Study of Process Parameters Affecting the Diameter and Morphology of Electrospun Polyvinylidene Fluoride (PVDF) Nanofibers

Dhananjay D. Pise[1], Dr. B. B. Ahuja[2], Dr. S. M. Shendokar[3]

[1]M. Tech. Student, Department of Production Engineering and Industrial Management, College of Engineering, Pune.

[2]Professor, Department of Production Engineering and Industrial Management, Deputy Director, College of Engineering, Pune

[3]I/C Principal, Bharati Vidyapith's Group of Institutes, Technical Campus College of Engineering, Lavale, Pune.

Abstract: ***The recent developments in technology are to design and manufacture the devices of portable size with increase in efficiency, less energy consumption and more effectiveness. Fabrication of nanofibers of different polymer solution and their increasing use in wide range of applications is directing towards this. Out of different manufacturing techniques of nanofibers, electrospinning is the simple, more productive and low cost method. In this study, the nanofibers of polyvinylidene fluoride (PVDF) in solvent Dimethyl formamide (DMF) are spun with the help of electrospinning technique at different combination of input parameters such as concentration, voltage, flow rate and distance between collector and syringe tip. Taguchi method of design of experiments (L9) is used for combination of these input parameters. Further, the diameter and morphology of collected nanofibers are studied with the help of SEM images. The objective is being to study the effects of parameters and produce nanofibers of minimum diameter and defect free morphology by controlling the input parameters.***

Keywords: Electrospinning, PVDF nanofibers, process parameters, SEM images

1. Introduction

Nanoscience is the study of phenomena of materials at the atomic, molecule and molecular scale where properties change dramatically. Whereas, Nanotechnologies are the design, characterization, production and application of system, devices by controlling the structure at the nano scale [1].

In the last two decades, the advancement in the field of electronics have led to miniaturization of components and accompanied by challenges of manufacturing these parts at micron and sub-micron levels. In spite of these challenges nanoscience and nanotechnology have made unprecedented progress. Since, nanomaterials have found commercial applications a great focus is on to find new methods and techniques in the preparation and characterization of nanomaterials, a lot of research has been carried out to find the functional application of these nanomaterials. Nanofibers are one dimensional nanomaterial, they have some distinguished properties such as extremely high specific surface owing to their very small diameters, nanofiber membranes are highly porous with excellent pore interconnectivity, they are very light in weight and has the capability to form mesh at submicron level [2].

Nanofibers are of very large length as compared to diameter. The different fabricating techniques of nanofibers are drawing, phase separation, templet synthesis, self-assembly, electrospinning. Among these electrospinning is the simple, low cost and high productive technique which is easy for commercial use. Electrospinning is the combination of electrospraying and conventional solution dry spinning of fibers. It does not require high temperature or coagulation chemistry to produce the threads which makes process suitable for production of fine fibers [2], [3]. Nanofibers are having characteristics such as very large surface area to volume ratio, high flexibility and surface functionalities and superior mechanical performance compared with any other known form of the material. These properties make the polymer nanofibers to be optimal candidate for many important applications [4]. Nanofibers have possible applications in the medical science field as a means of controlled release of drugs, in artificial blood vessels, directly applied to wound healing, for skin protection and also in the muscles and bone fracture healing. Nanofiber mats can be used for the protection of the environment as a means of pollution control in air and water and vice-versa it can be used for filtration purposes also. In chemical industries also, nanofibers find many applications like those of sensors. Nanofibers materials have found to have much higher energy conversion and storage efficiency than the larger sized materials. Nanofibers in the field of electronics have found potential applications in solar cells, fuel cells and mechanical energy harvesters which can be used for self-powering low consumption devices [5], [6]. In the above applications, nanofibers of different materials are used as a sensing material which are fabricated at the low cost as compared to other materials used previously. In the present paper, an attempt is made to study the effect of parameters on the variation of diameter and surface morphology of the nanofiber film fabricated using the multiple spinneret giving high production rate as compared to other methods having single spinneret. The polymer solution of polyvinylidene fluoride (PVDF) in the solvent dimethyl formamide (DMF) of different concentration are prepared and optimised parameters for minimum diameter of nanofibers are found.

2. Experimental Setup

2.1 The Basic Setup for Electrospinning

Figure-1 shows, the schematic setup for the electrospinning. High voltage power supply, spinneret (needle of syringe) and collector are the major components of the electrospinning machine. In present case, multiple spinneret setup with two syringe and rotating drum is used as a collector for carrying out the experiments. The solution of polymer material is prepared by mixing it in solvent at concentration of 16%, 18% and 20% w/v. The magnetic heating type stirrer is used for preparing the solution. The stirring was done for 30 minutes for the formation of homogenous solution.

The solution is fed in to the spinneret (here medical syringe have been used), held in the spinneret head assembly. The servo motor pumps polymer liquid at constant flow rate to the tip of syringe. This tip of the syringe is kept as positive terminal of high voltage supply whereas the rotating drum collector is the negative terminal at the potential difference of 15kV, 25kV and 35kV. The drop of polymer solution from the spinneret is held at tip of syringe due to its surface tension. When the high voltage supply is applied, the hemispherical drop is elongates and forms inverted cone shape called as Taylor cone. When this high voltage passes the critical value, electrostatic forces overcomes the surface tension forces, a jet of polymer solution ejected from tip of Taylor cone. Solvent having low melting point evaporates in to atmosphere when the jet is stretched. The nanofiber threads are wrapped on foil applied onto drum collector which appears like a nanofiber film. The different parameters affecting the electrospinning processes are the properties of solution such as concentration, viscosity and surface tension whereas the voltage, flow rate, distance (distance between spinneret tip and collector) and rotating speed of drum collector are the operational parameters.

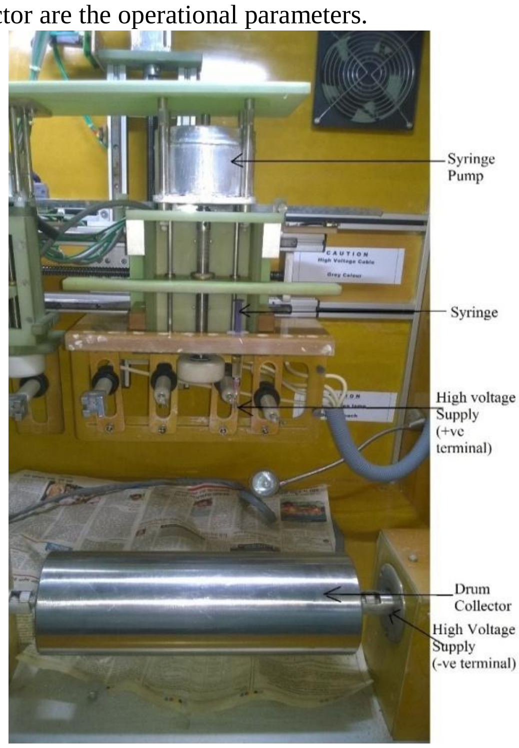

Figure 1: Basic setup of multi spinneret electrospinning

In present study, the effect of concentration of solution, flow rate, voltage and distance (distance between syringe tip and collector) are considered for study and other parameters have been kept constant. It have been found that all parameters are affecting the surface morphology and diameter of nanofibers [6], [7].

2.2 Experimental Design

As discussed above, there are different parameters which are affecting the morphology and diameter of nanofibers. But, it have been found that only few parameters are to be optimised to control the diameter of nanofibers [7], [8], [9]. In the present experiments, high voltage supply (D.C. power circuit), concentration of solution (PVDF in solvent DMF), flow rate (feed rate of polymer solution with the help of syringe pump), and distance (distance between spinneret and collector) are considered to study the effect on diameter whereas syringe translation speed and speed of rotating drum are kept constant. For carrying out experiments, Taguchi method of design of experiments (L9) was used. All the parameters are considered at three different levels as high, medium and low level [10].

3. Experimentation

For experimentation, the solution of polyvinylidene fluoride (PVDF) in solvent dimethyl formamide (DMF) is prepared at different concentration using magnetic stirrer of heating plate type. The stirring is carried out for 30 minutes till homogenous solution is formed. Table-I shows the different input parameters used for experimentation at different levels. The prepared solution is fed in to the two syringes of 2ml and held in the multi spinneret head for each run of the experiment. During experiments four parameters were varied as shown in Table-I while other parameters were kept constant.

Table 1: Parameters of PVDF experimentation

Parameter	Voltage (kV)	Flow rate (ml/hr)	Distance (cm)	Concentration (%)
High (1)	35	1.00	20	16
Medium (0)	25	0.75	17.50	18
Low (-1)	15	0.50	15.00	20

The parameters which were kept constants are, Rotating speed of drum collector: 600rpm Syringe translational speed: 0.25 m/min. It have been found that the above parameters are not affecting much on the morphology and diameter of nanofibers but the orientation of fibers collected on the film is depends on the rotation speed of the cylindrical drum collector[9], [10]. The nanofibers were spunned for 4 hours. Aluminium film was wrapped on the drum collector for ease of handling nanofibers mats.

4. Experimental results and analysis of pvdf nanofibers

To study the morphology and diameter of nanofibers, images from Scanning Electron Microscope (SEM) of 10nm visibility are analysed. The specimen images were taken from electrospun mesh sample of dimension 10mm*10mm cut from the deposited sheet. To improve electron dispersion from PVDF nanofiber surface gold coating of samples was done for about 60 seconds. After that SEM images were taken at magnification of 10KX and high electric voltage (EHT) of 3.00kV. Electron micrographs for experimental combination of different input parameters were analysed. The experimental combination of different input parameters and associated nanofiber diameters are as shown in TableII. Table-II shows the average diameter of PVDF nanofiber measured from 10 observations. From the Table-II, it is observed that the diameter range of nanofibers is 80nm to 190nm. The minimum diameter of nanofibers is found in sample number 3 which is having input parameters as 15KV high voltage D. C. power supply, flow rate of 1ml/hr, distance (distance between syringe tip and collector) and concentration of polymer solution at 16%.

Table 2: Experimental parameters

Input Parameters					Output Parameter
Sr. No.	Voltage (kV)	Flow rate (ml/hr)	Distance (cm)	Concentration (%)	Diameter (nm)
1	15	0.50	15	16	100
2	15	0.75	17.5	18	160
3	15	1.00	20	20	190
4	25	0.50	17.5	20	180
5	25	0.75	20	16	100
6	25	1.00	15	18	150
7	35	0.50	20	18	120
8	35	0.75	15	20	160
9	35	1.00	17.5	16	80

The regression statistics for above experimental parameters is as shown in Table-III

Table 3: Regression Statistics

Regression Parameter	Value
R square	0.9750
Adjusted R square	0.9500
Standard error	8.975
Observations	9

R^2 is percentage of response variable variation that is explained by its relationship with one or more predictor variables. In general, the higher the R^2, the better the model fits your data. R^2 is always between 0 and 100%. It is also known as the coefficient of determination. Adjusted R^2 is percentage of response variable variation that is explained by its relationship with one or more predictor variables, adjusted for the number of predictors in the model. This adjustment is important because the R^2 for any model will always increase when a new term is added. The adjusted R^2 is a useful tool for comparing the explanatory power of models with different numbers of predictors. The adjusted R^2 will increase only if the new term improves the model more than would be expected by chance. It will decrease when a predictor improves the model less than expected by chance.

SE Coefficient is the standard deviation of the estimate of a regression coefficient. It measures how precisely the data can estimate the coefficient's unknown value. Its value is always positive, and smaller values indicate a more precise estimate. The standard error of a coefficient helps to determine whether the value of the coefficient is significantly different than zero – in other words, whether the predictor has a significant effect on the response [11], [12].

From the Table-III, the value of R^2 is greater than 70% which shows that experimentation is valid and all the above parameters are affecting the diameter of nanofibers [11]. The regression analysis is the statistical process for estimating relationship between the dependent and independent variables. Regression model helps to understand how typically the value of dependent variable changes with respect to the independent variable [11], [12]. To analyse the effect of individual parameter on the diameter, the regression model can be given in equation form as,

$Y = \beta_0 + \beta_1 V + \beta_2 F + \beta_3 D + \beta_4 C$----------------------------- (I)

Where, β_0,β_1,β_2,$\beta_3$and $\beta_4$are the constants coefficients of regression equation,

Y = diameter of nanofibers (nm),

V= high voltage supply (KV),

F = flow rate (ml/hr),

D = distance (cm) (distance between syringe tip andcollector),

C = concentration of polymer solution (%)

The regression coefficients can be find out by using least square method. The regression estimator β can be is given as,

$[\beta] = [X^T X]^{-1} X^T [Y]$-- (II)

Where, $[\beta]$ = Regression Coefficient Matrix

$[X^T]$ = Transpose of matrix [X],

$[X^T X]^{-1}$ = Inverse of matrix $[X^T X]$,

[Y] = Response matrix.

Where,

$$\text{Where, } X = \begin{bmatrix} 1 & 15 & 0.50 & 15 & 16 \\ 1 & 15 & 0.75 & 17.5 & 18 \\ 1 & 15 & 1.00 & 20 & 20 \\ 1 & 25 & 0.50 & 17.5 & 20 \\ 1 & 25 & 0.75 & 20 & 16 \\ 1 & 25 & 1.00 & 15 & 18 \\ 1 & 35 & 0.50 & 20 & 18 \\ 1 & 35 & 0.75 & 15 & 20 \\ 1 & 35 & 1.00 & 17.5 & 16 \end{bmatrix} \text{ and } Y = \begin{bmatrix} 100 \\ 160 \\ 190 \\ 180 \\ 100 \\ 150 \\ 120 \\ 160 \\ 80 \end{bmatrix}$$

On substituting the values in the above equation and then solving it we get the values of the coefficients in the form of output matrix as,

$$\beta = \begin{bmatrix} -210.00 \\ -1.50 \\ 13.30 \\ 0.0 \\ 20.80 \end{bmatrix}$$

Now, the equation-I becomes,

Y = – 210 – 1.50V + 13.3F + 0.0D + 20.8C

From the above equation, theoretical values of PVDF nanofibers is calculated and tabulated. The % error in the actual values and theoretical values of diameter of PVDF nanofibers are calculated as,

$$\% \text{ Error} = \frac{\text{Actual diameter} - \text{theoretical diameter}}{\text{actual diameter}} \times 100$$

The % error of each sample and the mean % error in diameter of nanofibers is as shown in Table-IV.

Table 4: Comparison of actual values and theoretical values of PVDF nanofibers

Sr. No.	Actual Diameter (nm)	Theoretical Diameter (nm)	% Error
1	100	106.95	-6.95
2	160	151.87	5.078
3	190	196.8	-3.579
4	180	175.15	2.70
5	100	95.275	7.046
6	150	140.20	4.725
7	120	118.22	1.20
8	160	163.47	-2.172
9	80	83.60	-4.50
Total %		Error	3.548
Mean %		Error	0.40

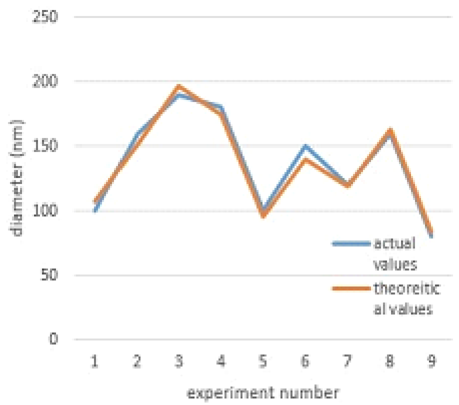

Figure 2. Comparison of Actual versus Theoretical values of PVDFnanofibers

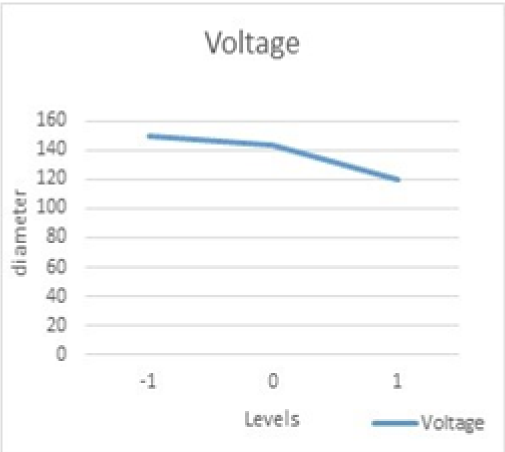

Figure 3. Main effect plot of diameter versus voltage

Figure-2 shows the comparison of actual diameter versus theoretical diameter of nanofibers. It can be seen that the actual and theoretical values are almost same. Comparing the experimental values and theoretical values the mean error of 0.40 % is found which is negligible and thus, it can be concluded that the regression equation gives the correct values for voltage, flow rate, distance and concentration.

To study the effect of individual parameters on diameter of PVDF nanofibers at each level, the main effects plot of means of diameter versus parameter is considered. If the nature of graph is,

1) Horizontal, it is said that there is no main effect. Each level of the factor affect the response in the same way and the response mean is the same across all the factors.
2) When the line is not horizontal, then there is main effect. Different levels of factors affect the response differently.

The steeper the slope of line, greater the magnitude of main effect [11].

The mean values of diameter for each parameter at levels are calculated and tabulated as below and main effects plot for each parameter verses diameter are as shown in below,

Table 5: Means of diameter for each parameter

Level	Voltage	Flow Rate	Distance	Concentration
Low (-1)	150.00	133.33	136.67	93.33
Medium (0)	143.33	140.00	140.00	144.33
High (+1)	120.00	140.00	136.67	176.67

4.1 Effect of Voltage

As seen in Table-II, the high voltage D. C. power supply have been varied in three levels as 15KV, 25KV & 35KV. The main effect plot for voltage against mean diameter of nanofibers at each level is as shown in Figure-3 which shows that the diameter of nanofibers decreases as voltage increased and beads free smooth fibers are spunned.

4.2 Effect of Flow Rate

The flow rate was varied as 0.5ml/hr, 0.75ml/hr and 1.00ml/hr. From the Figure-9 it can be say that the diameter of nanofibers remains same but the beads-free fibers are deposited on the aluminium foil. With minimum flow rate the fibers take more time to deposit on collector and solvent gets evaporates in atmosphere in time period between syringe tip and collector. Due to this, beads-free and smoother nanofibers are collected. The main effect plot of mean diameter versus flow rate at each level is as shown in Figure4 from which it is concluded that there is not much effect of change of flow rate on the diameter on PVDF nanofibers, as the line is almost horizontal.

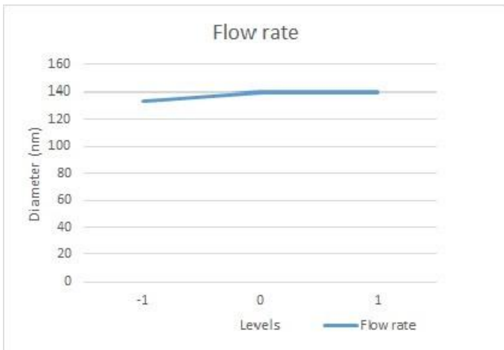

Figure 4: Main effect plot of flow rate versus diameter

4.3 Effect of Concentration

The polymer solution of solute PVDF in solvent DMF at 16%, 18% and 20% concentration is considered to study the effect of concentration on the diameter and morphology of nanofibers. From Table-II, it is seen that concentration of solution increases, the thicker fibers are formed. The SEM images of the samples are as shown in Figure-9, at more concentration of solution the beads-free nanofibers can be fabricated. The main effect plot of concentration of solution versus mean diameter of PVDF nanofibers at each level is as shown in Figure-5. From the nature of graph it is concluded that as the concentration of solution increases, thicker nanofibers are formed.

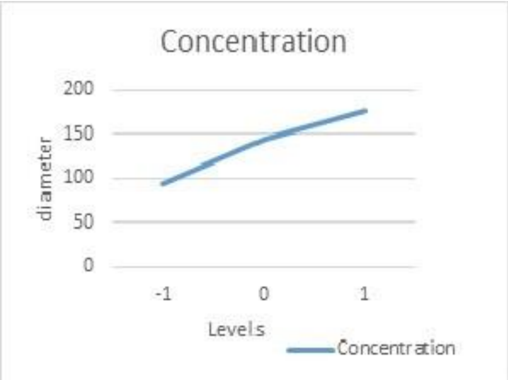

Figure 5: Main Effect plot of diameter versus concentration of solution

4.4 Effect of Distance (distance between syringe tip andcollector)

The main effects plot of distance and the mean diameter of nanofibers at each level is as shown in Figure-6, which suggests that there is not much effect of distance on the nanofibers diameter. The nature of graph is almost parallel to horizontal axis. But as the distance increases, solvent gets more time for evaporation and the beads free nanofibers are deposited on drum collector covered with aluminium foil used for ease in handling nanofibers.

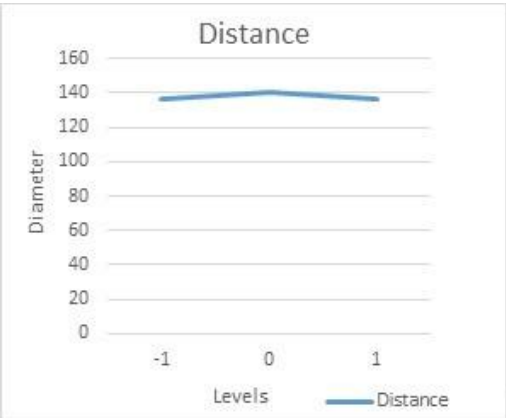

Figure 6: Main effect plot of diameter versus distance

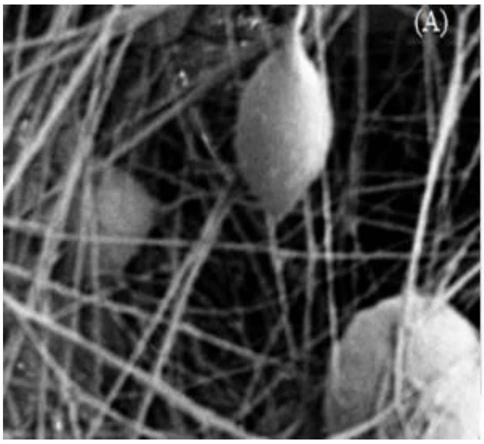

Figure 7: Effect of concentration on the morphology of nanofibers, (A)16% concentration

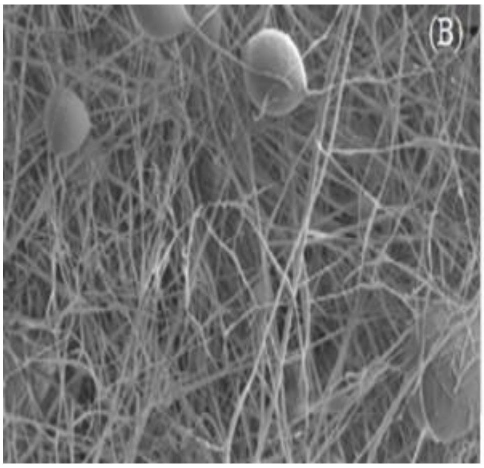

Figure 8: Effect of concentration on the morphology of nanofibers, (B) 18% concentration

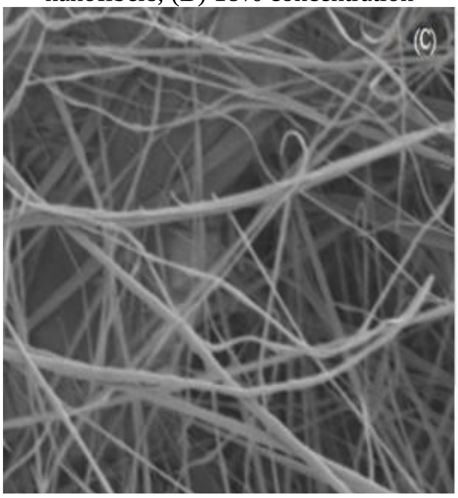

Figure 9: Effect of concentration on the morphology of nanofibers, (B) 18% concentration and (C) 20% concentration

The Table-VI shows the summary of effects of different process parameters affecting the morphology and diameter of PVDF nanofibers fabricated using electrospinning technique.

Table 6: Effect of process parameters affecting the morphology of PVDF nanofibers

Sr. No.	Parameter	Effect on morphology of PVDF nanofibers
1	Concentration	Increase in fiber diameter as concentration increased, disappearance of beads
2	Voltage	Decrease in fiber diameter as voltage increased
3	Flow rate	Decrease in beads formation as flow rate increases and fiber diameter increases
4	Distance	Decrease in beads formation as distance increases

5. Conclusion

From the main effect plot of diameter versus individual parameters, it can be seen that high voltage supply and flow rate are the more influencing parameters on the diameter of nanofibers. From the Figure-3, as the voltage increases the minimum diameter nanofibers can be fabricated which is same in case of flow rate as shown in Figure-4. Whereas the concentration of polymer solution and the distance (distance between spinneret and collector) are the parameters which are affecting the morphology of nanofibers as shown in Figure-9. With proper viscous solution, beads-free nanofibers can be fabricated. In this present study from the Table-II, the minimum diameter of nanofibers of PVDF are fabricated at following parameters,

- 35KV voltage (high voltage D. C. power supply)
- 1ml/hr flow rate
- 17.5 cm distance (distance between spinneret and collector)
- 16% concentration of PVDF in DMF.

6. Future Scope

Polyvinylidene fluoride (PVDF) nanofibers is the polymer material having the piezoelectric properties. In future scope, the nanofibers would be tested for piezoelectric properties feasible applications of nanofibers related to energy are envisage. There are hundreds of polymer variants from which nanofibers are produced by electrospinning, but very few publications are available related to study of electrospinning based on ANOVA or DOE.

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