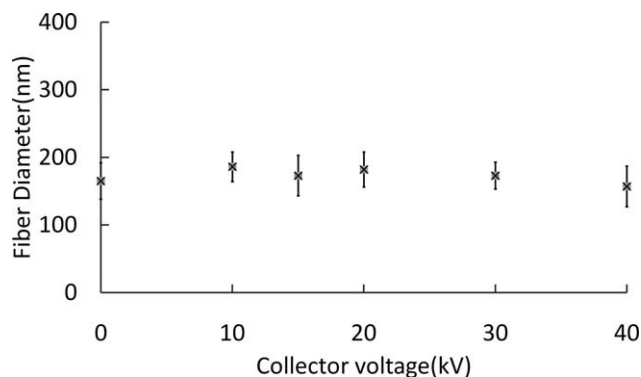


Figure 7 Effect of collector voltage on fiber diameter at MEV for 10% PAN concentration and 0.5 ml/h flow rate.

influence of NV on electrospinning has been indicated in the literature,¹⁶ where it was found that higher flow rate could be realized when the needle was charged and the collector was grounded compared with when the collector was charged and the needle grounded.

The effect of varying CV on diameter of the fibers was studied while maintaining the MEV condition as per eq. (4). The mean diameter of the nanofibers and its standard deviation is shown in Figure 7. From the results, it can be clearly seen that neither the fiber diameter nor the diameter variability (as seen from the standard error values plotted as error bar) changes significantly. Therefore, it may be inferred that nanofibers electrospun satisfying the MEV condition have the same diameter irrespective of the fact that the spinning polymer solution is charged by conduction or induction. However, charging the dope partly by induction has been found to control the spread of nanofibers on the collector plate without altering fiber diameter, which can have significant practical implication in controlling the morphology (pore size distribution) of the nanoweb for application such as filtration.

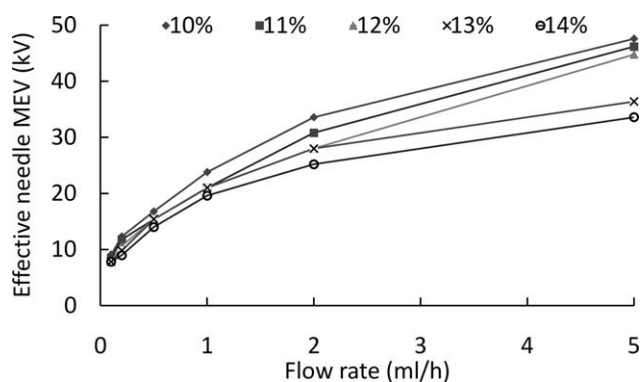


Figure 8 Effect of flow rate on MEV.

Effect of flow rate

The effect of flow rate of polymer solution on fiber diameter was studied over a wide range from 0.1 to 5 mL/h while maintaining the MEV condition. The effect of increasing flow rate on MEV is shown in Figure 8. The MEV was calculated from the needle and CV as per eq. (4). It was observed that with increase in flow rate of the polymer solution, the MEV increased sharply. The increase in MEV with increase in flow rate can be explained by the fact that higher amount of charge/unit time would be required to extend higher amount of polymer solution. As expected, it can be seen from Figure 9(a–c) that when the polymer is electrospun under MEV condition, there is no significant change of nanofiber diameter even with increase in flow rate from 0.1 to 5 mL/h. The result is reproducible at concentrations

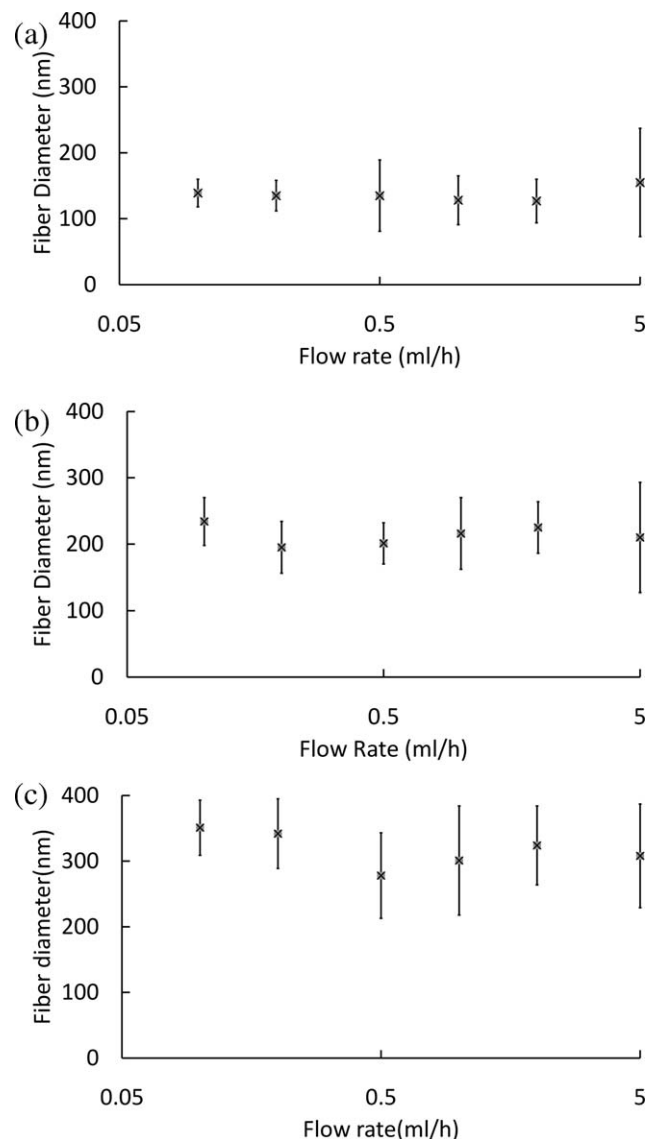


Figure 9 Effect of flow rate on fiber diameter for (a) 10%, (b) 12%, (c) 14% PAN concentrations.

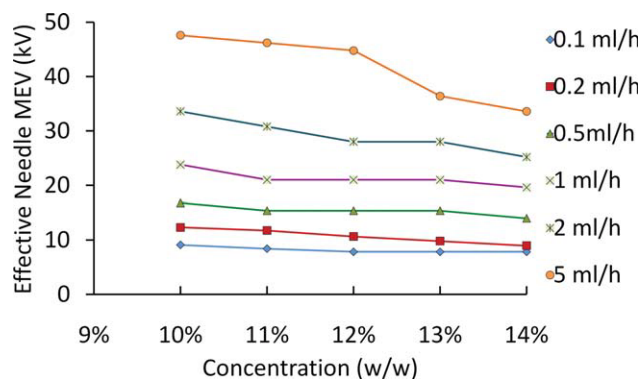


Figure 10 Effect of polymer dope concentration on MEV at different flow rates [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

in the range of 10–14 wt % of PAN solution being injected into the spinning zone.

Effect of polymer concentration

The effect of polymer solution concentration on the MEV and diameter was studied for the polymer concentrations from 10 wt % to 14 wt % and is shown in Figures 10 and 11, respectively. The experiments were also performed at different flow rates. The MEV was found to decrease while diameter increased with increase in polymer concentration. From the figures, it can be seen that for a flow rate of 1 mL/h, the diameter of nanofibers increased from 129 to 296 nm, while the MEV decreased from 23.8 to 19.6 KV on increasing the concentration from 10 to 14%. The behavior was reproducible at all flow rates from 0.1 to 5 mL/h. The decrease in MEV with increase in concentration can be ascribed to the fact that lower amount of charge is required to split the polymer fluid jet to a higher diameter (i.e., smaller surface area). Although the increase in diameter with an increase in polymer concentration is likely

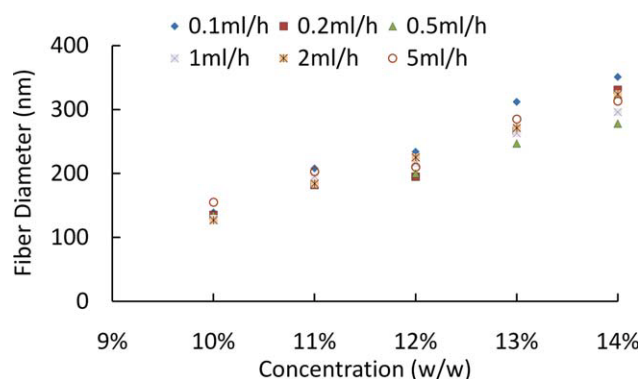


Figure 11 Effect of varying PAN dope concentration on fiber diameter at varying flow rates [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

due to an increase in entanglement density, which possibly prevented the dope from getting further split or drawn into finer nanofibers. Therefore, lower charge, generated at lower voltage, was sufficient to completely convert the polymer solution of higher concentration into nanofibers of higher diameter.

From the above discussion, it is clear that the electrospinning process parameters such as voltage and polymer flow rate do not affect the final nanofiber diameter. The surface tension of DMF at different PAN concentrations has been reported and is found to vary in a narrow range.¹⁷ Therefore, the effect of surface tension in determining the fiber diameter is unlikely to be significant. Elasticity of the polymer solution, which is a function of entanglement density of the polymer chains, could be one of the important factors that may determine the drawability/splitability of the polymer dope into nanofibers. Therefore, dependence of diameter on the entanglement density was investigated. The entanglement number was calculated using eq. (1) for all the PAN solutions from 8 to 14 wt %, taking M_e , the entanglement average molecular weight as 3120 from the literature.¹⁸ The number of entanglements per chain was plotted against the nanofiber diameter and is shown in Figure 12. From the graph, it is interesting to observe that the nanofiber diameter was linearly dependent on the number of chain entanglements per chain. From the results, it appears that polymer solution with higher entanglement density is unable to draw to finer diameters due to locking of polymer chains in an elastic network.

For 8 wt % and 9 wt % PAN solution in DMF, the number of entanglements per chain was found to be 1.2 and 1.4, respectively. As the weight average molecular weight of the polymer was considered for calculating the average entanglements, the lower molecular weight fraction of the polymer is unlikely to have any entanglements at these polymer concentrations. This fraction would result in formation of

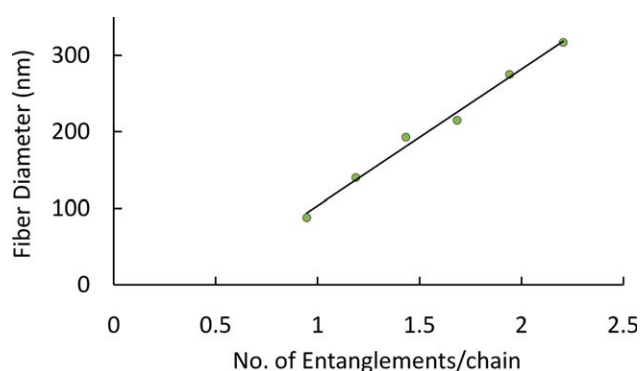


Figure 12 Plot of diameter of nanofibers against number of entanglements per chain ($R^2 = 0.991$) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

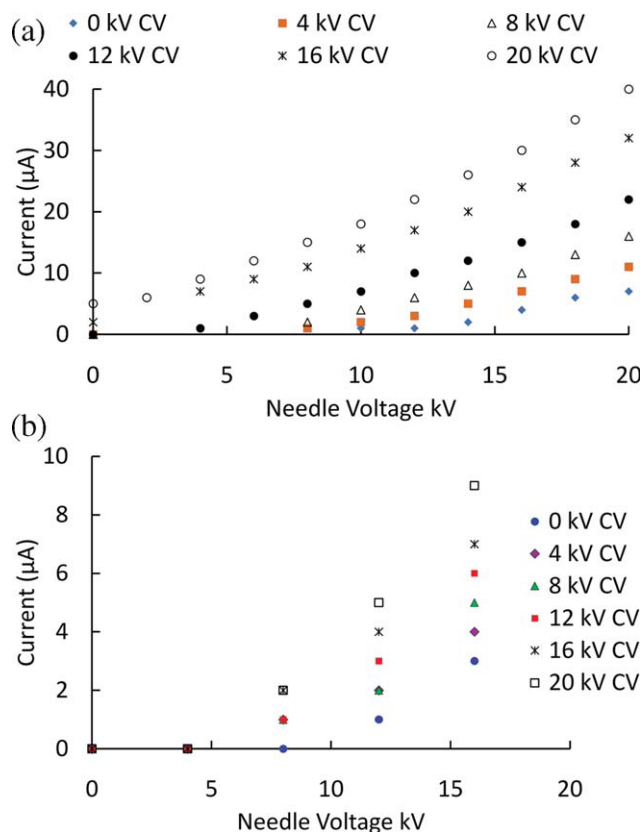


Figure 13 Plot of leakage current against needle voltage at needle to collector distance of (a) 11cm and (b) 21 cm at different collector voltage [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

droplets in spite of spinning the solutions above their respective MEV. This is clearly depicted in Figure 2, where 8 wt % and 9 wt % polymer solutions could not be completely converted to nanofibers and gave a maximum of 78 and 85% conversion, respectively. Therefore, the formation of droplets, the unconverted fraction of polymer, would depend on the lower molecular weight fraction of the polymer chains that are not entangled with each other. At higher polymer concentration of 10–14 wt %, average entanglement density ranges from 1.5 to ~ 2.5 , which appears to be high enough to allow full conversion of polymer solution to nanofibers.

Thus, the average molecular weight, its distribution and polymer concentration in solution assumes significant importance in the formation of defects/droplets in electrospinning of polymer solutions.

In a spinning system, the entanglement density is likely to change with the path of spinning due to the evaporation of the solvent. Therefore, in our opinion, the final diameter of the electrospun nanofibers should depend on the final value of entanglement density in the spinning path. In our case, the linear dependence of diameter on entanglement density of

the initial polymer solutions is likely due to the fact that evaporation of DMF is expected to be low compared with the rates of extension during electrospinning process. The variation in rate of evaporation of solvents during electrospinning may be responsible for the different observations reported in the literature. In studies, where the rate of solvent evaporation is significantly high, the diameter of the nanofiber would appear to vary with other process parameters at a given polymer concentration.

Correlation of surface formation rate with MEV

The current flowing through the electrospinning circuit, when electrospinning was not taking place, was measured using ammeters for different NVs. Figures 13(a,b) show the leakage (discharge) current measured at needle to collector distances of 11 cm and 21 cm, respectively.

The discharge current was found to increase with increase in NV for both the distances. The discharge current also increased with decrease in needle to collector distance. In other set of experiments, it was found that this discharge current was also a strong function of relative humidity of the surrounding environment. When the electrospinning was started with PAN solution in DMF using the above system, the change in current readings was insignificant, and dropped as concentration of DMF vapors increased with electrospinning time. From this, it was inferred that the large change in leakage current (in μA) observed in the given circuit compared with much small current (in nA) expected due to electrospinning makes the estimation of later extremely difficult.

The surface formation rates for different flow rates in the range of 0.1–5 mL/h and for different concentrations in the range of 10 wt % to 14 wt % were calculated from the mean diameter and the feed rates as discussed in the Experimental section. Figure 14 shows the plot of surface formation rate against

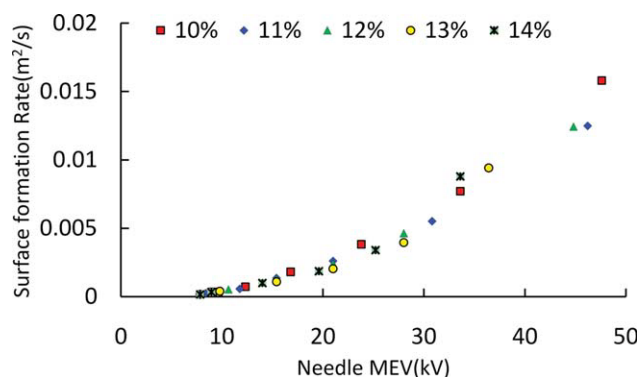


Figure 14 Plot of surface formation rate against MEV at different flow rates and concentrations [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

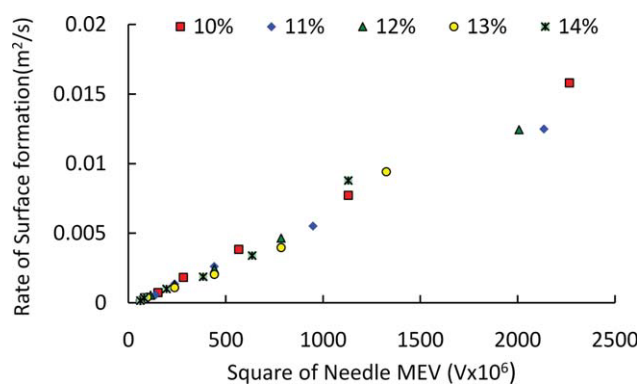


Figure 15 Plot of surface formation rate against square of MEV at different flow rates and concentrations [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

MEV. Interestingly, there is a strong correlation between the two parameters.

During electrospinning a polymer droplet is stretched into a fiber having high surface area using electrical force in the process. The electrical force (F_E) overcomes the total cohesive forces (F_T) in the form of surface tension (F_{ST}) and rheological force (F_R) during this process.

$$F_T = F_{ST} + F_R \quad (5)$$

The mechanical power P_M required to create this surface would then be given by¹⁹

$$P_M = F_T \times S \quad (6)$$

where S is the rate of surface area formation

This may be related to electrical power (P_E) spent in the process

$$P_M = \eta \times P_E \quad (7)$$

where η is efficiency of conversion of electrical to mechanical power.

When S was plotted against MEV, an exponentially increasing curve was obtained as shown in Figure 14. The square of voltage is proportional to the electrical power in a circuit obeying Ohm's Law. Therefore, P_E may be equated to

$$P_E = C(\text{MEV})^2 \quad (8)$$

where C is some constant related to the inverse of resistance of the system. Using eqs. (6)–(8),

$$S = (\eta \times C/F_T) \times (\text{MEV})^2$$

Increase in MEV indicates increase in surface formation rate in a spinning system. From the above relation, S should linearly depend on MEV^2 for a

given polymer solution. As both MEV^2 and surface formation rate are expression of power, their slope can provide the efficiency of the system for a given polymer solution. However, for different polymer solutions, F_T is expected to vary, which in turn has resulted in series of closely spaced straight lines for different solutions as shown in Figure 15. The differences between the slopes obtained for various polymer solutions are expected to be small on account of the following reasons: (a) as mentioned earlier, F_{ST} is nearly similar for all polymer concentrations and has a very small contribution to F_T ; (b) The change in values of F_R are expected to be very small compared with the order of magnitude change in the values of $(\text{MEV})^2$. Therefore, the slope given by $(\eta C/F_T)$ is not expected to change significantly for various polymer concentrations for a given system. However, for a different spinning system, MEV may change significantly, and accordingly, the slope may change. The above relation appears to be also supported by the fact that the lines are passing very close to the origin.

From the above discussion, it emerges that MEV is an important parameter in electrospinning, because at this condition, the electrical power supplied to the system is usefully utilized to do mechanical work on the extruded polymer dope. Also, at this condition, the nanofiber diameter is found to be solely dependent on polymer solution properties.

CONCLUSIONS

It has been experimentally established that while carrying out electrospinning with a steady flow system, a minimum voltage, termed as MEV, is required to completely convert the polymeric fluid into nanofibers. The conversion percentage from polymer fluid into nanofibers increases with increase in voltage until MEV is reached. Electrospinning at higher voltage than MEV does not cause any significant change in the fiber diameter or defect formation. MEV can be reached either by charging the needle (NV) or collector (CV) by a suitable voltage. A stronger quantitative dependence of MEV was observed on NV than on CV. However, irrespective of the fact that the polymer fluid was charged by conduction or induction, nanofibers formed satisfying the MEV, had the same diameter. Changing the flow rate, while maintaining MEV, did not affect the fiber diameter. However, increase in polymer concentration increased the nanofiber diameter, even while maintaining MEV. The nanofiber diameter was found to have a strong correlation with the entanglement density of the polymeric fluid. Formation of droplets could be quantitatively linked to the number of entanglements per chain. MEV showed a strong correlation with the surface formation rate. The square of MEV, which is a measure of the

electrical power supplied, was found to vary directly with the surface formation rate of the nanofibers. MEV can, therefore, be considered as an important concept to understand the nanofiber formation in electrospinning. The model system of PAN/DMF used in this study show-cased the above findings. Any radical change in terms of volatility of solvent or moisture absorption by solvent causing either change in the entanglement density or premature precipitation of polymer in the spin-line may affect the findings applicable to this model system. We are trying to extend this study to other polymer solvent systems and establish the effect of other spinning parameters on nanofiber morphology at MEV.

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