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Research Article

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Design of ultrafine nanofibers/nets for varied textile applications

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Keywords

Ultrafine Nanofibers, electrospinning, Textile applications,

Abstract

Ultrafine Nanofibers generally have diameter ranging from 10-100 nm. With such small diameters come high specific surface area and porous aggregation, which makes them highly desirable for Tissue Scaffolds, Filters, Drug Delivery, etc. These Ultrafine nanofibers are spun using the method of electrospinning. This process of electrospinning exploits the polar nature of the polymers and hence there charge density for spinning of thin fibers.

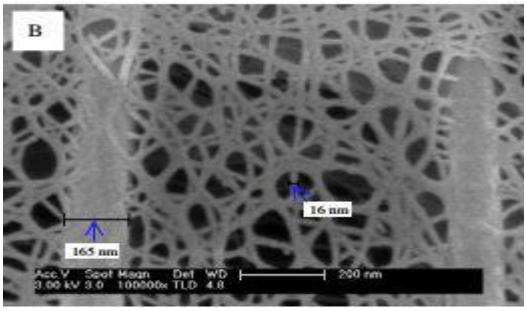
An electric field is applied to a capillary/needle containing a polymer solution. As the intensity of the electric field is increased, the hemispherical surface of the solution at the tip of the needle extends to form a polarized conical shape (Taylors' Cone) through which a jet is ejected. This jet due to instability in the polymer solution further splits into nanofibers which are collected on the collector plate, producing a non-woven web. By modifying several process parameters, diameter and hence porosity of the nanofibers can be changed.

However there are various challenges in this process. Firstly, uniformity amongst nanofibers is not maintained in this process, large-scale and extremely small diameter (<50 nm) nanofibers.

Various approaches, such as decreasing the polymer concentration, elevating the solution temperature, and increasing the net charge density of the solution, have been utilized to reduce the diameter of electrospun nanofibers. However, these methods typically produce nonuniform fibers with poorly defined structures and the objective of reducing fiber diameter down to 50 nm was rarely achieved.

To solve the problem of fabrication of Ultrafine nanofibers, the method of Electro-spinning/netting (ESN) was first observed by Ding [1] for the first time in 2004. With this method one can fabricate both normal nanofibers of higher diametric range and ultrafine nanofibers of range less than 100nm, hence the resultant product of ESN is nano-nets, supported by the conventional electrospun nanofibers in the nano-fiber/nets (NFN) membranes. These NFNs exhibit several distinguishing characters, few among them are extremely small diameter, high porosity and Steiner tree network geometry. Such characteristics make NFNs highly suitable for many textile applications such as filtration, protective clothing, scaffolds, etc.

Introduction



Nylon Nanonets. [2]

Source: Formation of novel 2D polymer nanowebs via electrospinning. Bin Ding, Chunrong Li, Yasuhiro Miyauchi, Oriha Kuwaki and Seimei Shiratori.

Literature Review:

In the review paper, "Electro-spinning/netting: A strategy for the fabrication of three-dimensional polymer nano-fiber/nets", published by Xianfeng Wang, Bin Ding, Gang Sun, Moran Wang, Jianyong Yu. Due to absence of the exact theoretical model of NFNs, they have proposed multiple possible mechanisms through which NFNs are formed. The very first and widely accepted amongst them is phase separation of charged droplets. They have argued that during the flight of charged droplet from tip to collector, the microsized droplet gets distorted and expanded into a thin film due to the comprehensive effects of the forces acting on it. This thin film then splits into nano-nets due to the rapid phase separation between polymer and solvent and to the fast evaporation of solvent at lower humidity. This claim is also supported by several published papers where effect of humidity on ESN is studied.

The second proposed mechanism is ion initiated splitting up of electrospun fibers. According to it, the nanonets formed are nothing else but connections between two nanofibers, formed due to attractions between the two charges. So, addition of ionic salts in polar polymer solution, would create these connections/joints (nanonets) at taylor's cone. The other two proposed mechanisms were intermolecular hydrogen bonding in the polymer systems leading to formation of connections and intertwining among branching jets.

In, Formation of novel 2D polymer nanowebs via electrospinning by Bin Ding, Chunrong Li, Yasuhiro Miyauchi, Oriha Kuwaki and Seimei Shiratori, authors have successfully fabricated nylon-6 (in formic acid) nanowebs with average diameter of nanowebs of 17nm. It was observed at 20% w/w and at 25kV effective potential.

Also, in research paper, Recent Progress on the Fabrication of Ultrafine Polyamide-6 Based Nanofibers Via Electrospinning: A Topical Review by R. Nirmala, R. Navamathavan, Soo-JinPark and HakYongKim, the authors have publishes the effect of various parameters on nanoweb formation. It was observed that by changing the solvent system to a more volatile system, i.e, introduction of acetic acid in the nylon-6/formic acid, increases the coverage area of nanowebs. Also, addition of inorganic salts add to the phenomenon of nanoweb formation. It was established in the paper by adding small amounts of NaCl to the polymer system. The effect of humidity was also studied in the paper, and it was concluded that the nanoweb formation needs lower humidity, this is ensured to avoid formation of films instead of nanowebs, as lower humidity implies faster evaporation of the volatile solvent.

In [4], for bipolar power sources the effective voltage has been related to the distance between collector plate and needle and the collector-needle potential.

Effective potential= Needle voltage + Slope*Collector voltage; where slope is 0.4 for 20 cm , 0.5 for 15 cm and 0.6 for 10 cm distance between collector plate and needle.

Summary of process parameters for ESN:

	Parameter	Requirement
1.	Charge Density	High; Highly Polar Polymer or Polymer-Solvent System
2.	Distance from Needle to Collector	Decrease in diameter with increase in distance. Extensively low distance leads to improper evaporation and hence film defects are visible.
3.	Solution Viscosity	Not too low, not too high
4.	Polymer Conc.	Low; Ensuring no bead formation
5.	Solvent	Highly volatile to ensure fast evaporation
6	Relative Humidity	Low; 20-30% (to ensure rapid evaporation)
7	Potential	High for ESN

Objective:

To understand the mechanism of Nano-net formation

Experiment:

Materials Used:

Low molecular weight nylon pellets purchased from Sigma Aldrich was used as polymer for electrospinning along with formic acid (90%) and acetic acid (98%) as solvents, both of them purchased from Merck India. NaCl was purchased from Merck India.

Methods:

1) Spinning Setup:

For electrospinning, a bipolar system with high voltage power source was used. The positive terminal of which was connected with the spinning needle (spinneret), through which the polymer droplet was charged conductively, whereas the negative terminal connected with collector plate inductively charged the polymer droplet. Polymer solution was passed through a syringe pump, a 2mL syringe and a blunt needle. The fibers formed were deposited on an aluminium plate (collector).

2) Preparation of Solutions:

Procured Nylon was weighed in a glass vial and Formic acid was added to it, such that the total solution weighed 5gm. For dual solvent system after Formic acid, acetic acid was added maintaining a weight ratio of 4:1 amongst them.

In two of the solutions, 1.5% NaCl was added in the solution. This addition was with respect to the weight of the solution.

After preparing the solutions they were left for overnight stirring.

Details of the solutions prepared are mentioned in Table 1:

Table 1: Solutions prepared

Nylon Conc. (%w/w)	Weight of Nylon in 5gm solution	Solvent	NaCl (%w/wrt solution)
15%	0.75 gm	Formic Acid	-
18%	0.9 gm	Formic Acid	-
20%(1)	1 gm	Formic Acid	-
20%(2)	1 gm	Formic Acid	-
20%	1 gm	Formic Acid	1.5%
20%	1 gm	Formic Acid+Acetic Acid	-
20%	1 gm	Formic Acid+Acetic Acid	1.5%
15% (HMW)	0.75 gm	Formic Acid	-

3) Electrospinning of Nylon Solutions:

The above prepared solutions were electrospun in three different experiments (I,II,III) and a total of 20 samples were made. These 20 samples had different parameters as shown in Tables 2,3 and 4.

*The samples are coded using the following abbreviations:

N15FA/AA-EV35-Na :: Where N15 represents the concentration of nylon-6 in solution, FA/AA represents solvent system of formic acid and acetic acid, EV35 represents the effective voltage applied on the electrospinning system and Na represents the presence of Sodium salt in the solution in the proportion mentioned above.

Experimental Parameters:

I. Flow Rate: 0.25 mL/hr
Temperature: 28.9℃
Relative Humidity: 55%

Table 2: Experiment I

Sample	Nylon Conc.	Solvent	Needle to plate distance	Collector/Needle Voltage (kV)	Effective potential (kV)
N15FA-EV35	15%	FA	20cm	25/25	35
N15FA-EV28	15%	FA	20cm	20/20	28
N15FA-EV37.5	15%	FA	15cm	25/25	37.5
N18FA-EV37.5	18%	FA	15cm	25/25	37.5
N18FA-EV30	18%	FA	15cm	20/20	30
N18FA-EV28	18%	FA	20cm	20/20	28
N20FA-EV22.5	20%	FA	15cm	15/15	22.5
N20FA-EV21	20%	FA	20cm	15/15	21

Table 3: Experiment II

II. Flow Rate: 0.25 mL/hr
Temperature: 30℃
Relative Humidity: 58%

Sample	Nylon Conc.	Solvent	NaCl	Needle to plate distance	Collector/Needle Voltage (kV)	Effective potential (kV)
N20FA-EV30	20%	FA	-	15cm	20/20	30
N20FA-EV37.5	20%	FA	-	15cm	25/25	37.5
N20FA-EV37.5-Na	20%	FA	1.5%	15cm	25/25	37.5
N20FA-EV35-Na	20%	FA	1.5%	20cm	25/25	35
N20FA-EV30-Na	20%	FA	1.5%	15cm	20/20	30
N20FA/AA-EV30	20%	FA+AA	-	15cm	20/20	30
N20FA/AA-EV30-Na	20%	FA+AA	1.5%	15cm	20/20	30
N20FA/AA-EV25.5-Na	20%	FA+AA	1.5%	15cm	17/17	25.5
N20FA/AA-EV37.5-Na	20%	FA+AA	1.5%	20cm	25/25	37.5

Table 4: Experiment III

III. Flow Rate: 0.25 mL/hr
Temperature: 32.8℃
Relative Humidity: 55%

Sample	Nylon Conc.	Solvent	NaCl	Needle to plate distance	Collector/Needle Voltage (kV)	Effective potential (kV)
N20FA/AA-EV37.5	20%	FA+AA	-	15cm	25/25	37.5
N20FA/AA-EV37.5-Na*	20%	FA+AA	1.5%	15cm	25/25	37.5
N20HMWFA-EV45	20%(HMW)	FA	-	15cm	30/30	45

4) Characterization of samples:

Field Emission Scanning Electron Microscopy(FESEM), SMITA research lab was used to observe the electrospun samples.

Results:

Amongst the results of experiment I (refer table 2), no visible nanonets were observed at low concentration samples, i.e, N15FA-EV35, N15FA-EV28 and N15FA-EV37.5, as shown in Fig. 2. Fig.3 too has no visible nanonets despite high concentration possibly due low effective potential. Whereas on increasing the concentration to 18%, nanonets were visible but in extremely low area. Figure 4 shows sample N18FA-EV37.5, in which the concentration is moderate, the effective potential was high and coverage area of the nanowebs formed was low

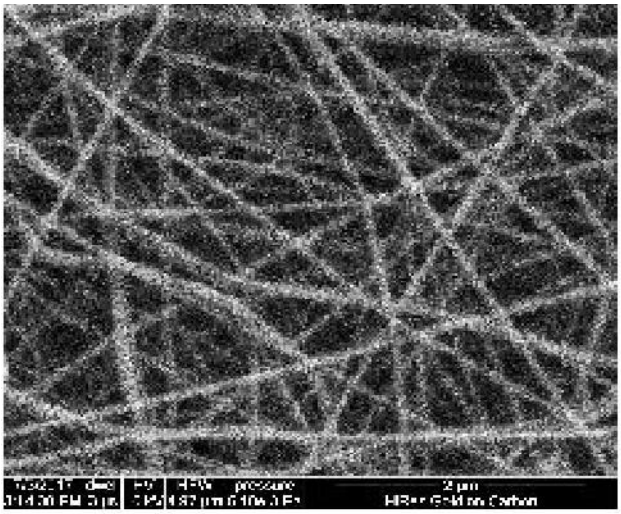


Figure 2.N15FA-EV35 Average dia: 46 nm SD 11nm

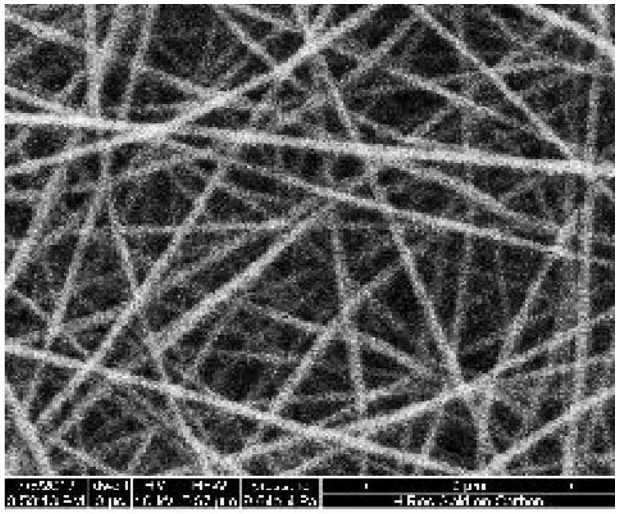


Figure 3. N20FA-EV22.5 Average dia: 59nm SD 9nm

Thus, from experiment I it was concluded that lower concentration and lower potential both act against the phenomenon of ESN. This was the very basis of experiment II, in which the concentration of Nylon in formic acid was fixed at 20% (w/w).

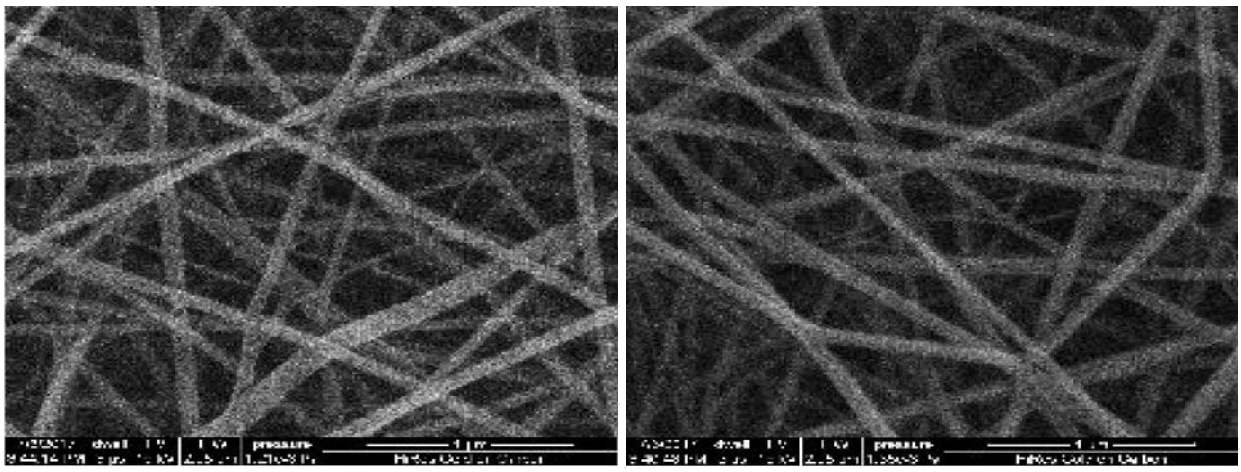


Figure 4. N18FA-EV37.5 Average dia:83nm SD 14nm Web dia: 20nm

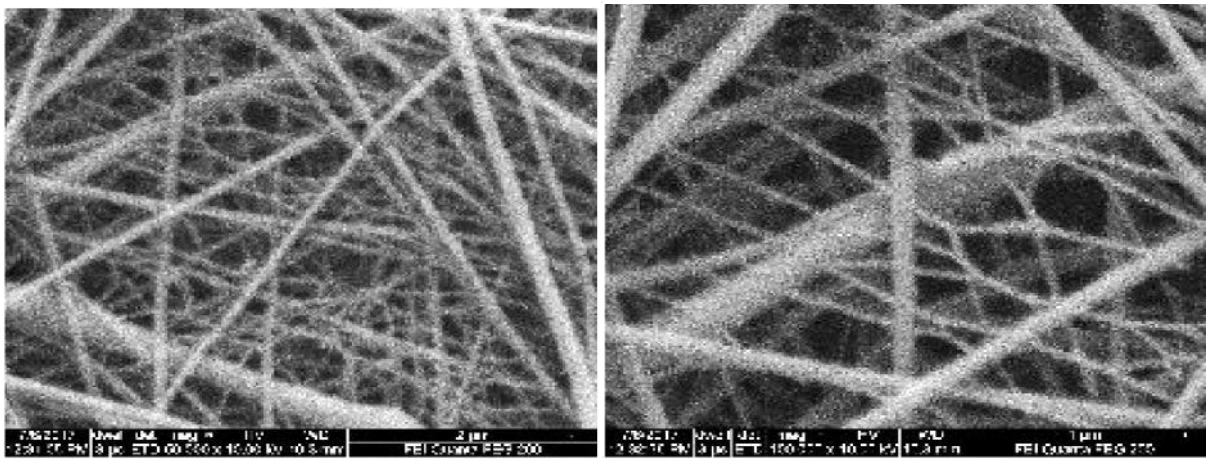


Figure 5. N20FA-EV30 Average fiber dia: 110nm SD 15nm Web dia: 35nm(approx)

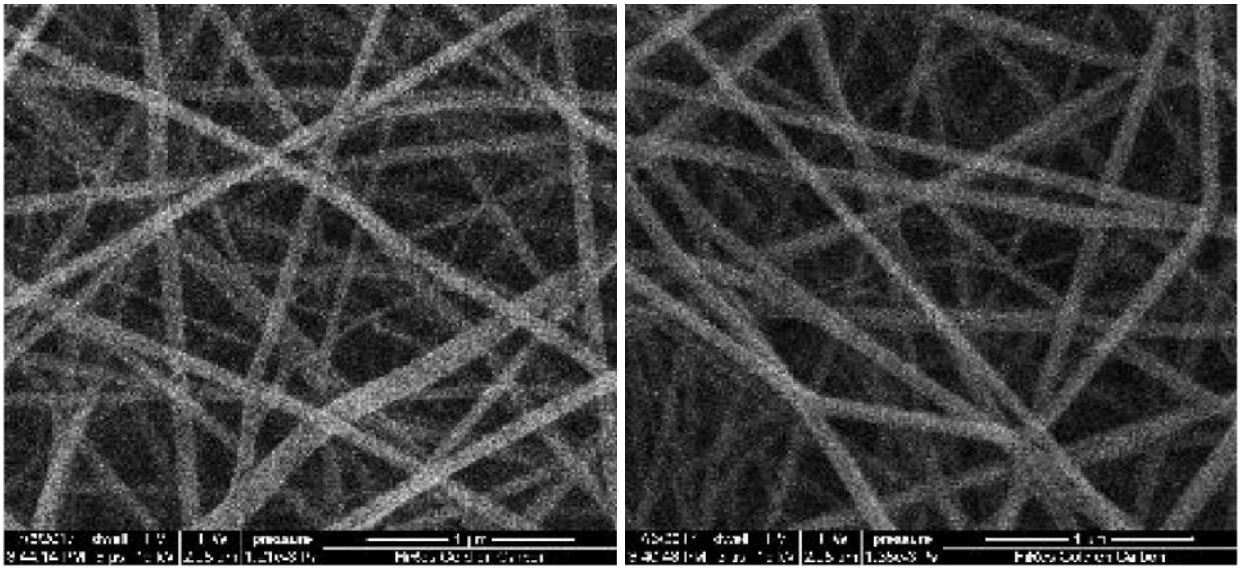


Figure 4. N18FA-EV37.5 Average dia:83nm SD 14nm Web dia: 20nm

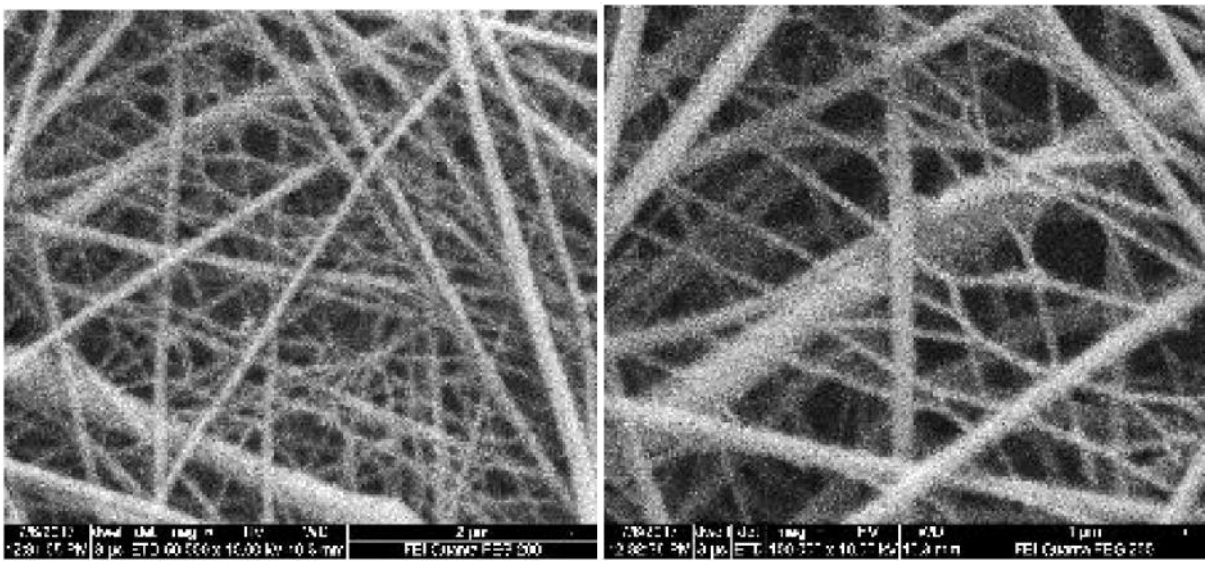


Figure 5. N20FA-EV30 Average fiber dia: 110nm SD 15nm Web dia: 35nm(approx)

Fig. 5 have the SEM images of N20FA-EV30 at the magnification of 2µm and 1µm. The nanowebs produced had much more coverage area than the previous samples but were still not found in the complete sample. Also, the average web diameter was high, i.e., 35 nm.

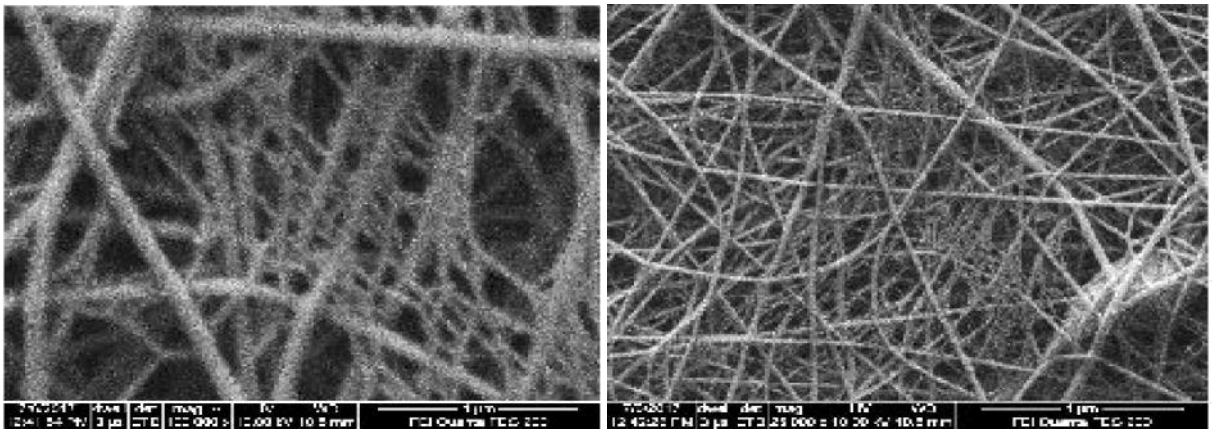


Figure 6. N20FA-EV37.5 Average fiber dia: 102nm Web dia: 30nm(approx)

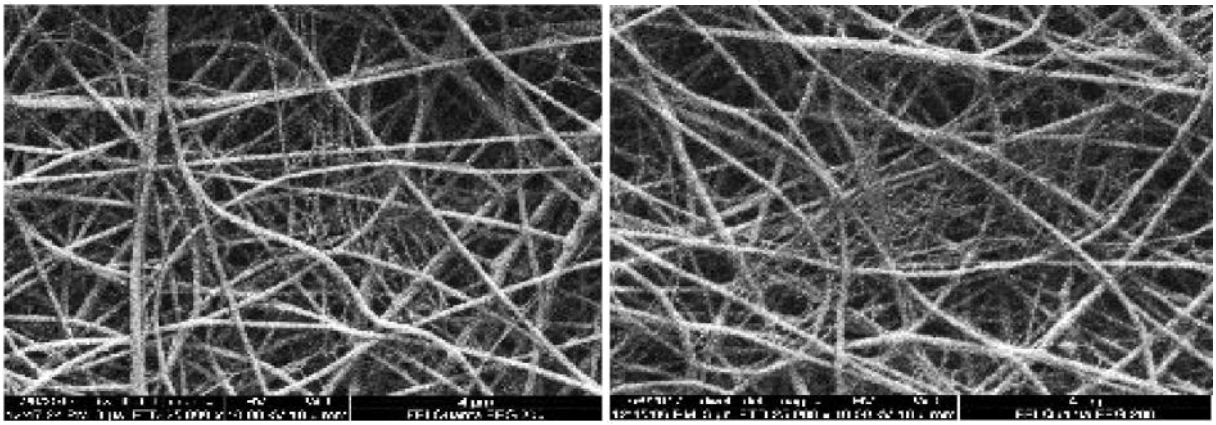


Figure 7. N20FA-EV37.5-Na

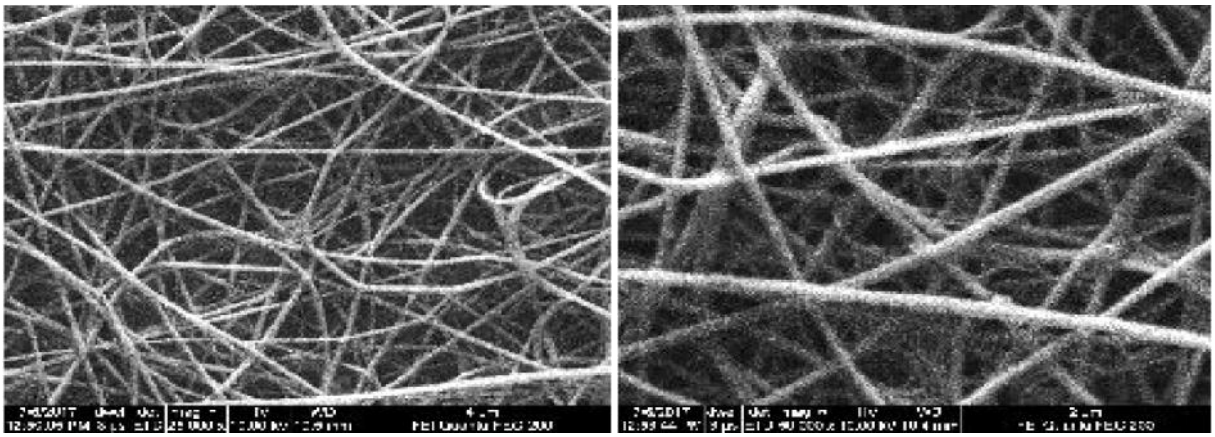


Figure 8. N20FA-EV35-Na

Figure 9. N20FA-EV30-Na

Samples N20FA-EV37.5 and N20FA-EV37.5-Na have been shown in Fig.6 and 7 respectively. The only difference in the two samples is of the presence of sodium salt in the latter. This inorganic salt had effectively negligible effect on the nanoweb formation, as both the samples had similar coverage area.

In the samples, N20FA-EV35-Na and N20FA-EV30-Na the deposition time taken was less, i.e., of less than 5 minutes. Whereas, deposition time taken for other samples is on average around 10 minutes. Low deposition led to incomplete formation of nanowebs as visible in Fig. 8 and Fig.9. It is clearly visible in Fig. 9 that the formation of nanowebs was not fully completed as they have broken ends and low coverage area.

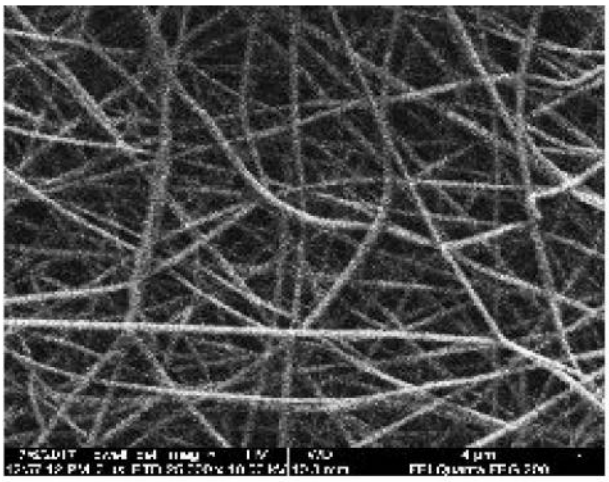


Figure 10. N20FA/AA-EV30

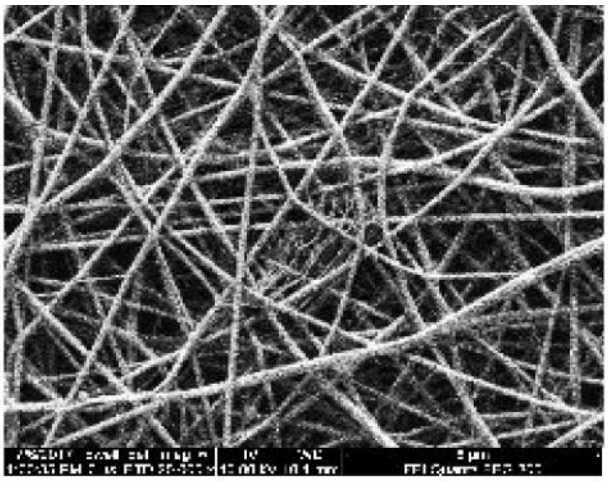


Figure 11. N20FA/AA-EV30-Na

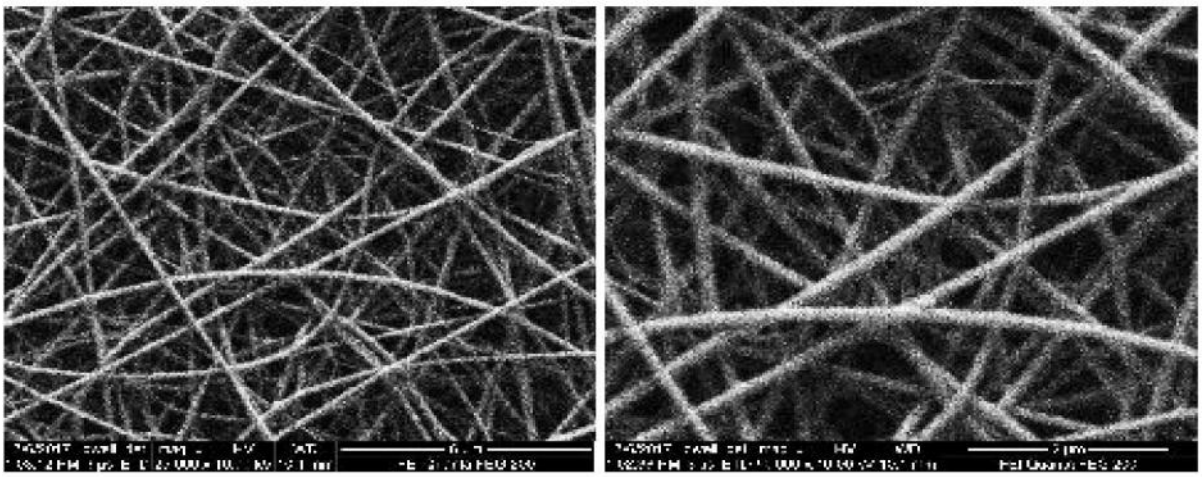


Figure 12. N20FA/AA-EV25.5-Na

Fig. 10. shows nanowebs not uniformly spread over the sample possibly due to moderate effective potential, i.e, of 30kV, also better but similar results were found in sample N20FA/AA-EV30-Na (Fig. 11). By decreasing the effective potential from 30kV in sample N20FA/AA-EV30-Na to 25.5 kV in N20FA/AA-EV25.5-Na (Fig. 12), the expected results were seen, i.e, decrease in nanoweb formation, due to decrease in potential.

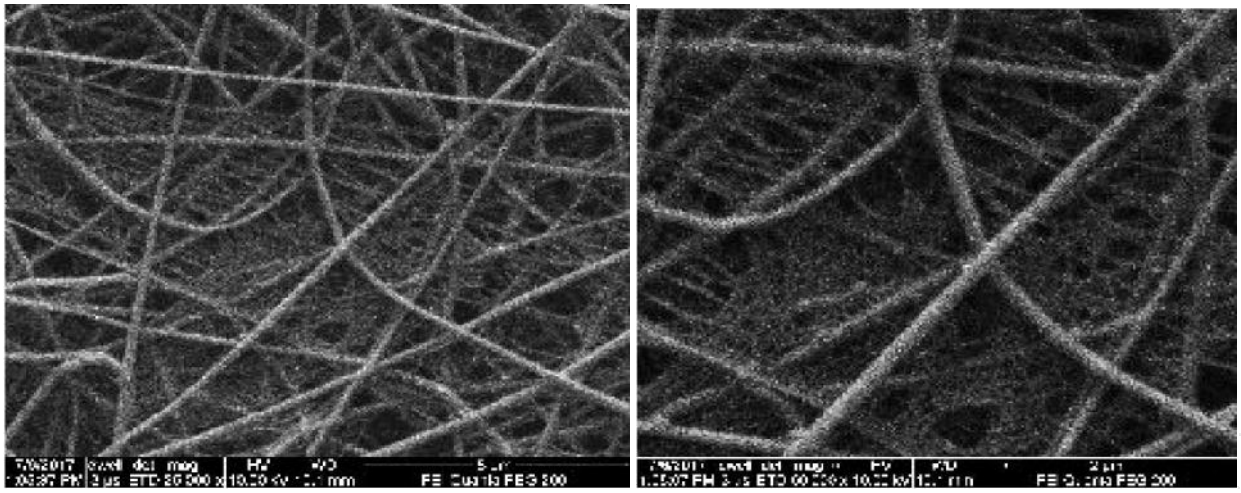


Figure 13. N20FA/AA-EV37.5-Na Fiber Dia: 83nm SD 11nm Web Dia: 20nm(approx)

Fig. 13. shows the sample N20FA/AA-EV37.5-Na which has very good coverage area and also the average nanoweb diameter achieved was 20nm. This is possibly due to several factors such as, high potential, addition of sodium salt and usage of dual solvent system. These webs could have been more individualized by decreasing the relative humidity (less than 40%) and hopefully the average diameter of the webs would have also decreased.

Conclusion

As observed that apart from the right effective potential, which is chosen in accordance with the molecular weight of polymer being spun, other contributing factors like concentration of polymer solution, viscosity and volatility of the polymer solution play an equally important role. Also, presence of salts improve the web density by helping form more connections between two nanofibers.

Apart from these, the environmental factors namely temperature and humidity modify the structure of formed fibers. The best suited factors for low molecular weight nylon are:

Effective Potential- 37.5 V
Nylon Conc.- 20%
Solvent System- Formic Acid +Acetic acid (3:1 w/w)
Salt Conc.- 1.5%
Humidity- 55% (lower humidity is more preferred as evaporation rate improves)
Temperature- RT

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[1] Electro-spinning/netting: A strategy for the fabrication of three-dimensional polymer nano-fiber/nets. Xianfeng Wang, Bin Ding, Gang Sun, Moran Wang, Jianyong Yu
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