Experimental Investigation into Effect of Process Parameters in Manufacturing PolymBlend Nanofibers and Its Morphology

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Abstract

Fabrication of nanofibers of different polymer solution and their increasing use in wide range of applications requires detail study of a manufacturing process. Various manufacturing techniques of preparation of nanofibers are available. However, electrospinning is the simplest, more productive and low cost method. Electrospinning uses an electrical charge to draw very fine (typically on the Micro or Nano scale) fibres from a liquid. In this study, an attempt is made to study the effect of process parameters on preparation of nanofibers of minimum diameter and defect free morphology by controlling the input parameters. A new PolymBlend solution i.e. blend of Methyl Methacrylate-co-Hydroxyethyl Methacrylate and Methyl Acrylate-co-Hydroxyethyl Acrylate in solvent Dimethyl Formamide (DMF) are spun with the electrospinning technique at different combination of input parameters such as voltage, flowrate, speed of drum collector and distance between collector and syringe tip. Design of experiments is used for conducting the experiments. Scanning electron microscope is used for observation of collected nanofibers. Further, the diameter and morphology of collected nanofiber samples are studied with the help of SEM images.

Keywords: Electrospinning, PolymBlend nanofibers, SEM.

1. INTRODUCTION

Nanoscience is the study of structures and materials on the scale of nanometers. Whereas, Nanotechnology is the science, engineering, application and technology conducted at the nano scale [1].

Nanoscience and nanotechnology have made much 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 fibers with diameters in nanometer range, they can be generated from different polymers and hence have different physical properties and applications, nanofiber membrane have excellent pore interconnectivity, they are very light in weight [2].

The different fabricating techniques of nanofibers are electrospinning, templet synthesis, drawing, phase separation, self-assembly. Among these electrospinning is the simple and high productive technique. Electrospinning is the combination of conventional solution dry spinning of fibers and electrospraying.

It doesn't need high temperature or coagulation chemistry to produce the threads which makes process easy and suitable for production of fine fibers [3]. Nanofibers are having characteristics such as surface functionalities, high flexibility and superior mechanical performance compared with any other known form of the material. For many important applications properties of polymer nanofibers are optimal [4]. Nanofibers have applications in the medical science field as a means of controlled release of drugs, directly applied to wound healing, for skin protection, in artificial blood vessels 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. Nanofibers in the field of electronics have found applications in fuel cells, solar cells, mechanical energy harvesters [5], [6]. 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. The polymer solution of PolymBlend in the solvent Dimethyl Formamide (DMF) 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, collector and spinneret (needle of syringe) 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 Methyl Methacrylate-co-Hydroxyethyl Methacrylate (Copolymer A), Methylacrylate-co-Hydroxyethyl Acrylate (Copolymer B) in 1:1 ratio in DMF solvent i.e. 5gm each copolymer for 67gm of solvent. The magnetic stirrer is used for preparing the solution. The stirring was done for 24 hours and after that added 45µl HCL 37% and maintained magnetic stirring for 1 hour more for the formation of homogenous solution.

The solution is fed in to the spinneret (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 9kV, 12kV and 15kV. 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

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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 viscosity, concentration and surface tension whereas the voltage, distance (distance between spinneret tip and collector), flow rate and rotating speed of drum collector are the operational parameters.

In present study, the effect of voltage, flow rate, distance (distance between syringe tip and collector) and speed of drum 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.

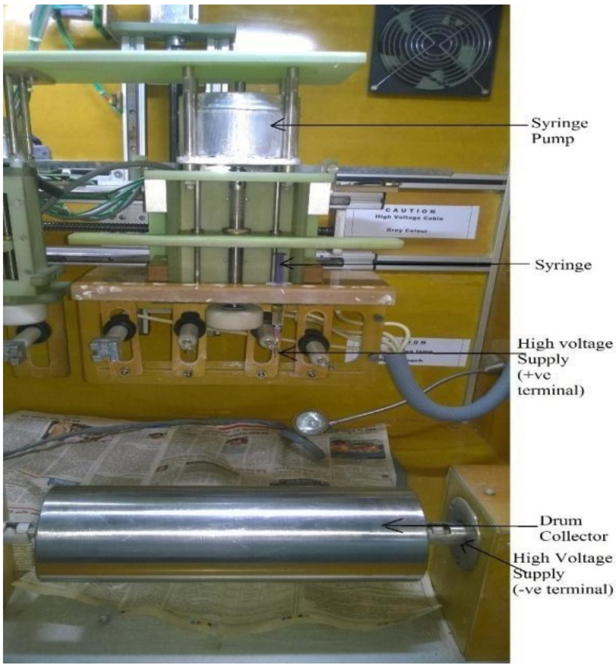


Fig. 1. Basic setup of multi spinneret electrospinning

2.2. Experimental Design

As discussed above, there are different parameters which are affecting the morphology and diameter of nanofibers. In the present experiments, high voltage supply (D.C. power circuit), flow rate (feed rate of polymer solution with the help of syringe pump), distance (distance between spinneret and collector) and speed of drum collector are considered to study the effect on diameter whereas syringe translation speed and concentration of solution are kept constant. For carrying out experiments, design of experiments 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 PolymBlend (Methyl Methacrylate-co-Hydroxyethyl Methacrylate and Methyl Acrylate-co-Hydroxyethyl Acrylate) in solvent Dimethyl Formamide (DMF) is prepared using magnetic stirrer. The stirring is carried out for 24 hours 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 5ml and held in the multi spinneret head for each run of the experiment.

Table 1 Parameters of PolymBlend experimentation

Parameter	Voltage (kV)	Flow rate (ml/hr)	Distance (cm)	Speed (rpm)
High (1)	15	1.30	26	1100
Medium (0)	12	1.00	23	800
Low (-1)	9	0.70	20	500

The nanofibers were spunned for 1 hour. Aluminium film was wrapped on the drum collector for ease of handling nanofibers mats.

Table 2 Experimental parameters

Input Parameters					Output Parameter
S. No.	Voltage (kV)	Flow rate (ml/hr)	Distance (cm)	Speed (rpm)	Diameter (nm)
1	9	0.70	20.0	500	490
2	9	0.70	20.0	500	380
3	9	0.70	20.0	500	440
4	9	1.00	23.0	800	540
5	9	1.00	23.0	800	480
6	9	1.00	23.0	800	510
7	9	1.30	26.0	1100	540
8	9	1.30	26.0	1100	430
9	9	1.30	26.0	1100	480
10	12	0.70	23.0	1100	470
11	12	0.70	23.0	1100	400
12	12	0.70	23.0	1100	440
13	12	1.00	26.0	500	480
14	12	1.00	26.0	500	430
15	12	1.00	26.0	500	460
16	12	1.30	20.0	800	490
17	12	1.30	20.0	800	400
18	12	1.30	20.0	800	440
19	15	0.70	26.0	800	450
20	15	0.70	26.0	800	320
21	15	0.70	26.0	800	370
22	15	1.00	20.0	1100	530
S. No.	Voltage (kV)	Flow rate (ml/hr)	Distance (cm)	Speed (rpm)	Diameter (nm)
23	15	1.00	20.0	1100	450
24	15	1.00	20.0	1100	480
25	15	1.30	23.0	500	530
26	15	1.30	23.0	500	500
27	15	1.30	23.0	500	500

4 EXPERIMENTAL RESULTS AND ANALYSIS OF POLYMBLEND NANOFIBERS

To study the morphology and diameter of nanofibers, images from Scanning Electron Microscope (SEM) of 10nm visibility are analysed. Table 2 shows the average diameter of PolymBlend nanofiber measured from 27 observations. From the Table 2, it is observed that the diameter range of nanofibers is 320nm to 540nm. The minimum diameter of nanofibers is found in sample number 20 which is having input parameters as 15KV high voltage D. C. power supply, flow rate of 0.7ml/hr, 26 cm distance (distance between syringe tip and collector) and speed of drum collector 800 rpm.

The regression analysis is the statistical process for estimating relationship between the dependent and independent variables. To analyse the effect of individual parameter on the diameter, the regression model can be given in equation form as,

$$Y = \beta_0 + \beta_1 V + \beta_2 F + \beta_3 D + \beta_4 S \text{--------------------------------- (I)}$$

Where, β_0, β_1, β_2, β_3 and β_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 and collector),
S = Speed of drum collector (rpm)
The regression coefficients can be find out by using least square method.

$$\beta = \begin{bmatrix} \beta 0 \\ \beta 1 \\ \beta 2 \\ \beta 3 \\ \beta 4 \end{bmatrix} = \begin{bmatrix} 452.22 \\ -2.96 \\ 101.85 \\ -2.59 \\ 0.0018 \end{bmatrix}$$

Now, the equation-I becomes,

$$Y = 452.22 - 2.96V + 101.96F - 2.59D + 0.0018S \text{---------(III)}$$

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

$$\%\ Error = \frac{Theoretical\ Diameter - Actual\ Diameter}{Theoretical\ Diameter} \times 100$$

The % error of each sample and the mean % error in diameter of nanofibers is as shown in Table 4.

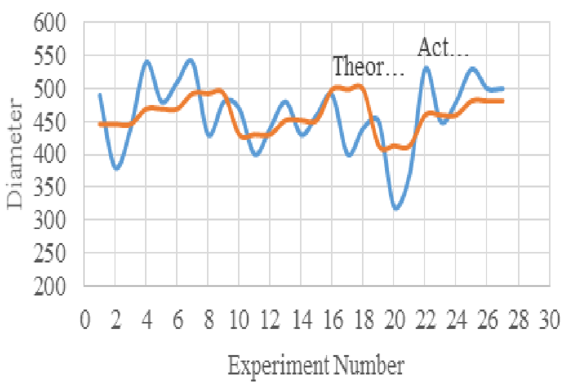


Fig. 2.Comparison of Actual versus Theoretical values of PolymBlend nanofibers

Table 4 Comparison of actual values and theoretical values of PolymBlend nanofibers

Sr. No.	Actual Diameter (nm)	Theoretical Diameter (nm)	% Error
1	490	445.9259	-9.88372
2	380	445.9259	14.78405
3	440	445.9259	1.328904
4	540	469.2593	-15.075
5	480	469.2593	-2.28887
6	510	469.2593	-8.68193
7	540	492.5926	-9.62406
8	430	492.5926	12.70677
9	480	492.5926	2.556391
10	470	430.3704	-9.20826
Sr. No.	Actual Diameter (nm)	Theoretical Diameter (nm)	% Error
11	400	430.3704	7.056799
12	440	430.3704	-2.23752
13	480	452.037	-6.18599
14	430	452.037	4.875051
15	460	452.037	-1.76157
16	490	498.7037	1.745266
17	400	498.7037	19.79205
18	440	498.7037	11.77126
19	450	413.1481	-8.91977
20	320	413.1481	22.54594
21	370	413.1481	10.44375
22	530	459.8148	-15.2638
23	450	459.8148	2.134515
24	480	459.8148	-4.38985
25	530	481.4815	-10.0769
26	500	481.4815	-3.84615
27	500	481.4815	-3.84615
	Total %	Error	0.4512
	Mean %	Error	0.0167

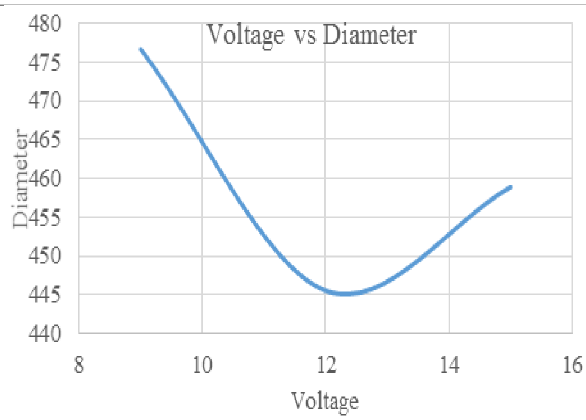


Figure 3. Main effect plot of diameter versus voltage

Figure-2 shows the comparison of actual diameter versus theoretical diameter of nanofibers. Comparing the experimental values and theoretical values the mean error of 0.0167 % 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 speed.

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	Speed
Low (-1)	476.67	417.78	455.56	467.78
Medium (0)	445.56	484.45	485.56	444.45
High (+1)	458.89	478.89	440.00	468.89

4.1 Effect of Voltage

As seen in Table 2, the high voltage D. C. power supply have been varied in three levels as 9KV, 12KV & 15KV. 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 spun.

4.2 Effect of Flow Rate

The flow rate was varied as 0.7ml/hr, 1.0ml/hr and 1.3ml/hr. 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 Figure 4 from which it is concluded that as flowrate is decreases diameter of nanofibers goes on decreasing.

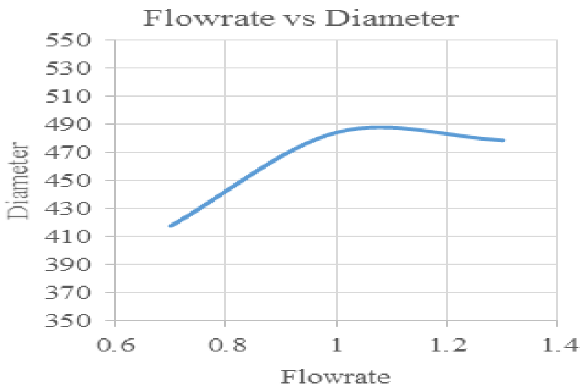


Fig. 4. Main effect plot of flow rate versus diameter

4.3 Effect of Distance (distance between syringe tip and collector)

The main effect plot of distance and the mean diameter of nanofibers at each level is as shown in Figure-5, 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.

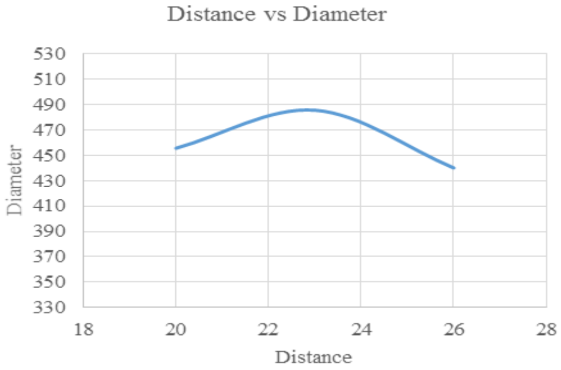


Figure 5: Main Effect plot of diameter versus distance

4.4 Effect of Speed of drum collector

The speed of drum collector varied as 500rpm, 800rpm and 1100rpm. The main effect plot of speed and the mean diameter of nanofibers at each level is as shown in Figure-6, which suggests that there is not much effect of speed on the nanofibers diameter. The nature of graph is almost parallel to horizontal axis. From the nature of graph it is concluded that at mean level of speed minimum diameter and beads free nanofibers are collected.

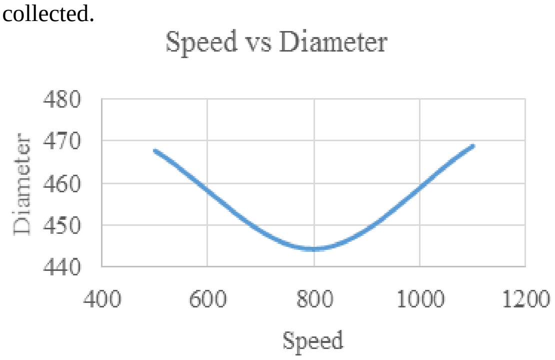
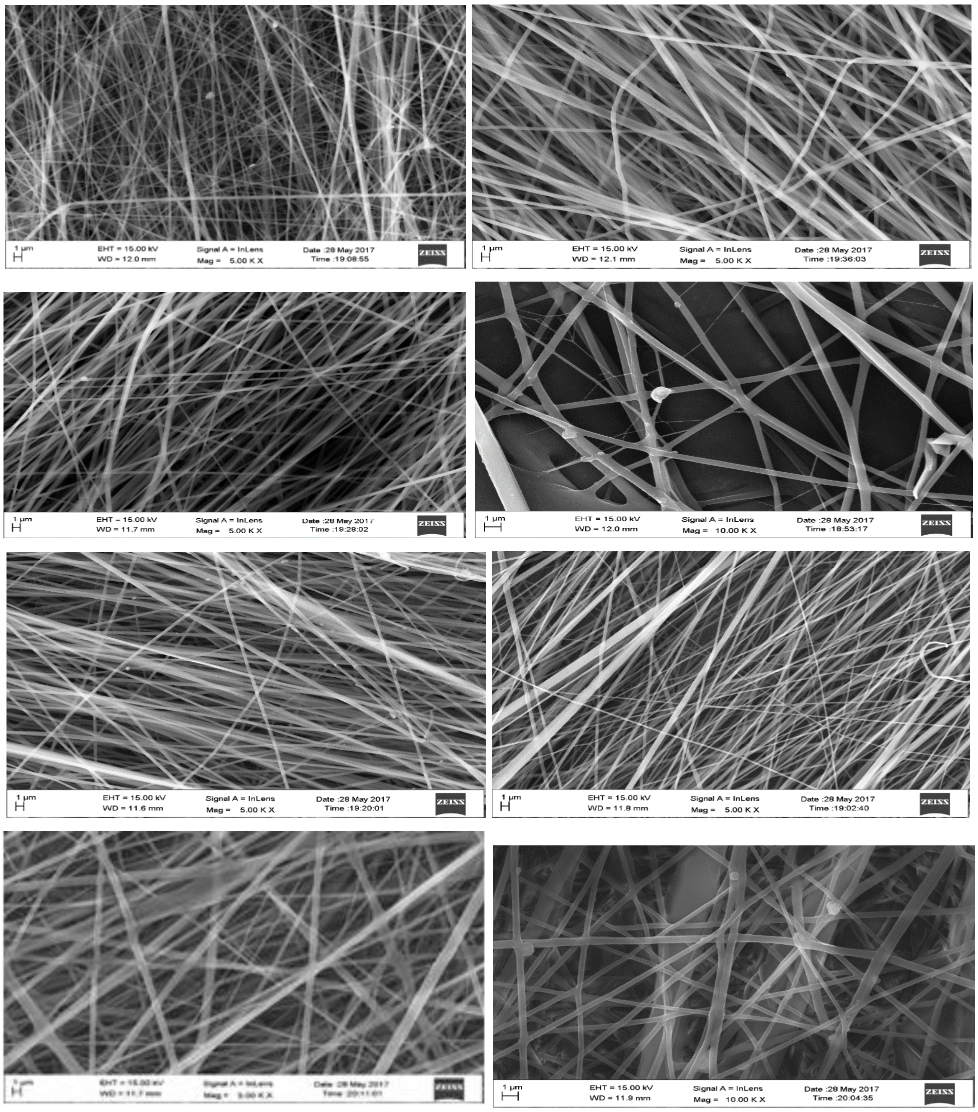


Fig. 6. Main effect plot of diameter versus speed

Table 6 Effect of process parameters affecting the morphology of PolymBlend nanofibers

Sr. No.	**Parameter**	**Effect on morphology of PolymBlend nanofibers**
1	Voltage	Decrease in fiber diameter as voltage increased
2	Flow rate	Decrease in beads formation as flow rate decreases and fiber diameter decreases
3	Distance	Decrease in fiber diameter as distance increases
4	Speed	Decrease in fiber diameter as Speed increased upto mean level, disappearance of beads

SEM IMAGES OF SAMPLES



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 and as the flow rate decreases the minimum diameter nanofibers can be fabricated shown in Figure-4. Whereas the speed of drum collector and the distance (distance between spinneret and collector) are the parameters which are less affecting the morphology and diameter of nanofibers. With proper viscous solution, beads-free nanofibers can be fabricated. In this present study from the Table 2, the minimum diameter of nanofibers of PolymBlend are fabricated at following parameters,

- 15KV voltage (high voltage D. C. power supply)
- 0.7ml/hr flow rate
- 26 cm distance (distance between spinneret and collector)
- 800rpm speed of drum collector.

6 FUTURE SCOPE

Mechanical properties of the PolymBlend nanofiber mat could be checked by Dynamic Mechanical Analyser (DMA). In future scope, the nanofibers would be tested for piezoelectric properties feasible applications of nanofibers related to energy are envisage. Different type of collectors can be used for handling the nanofiber mats and the change in fibers orientation can be studied. There are hundreds of polymer variants from which nanofibers are produced by electrospinning can be studied based on ANOVA or DOE.

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