Processing Conditions

•Another important parameter that affects the electrospinning process is the various external factors exerting on the electrospinning jet.

•This includes the voltage supplied, the feedrate, temperature of the solution, type of collector, diameter of needle and distance between the needle tip and collector.

•These parameters have a certain influence in the fiber morphology although they are less significant than the solution parameters.

Voltage

The high voltage will induce the necessary charges on the solution and together with the external electric field, will initiate the electrospinning process when the electrostatic force in the solution overcomes the surface tension of the solution.

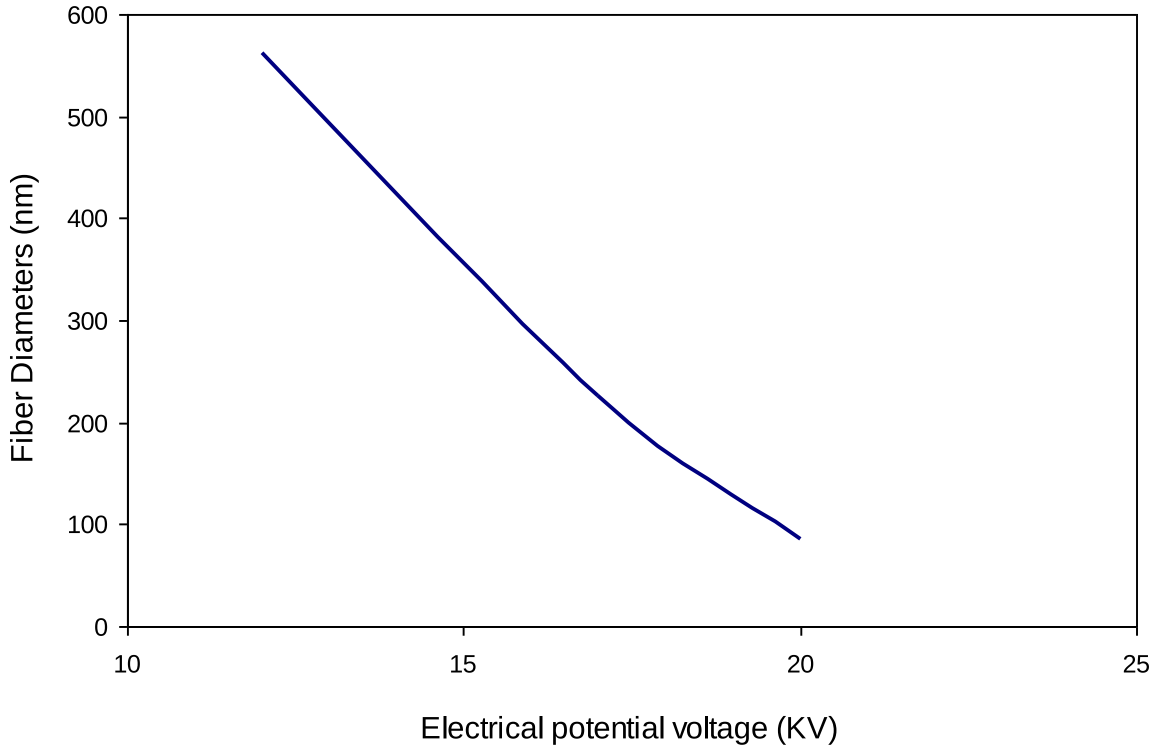
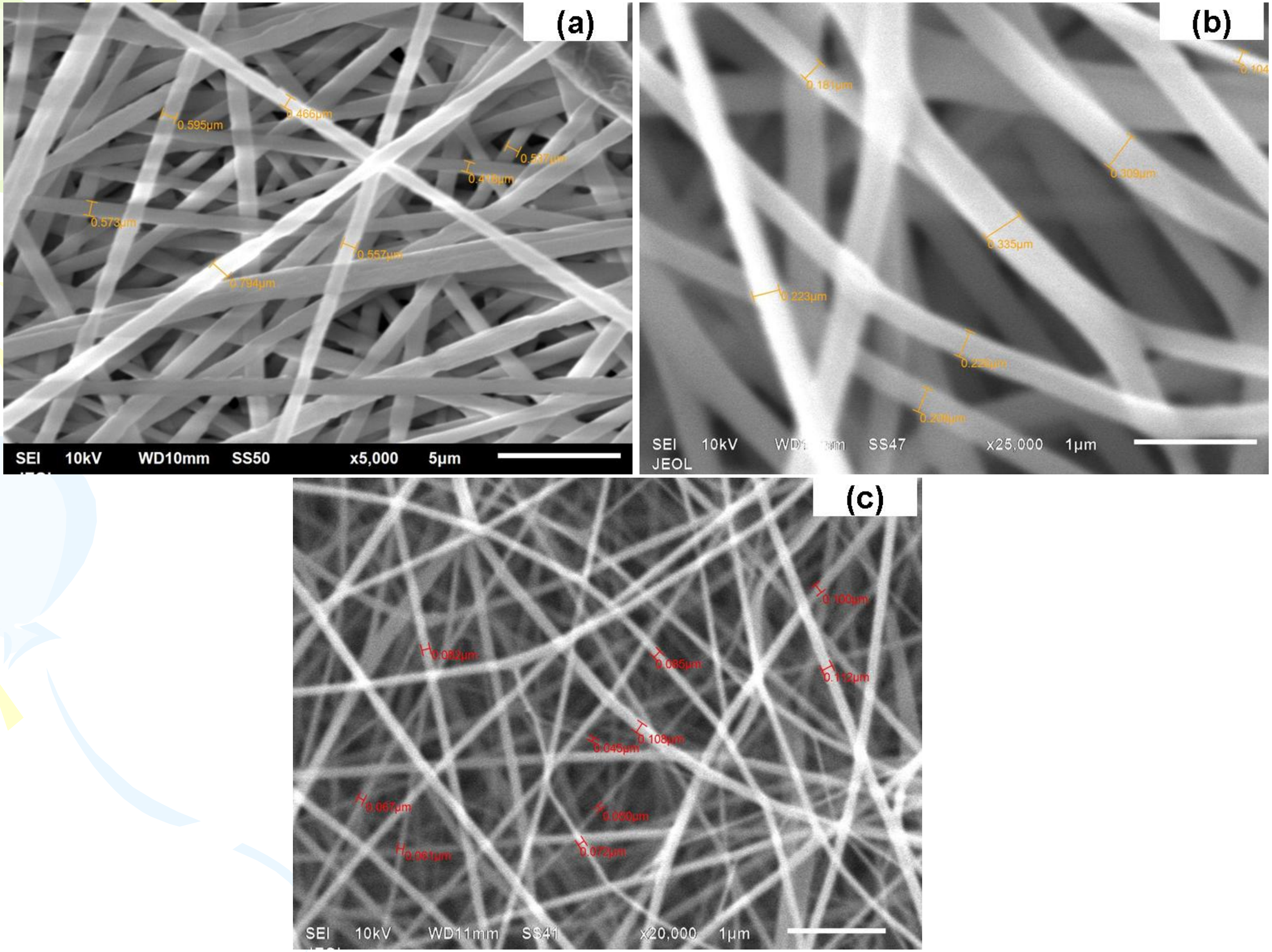


Figure: Effect of electric potential on fiber diameter

Electrical potential Voltage (KV)	12	17	20
Fiber Diameters (nm)	562	226	86



Microstructures showing the effect of electric potential on fiber diameter at constant flow rate, screen distance & concentration. (a) 12 KV, (b) 15 KV, and (c) 20 KV

- ***Feedrate***

- **When the feedrate is increased, there is a corresponding increase in the fiber diameter or beads size as shown in Fig.**

- **This is apparent as there is a greater volume of solution that is drawn away from the needle tip.**

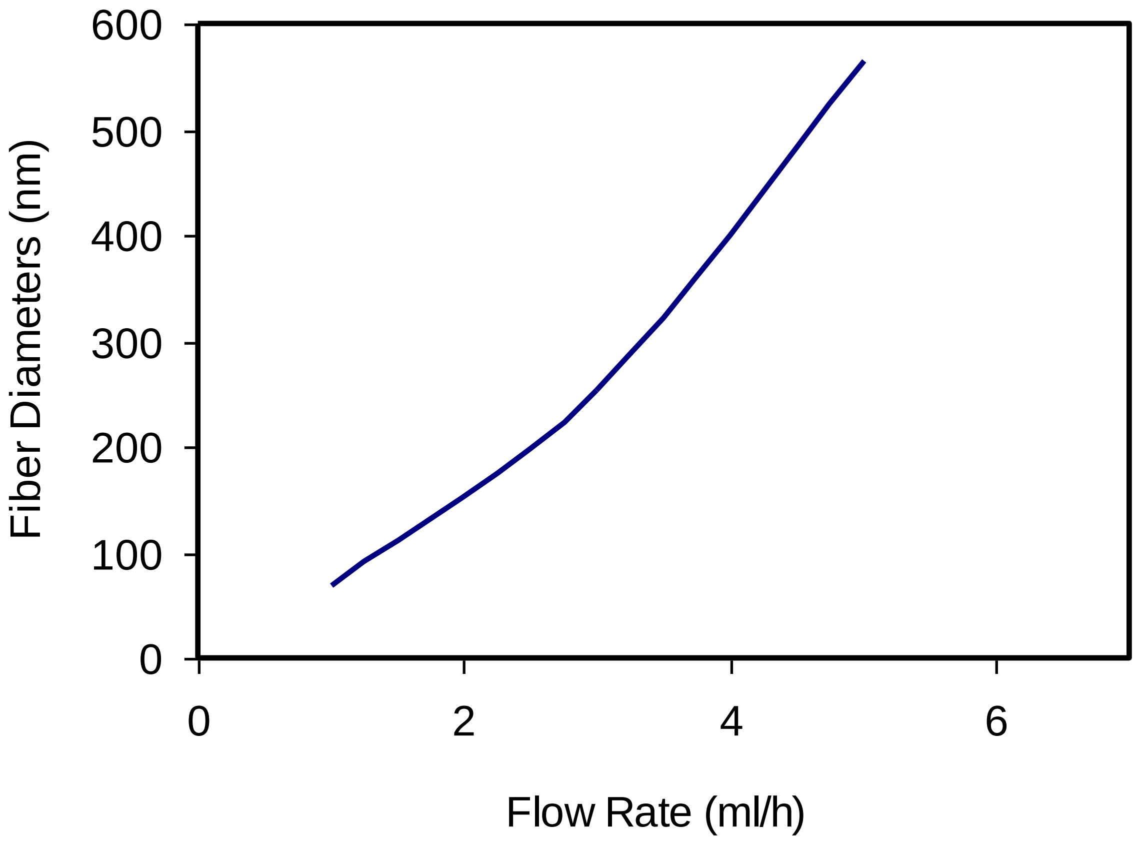
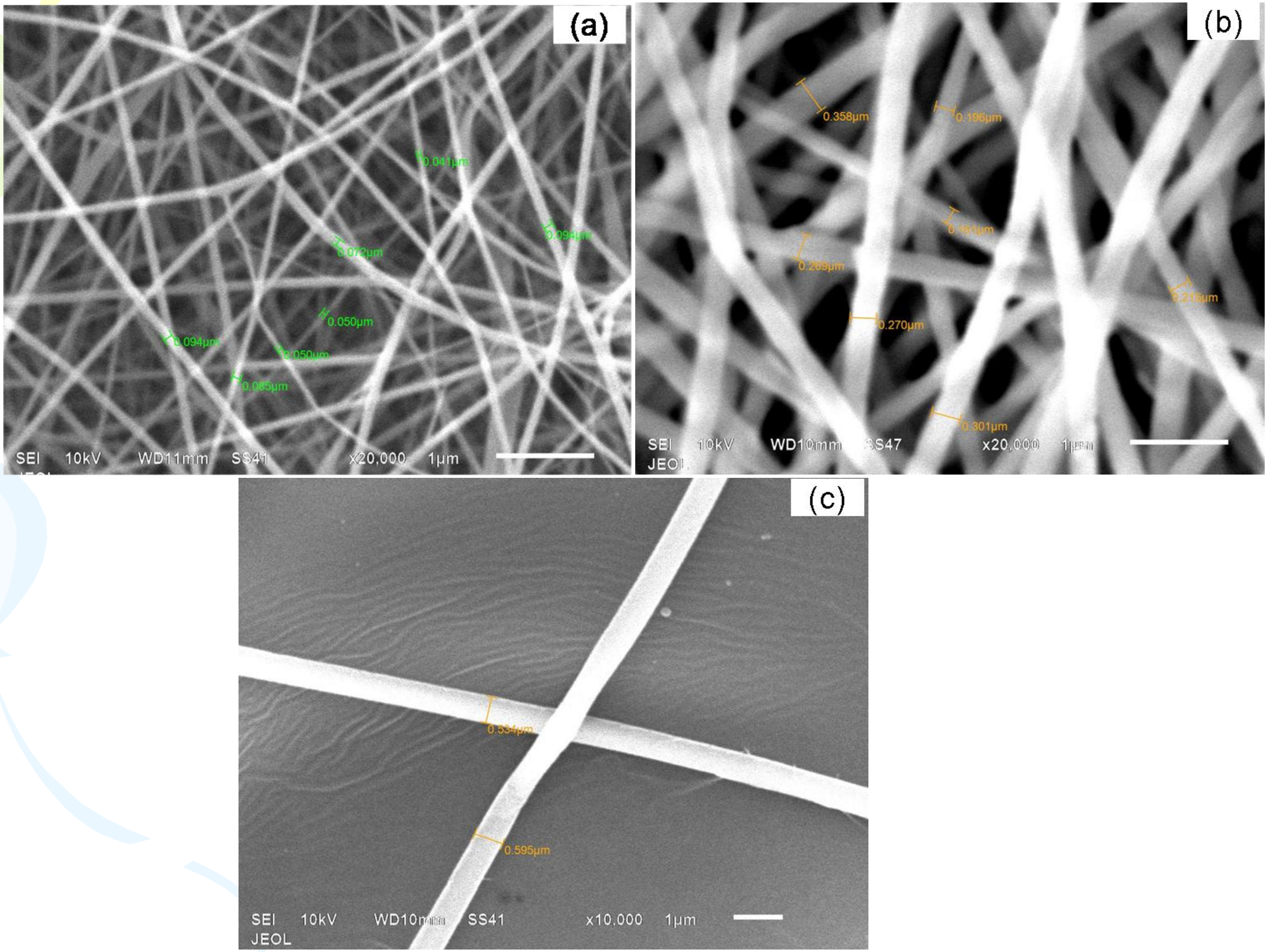


Figure: Effect of feedrate on fiber diameter.

FeedRate (ml/hr)	1	3	5
Fiber Diameters (nm)	69	252	564



Microstructures showing the effect of feedrate on fiber diameter at constant electric potential, screen distance & concentration. (a) 1 ml/h, (b) 3 ml/h, and (c) 5 ml/h

- ***Temperature***
- **The temperature of the solution has both the effect of increasing its evaporation rate and reducing the viscosity of the polymer solution.**

- ***Effect of Collector***
- **There must be an electric field between the source and the collector for electrospinning to initiate.**

- **Thus in most electrospinning setup, the collector plate is made out of conductive material such as aluminum which is electrically grounded so that there is a stable potential difference between the source and the collector.**

- ***Diameter of Pipette Orifice / Needle***
- **The internal diameter of the needle or the pipette orifice has a certain effect on the electrospinning process.**

- **A smaller internal diameter was found to reduce the clogging as well as the amount of beads on the electrospun fibers**

• *Distance between Tip and Collector*

- **Varying the distance between the tip and the collector will have a direct influence in both the flight time and the electric field strength.**
- **Increasing the distance results in a decrease in the average fiber diameter.**

- **The longer distance means that there is a longer flight time for the solution to be stretched before it is deposited on the collector.**

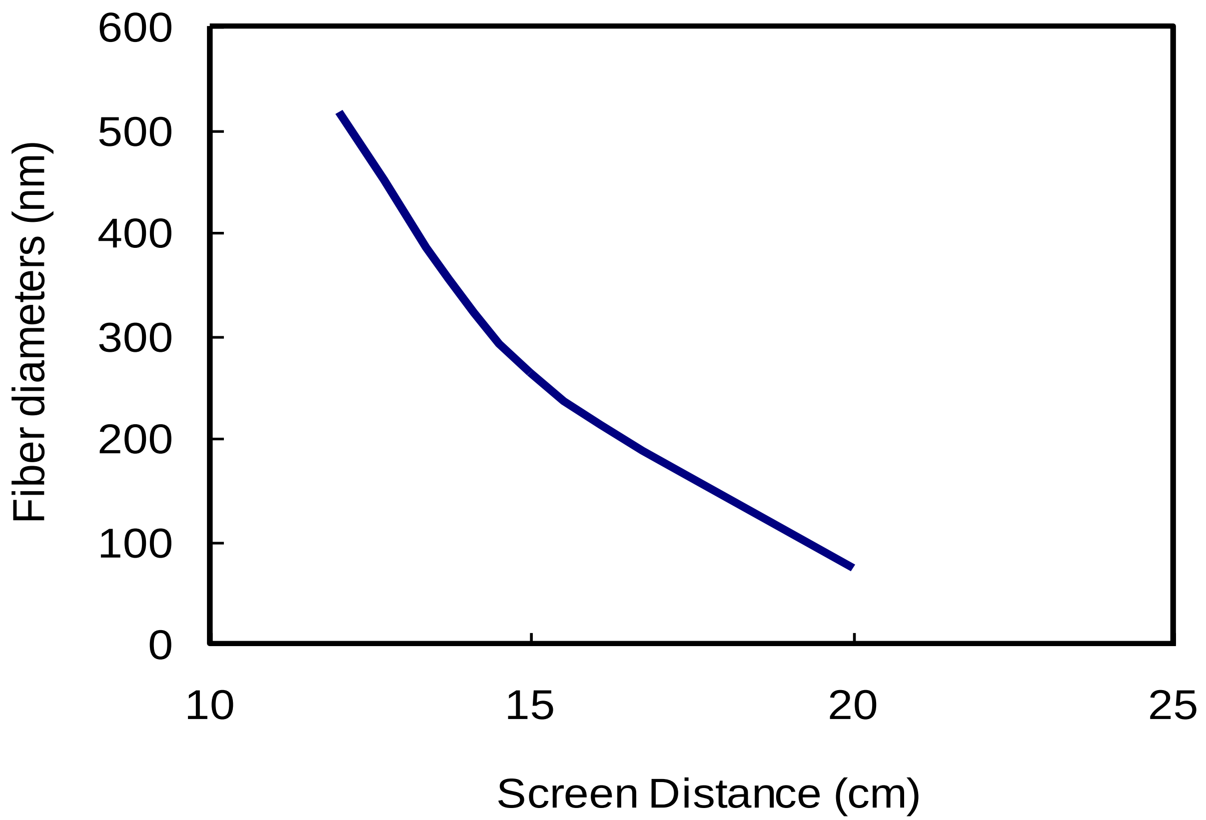
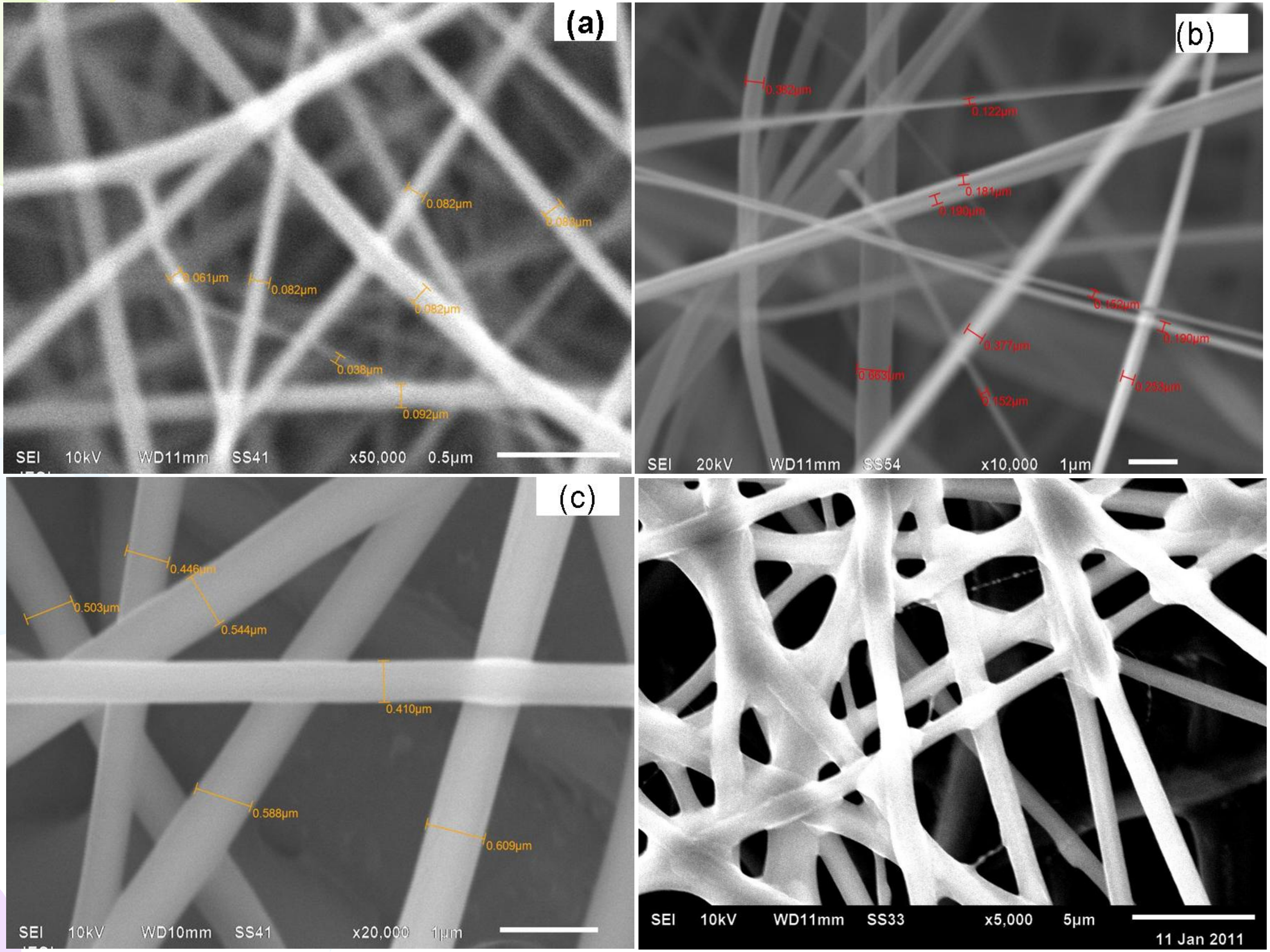


Figure: Effect of screen distance on fiber diameter at constant electric potential, flow rate & concentration

Screen Distance (cm	20	15	12
Fiber Diameters (nm)	74	264	516



Microstructures showing the effect of screen distance on fiber diameter at constant electric potential, flow rate & concentration. (a) 20 cm, (b) 15 cm, (c) 12 cm and (d) 10 cm

Ambient Parameters

•The humidity of the electrospinning environment may have an influence in the polymer solution during electrospinning.

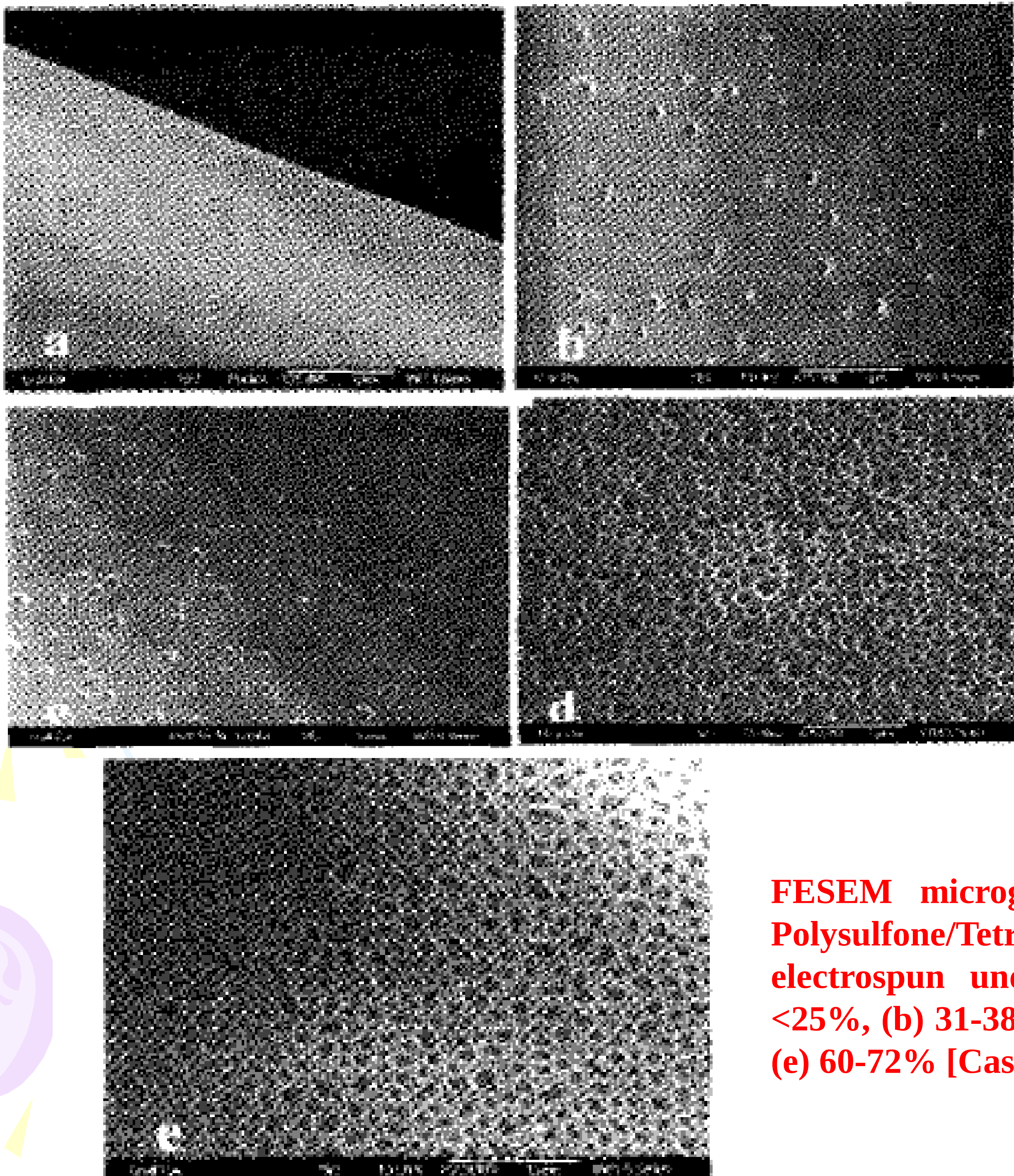
•At high humidity, it is likely that water condenses on the surface of the fiber when electrospinning is carried out under normal atmosphere.

•As a result, this may have an influence on the fiber morphology especially polymer dissolved in volatile solvents.

•However, an increased in the humidity during electrospinning will cause circular pores to form on the fiber surfaces.

•The sizes of the circular pores increases with increasing humidity until they coalescence to form large, non-uniform shaped structures.

•The humidity of the environment will also determine the rate of evaporation of the solvent in the solution.



FESEM micrographs of 190 000 g/mol Polysulfone/Tetrahydrofuran fibers electrospun under varying humidity: (a) <25%, (b) 31-38%, (c) 40-45%, (d) 50-29%, (e) 60-72% [Casper et. al. (2004)].

Type of Atmosphere

•The composition of the air in the electrospinning environment will have an effect on the electrospinning process. Different gases have different behavior under high electrostatic field.

•Pressure

•Under enclosed condition, it is possible to investigate the effect of pressure on the electrospinning jet.

•Generally, reduction in the pressure surrounding the electrospinning jet does not improve the electrospinning process.

•When the pressure is below atmospheric pressure, the polymer solution in the syringe will have a greater tendency to flow out of the needle and there causes unstable jet initiation.

•As the pressure decreases, rapid bubbling of the solution will occur at the needle tip.

•At very low pressure, electrospinning is not possible due to direct discharge of the electrical charges.

Electrical conductivity of solvents.

Solvent	Conductivity (mS/m)	Reference
1,2-Dichloroethane	0.034	Jarusuwannapoom et. al. (2005)
Acetone	0.0202	Theron et. al. (2004)
Butanol	0.0036	Prego et. al. (2000)
Dichloromethane/ Dimethylformamide (40/60)	0.505	Theron et. al. (2004)
Dichloromethane/ Dimethylformamide (75/25)	0.273	Theron et. al. (2004)
Dimethylformamide	1.090	Jarusuwannapoom et. al. (2005)
Distilled Water	0.447	Theron et. al. (2004)
Ethanol	0.0554	Prego et. al. (2000)
Ethanol (95%)	0.0624	Theron et. al. (2004)
Ethanol/Water (40/60)	0.150	Theron et. al. (2004)
Methanol	0.1207	Prego et. al. (2000)
Propanol	0.0385	Prego et. al. (2000)
Tetrahydrofuran/Ethanol (50/50)	0.037	Theron et. al. (2004)

To increase the conductivity of the solution at the same time reducing the surface tension, ionic surfactant [Lin et. al. (2004)] such as triethyl benzyl ammonium chloride can be added.

- ***Solution Conductivity***
- **If the conductivity of the solution is increased, more charges can be carried by the electrospinning jet.**
- **The conductivity of the solution can be increased by the addition of ions.**
- **Beads formation will occur if the solution is not fully stretched.**
- **Therefore, when a small amount of salt or polyelectrolyte is added to the solution, the increased charges carried by the solution will increase the stretching of the solution.**
- **Solution prepared using solvents of higher conductivity generally yield fibers without beads while no fibers are formed if the solution has zero conductivity**

Table 3.3. The boundary condition of electrical conductivity between uniform and beaded nanofibers.

Polymer	Molecular Weight	Solvent	Boundary Condition of Electrical Conductivity	Other Spinning Parameters
Poly(ethylene oxide), **PEO** [Fong et. al. (1999)]	Mw = 900,000	Water (NaCl addition)	Uniform Fibers: NaCl addition (0.3~1.5 wt%) Solution Resistivity (1.9~0.462 Wm) Beaded Fibers: NaCl addition (0.0015~0.15 wt%) Solution Resistivity (83.4~3.61 Wm)	Polymer Concentration: 3 wt% Voltage: 15 kV Distance: 21.5 cm
Collagen-Polyethyleneoxide, **Collagen-PEO** [Huang et. al. (2001a)]	900 kDa	Hydrogen Chloride (NaCl addition)	Uniform Fibers: NaCl addition (68 mmol/l) Solution Conductivity(--- ms) Beaded Fibers: NaCl addition (15~34 mmol/l) Solution Conductivity(1.5 ~2.3 ms)	Polymer Concentration: 2 wt% Voltage: 18 kV Distance: 15 cm Feed Rate: 6 ml/h
Poly(D,L-lactic acid), **PDLA** [Zong et. al. (2002)]	----------	DMF (1wt% KH_2PO_4, NaH_2PO_4 and NaCl addition)	Uniform Fibers: KH_2PO_4 addition (AFD = 1000 nm) NaH_2PO_4 addition (AFD = 330 nm) NaCl addition (AFD = 210nm)	Polymer Concentration: 30 wt% Voltage: 20 kV *Distance: 15 cm* Feed Rate: 1.2 ml/h

- ***Dielectric Effect of Solvent***
- **The dielectric constant of a solvent has a significant influence on electrospinning. Generally, a solution with a greater dielectric property reduces the beads formation and the diameter of the resultant electrospun fiber.**
- **Solvents such as N,N-Dimethylformamide (DMF) may added to a solution to increase its dielectric property to improve the fiber morphology. The bending instability of the electrospinning jet also increases with higher dielectric constant. This is shown by increased deposition area of the fibers.**
- **This may also facilitate the reduction of the fiber diameter due to the increased jet path.**

Dielectric constant of solvents.

Solvent	Dielectric constant	Reference
2-Propanol	18.3	MERCK technical data sheet
Acetic acid	6.15	Wannatong et. al. (2004)
Acetone	20.7	Berkland et. al. (2004)
Acetonitrile	35.92-37.06	Wannatong et. al. (2004)
Chloroform	4.8	Berkland et. al. (2004)
Dichloromethane	8.93	Yang et. al. (2004c)
Dimethylformamide	36.71	Yang et. al. (2004c)
Ethyl acetate	6.0	Berkland et. al. (2004)
Ethanol	24.55	Yang et. al. (2004c)
m-Cresol	11.8	Wannatong et. al. (2004)
Methanol	32.6	MERCK technical data sheet
Pyridine	12.3	MERCK technical data sheet
Tetrahydrofuran	7.47	Wannatong et. al. (2004)
Toluene	2.438	Wannatong et. al. (2004)
Trifluoroethanol	27.0	Berkland et. al. (2004)
Water	80.2	MERCK technical data sheet

Table 3.1 (b). The boundary condition of polymer concentration between uniform and beaded nanofibers.

Polymer	**Molecular Weight**	**Solvent**	**Boundary Condition of Polymer Concentration**	**Other Spinning Parameters**
Poly(trimethylene terephthalate), PTT , [Khil et. al. (2004)]	----------	Trifluoroacetic Acid (TFA) / MC (50:50)	Uniform Fibers: 13~16 wt% Beaded Fibers: 5~10 wt%	Voltage: 13 kV Distance: 13 cm
Poly(ethlene terephthalate-co-ethylene *isophtalate*), PET-*co*-PEI [McKee et. al. (2003)]	Mw = 76,000	Chloroform / DMF (70:30)	Uniform Fibers: 20 wt% Beaded Fibers: 16~18 wt%	Voltage: 18 kV Distance: 24 cm Feed Rate: 3 ml/h
Poly(3-hydroxybutyrate-co-hydroxyvalerate), PHBV, [Choi et. al. (2004a)]	Mw = 680,000	Chloroform	Uniform Fibers: 20 wt% Beaded Fibers: 13~17 wt%	Voltage: 15 kV Distance: 15 cm Feed Rate: 5 ml/h
Polyamide-6, PA-6 [Mit-uppatham et. al. (2004)]	17,000 Da	Formic Acid	Uniform Fibers: 32~46 w/v% Beaded Fibers: 20~24 w/v%	Voltage: 21 kV Distance: 10 cm
Poly(vinyl chloride), PVC [Lee et. al. (2002)]	----------	THF / DMF (50:50)	Uniform Fibers: 15 wt% Beaded Fibers: 10 & 13 wt%	Voltage: 15 kV Distance: 10 cm
Polystylene, PS [Lee et. al. (2003c)]	Mw = 140,000	THF / DMF (50:50)	Uniform Fibers: 15 wt% Beaded Fibers: 7~13 wt%	Voltage: 15 kV Distance: 12 cm
Poly(methyl methacrylate, PMMA [McKee et. al. (2004)]	Mw = 210,000	Chloroform / DMF (40:60)	Uniform Fibers: 8~10 wt% Beaded Fibers: 5~7 wt%	Voltage: 22 kV Distance: 24 cm Feed Rate: 6 ml/h
Poly(methyl methacrylate-co-SCMHB methacrylic acid), PMMA-co-SCMHB [McKee et. al. (2004)]	Mw = 183,000	Chloroform / DMF (40:60)	Uniform Fibers: 8.5~9 wt% Beaded Fibers: 4~7 wt%	

Da (Dalton): A unit of mass that equals the weight of a hydrogen atom, or 1.657 x 10-24 grams

- ***Surface Tension***
- **The initiation of electrospinning requires the charged solution to overcome its surface tension.**
- **Solvent such as ethanol has a low surface tension thus it can be added to encourage the formation of smooth fibers.**
- **Another way to reduce the surface tension is to add surfactant to the solution.**
- **The addition of surfactant was found to yield more uniform fibers. Even when insoluble surfactant is dispersed in a solution as fine powders, the fiber morphology is also improved.**