EFFECT OF MOLECULAR WEIGHT ON THE MORPHOLOGY OF ELECTROSPUN POLY(VINYL ALCOHOL) NANOFIBERS

Çiğdem Akduman[1], **E.Perrin Akçakoca Kumabasar**[2], **Ahmet Çay**[2]
[1] *Pamukkale University / Denizli Vocational School of Technical Sciences /Denizli, Turkey*
[2] *Ege University /Faculty of Engineering, Department of Textile Engineering /Izmir, Turkey*
cakduman@pau.edu.tr

ABSTRACT

Morphological characteristics of electrospun PVA nanofibers were investigated in terms of polymer molecular weight was reported in this paper. The change in the morphology depending on the polymer concentration of electrospinning solution and the applied voltage were addressed. The fiber diameter increased with the increase in the molecular weight and polymer concentration and applied voltage and the average nanofiber diameter variation was found to be between 175.83 and 735.69 nm.

Key Words: Electrospinning, PVA, nanofiber, molecular weight

1. INTRODUCTION

PVA has the largest volume within the water-soluble polymer production of the world [1] and it is semi-crystalline, hydrophilic polymer with good chemical and thermal stability [2]. Due to biocompatibility, nontoxicity, hydrophilicity and ease of processability of PVA, electrospun PVA nanofibers have been one of the most extensively studied topics [3,4] and they are considered as a potential polymer for biotechnological applications [5-7]

Although PVA have advantageous properties, higher solubility in water results in stability problems thereby limiting its applications [8]. Therefore, crosslinking of PVA nanofiber web [9] is carried out to produce nanowebs with poorer solubility characteristics in which polymer chains are joined together to form three-dimensional network structure and improve mechanical properties. Crosslinking of PVA nanofibres can be carried out by two methods, including chemical and physical crosslinking techniques. The principle of chemical crosslinking is to create permanent and irreversible covalent bonds between the polymer chains [10, 11] while physical crosslinking is mainly based on the increase in crystallinity of resultant fibers.

Furthermore, PVA based nanofibers and nanofiber composites have been considered as an attractive choice in tissue scaffolding [6,12], filtration materials [13, 14], protective clothing, wound dressing [15], drug release [16], medical [17,18] and biosensor applications [19], and so on.

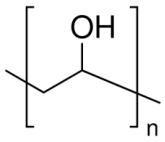
In this paper, morphological characteristics of electrospun PVA nanofibers were investigated in terms of polymer molecular weight. The change in the morphology depending on the polymer concentration of electrospinning solution and the applied voltage were also addressed.

2. EXPERIMENTAL

Three types of PVA (Figure 1) with average molecular weights of 89,000-98,000 g/mol, ~125,000 g/mol and 146,000-186,000 g/mol was obtained from Sigma Aldrich Chemical Company. PVA was dissolved in water at 100°C and stirred for 4 h with the concentrations given in Table 1. Electrospinning of the prepared solutions was carried out by a set-up consisting of a high-voltage DC power supply (Simco, MP Series CM5 30 P, Charging Generator Output 30 kV DC), a 10 ml syringe with a needle of 22 gauge flat-tipped stainless steel. Stationary rectangular metal collector covered by a piece of aluminum foil was used as the fiber collecting area. The electrostatic field strength was changed as 12, 15 and 18 kV at the tip to collector distance of 15 cm. The feed rate of the solutions was controlled at about 0.5 ml/h using a syringe pump. The complete electrospinning apparatus was enclosed in a glass box and the electrospinning of the nanofibers was carried out at room temperature.

a) b) c)

$[-CH_2CHOH-]_n$



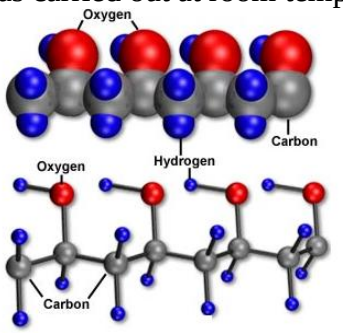


Figure 1 Linear Formula (a) and Molecular Structure (b) 3D ball representation (c) of Poly(vinyl alcohol) [12-13]

Table 1. Weight average molecular weight (Mw) and concentration of PVA used in this study

Average Molecular Weights of PVA (g/mol)	Concentration (w/v)
89,000-98,000	8%
	10%
	12%
~125,000	8%
	10%
	12%
146,000-186,000	6%
	8%
	10%

The morphological appearance of electrospun PVA mats was observed by Hitachi TM-1000 Tabletop Microscope. The mean diameter of the resultant fibers was calculated from the measurements of fiber diameters on the images of 10000× magnification by using Image J program. Approximately 30 measurements were carried out from the different parts of each sample. Incase of beaded nanofibers, largest parts of the beads and diameter of connecting nanofibers were measured.

3. RESULTS AND DISCUSSION

Figures 2, 3 and 4 illustrates the SEM images of collected elctrospun PVA mats with average molecular weight of 89,000-98,000 g/mol, ~125,000 g/mol and 146,000-186,000 g/mol, respectively. Based on these images, mean diameter of the fibers, standart error of mean, standart deviation, range, minimum and maximum values are given in Table 2.

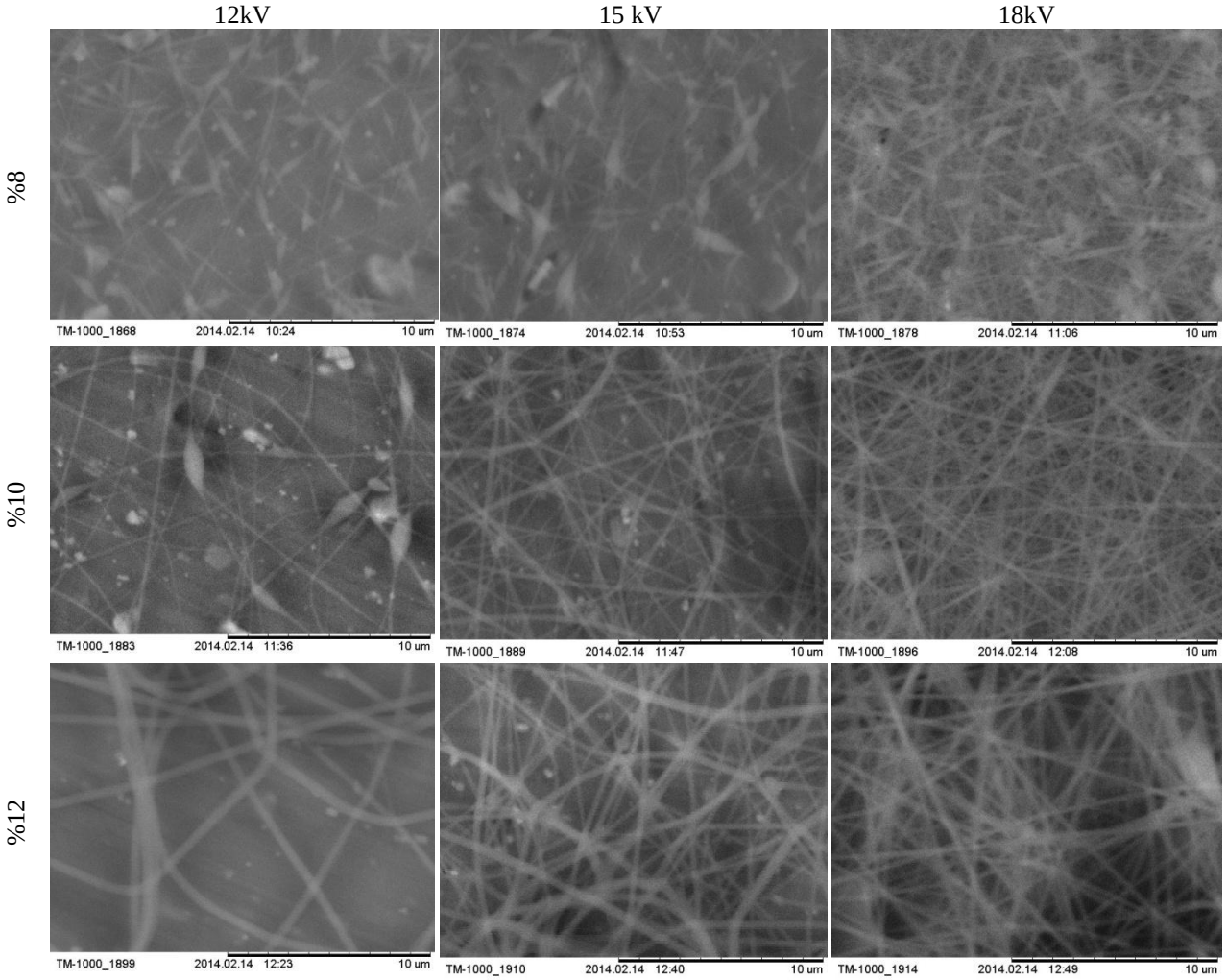


Figure 2 Images of average molecular weight of 89,000-98,000 g/mol at concentrations of 8-10 and 12% at 15 cm tip to collection distance with 0.5 ml/h feeding rate

Typical structures showing the effect of concentration are shown in Figure 2 for Mw 89,000-98,000 g/mol. At a constant molecular weight, as the applied voltage was increased, the structural features change from beaded fibers with round beads (8%- 12 and 15 kV) to beaded fibers with spindle-like beads (8%-18 kV). On the other hand as the concentration was increased, the structural features change from beaded fibers (8%-15 kV) to stable circular fibers (10%-15kV and 12%-15 kV). At 8% of polymer concentration, chain entaglements were not enough to maintain the continuity of the polymer jet. Increasing the applied voltage, favored the thinner fiber formation as it can be seen for 10 and 12 % polymer concentration (Table 2). A narrow distributions of fiber diameters were observed at voltages of 15–18 kV, while broad distribution in the fiber diameter was obtained at a lower applied voltage of

12kV. Additionally finest nanofibers from PVA with the molecular weight of 89,000-98,000 g/mol was obtained at %10 PVA concentration and an applied voltage of 18 kV with narrower distrubution (SE: 5.71, Table 2).

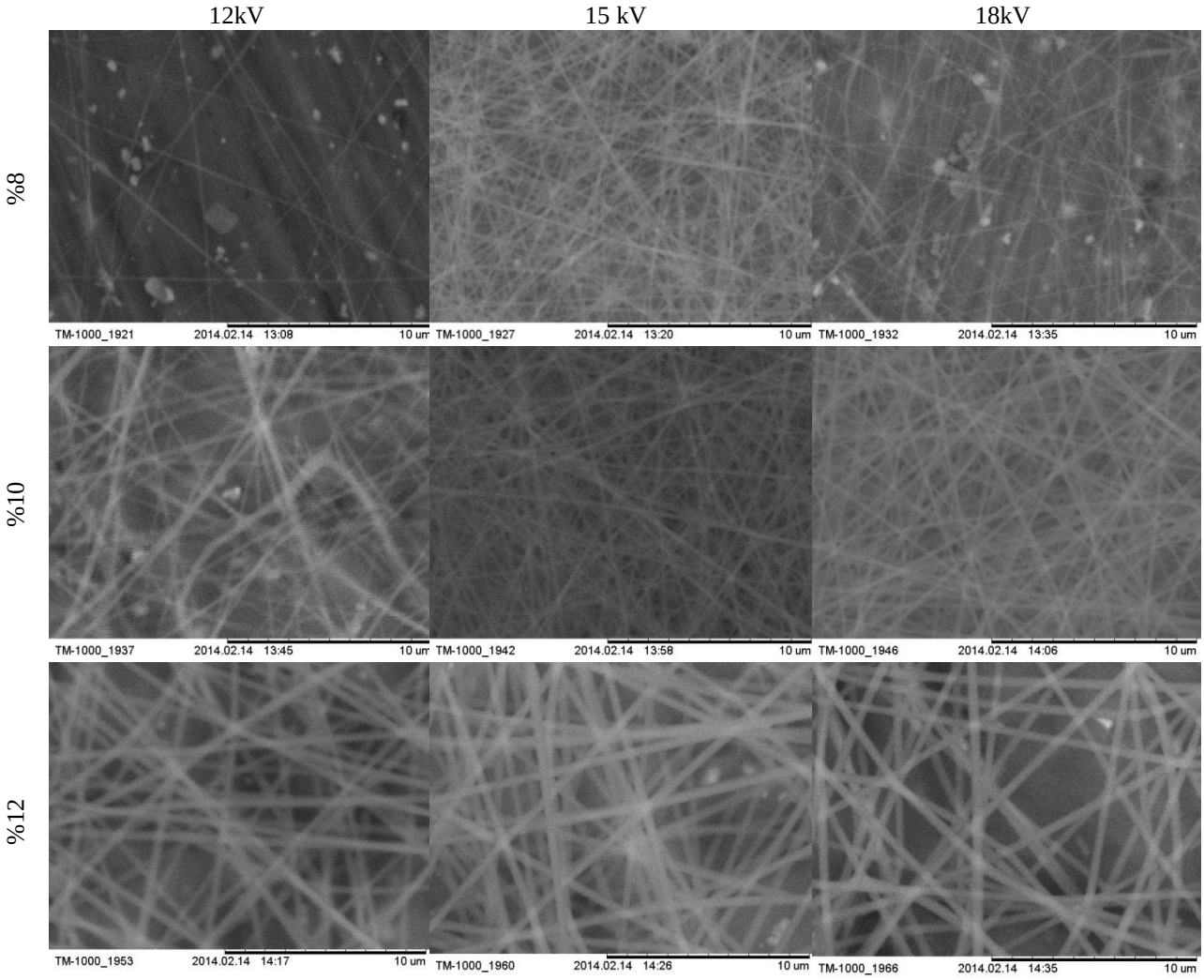


Figure 3 Images of average molecular weight of ~125,000 g/mol at concentrations of 8-10 and 12% at 15 cm tip to collection distance with 0.5 ml/h feeding rate

Comparing the images of Figure 2 and Figure 3, more uniform fibers were obtained with the increased molecular weight. Contrary to PVA with 89,000-98000 g/mol molecular weight, no bead formation was observed in any polymer concentration for PVA with ~125,000 g/mol molecular weight (Figure 3). There was a slight increase in average fiber diameter with increasing applied electric field. Because, when the applied voltage is higher, the greater amount of charges caused the jet to accelerate faster and more volume of PVA solution was drawn from the tip of the needle and resultant fiber diameters were thicker (Table 2). Also, as expected with increasing concentration, the average fiber diameter was also increased from 157.1 ± 6.32 nm (8%, 12 kV) to 403.03 ± 11.04 nm (12%, 18 kV) because of the increase in the viscosity. Finest fibers were obtained at 8% polymer concentration and applied voltage of 12 kV. However 12 kV was too low for optimum spinnability of the solution and a lot of

eruptions were seen. Therefore, it can be said that finest and most spinnable nanofibers were electrospun from 8% PVA (~125.000 g/mol) at 15 kV with lowest standart error (Table 2).

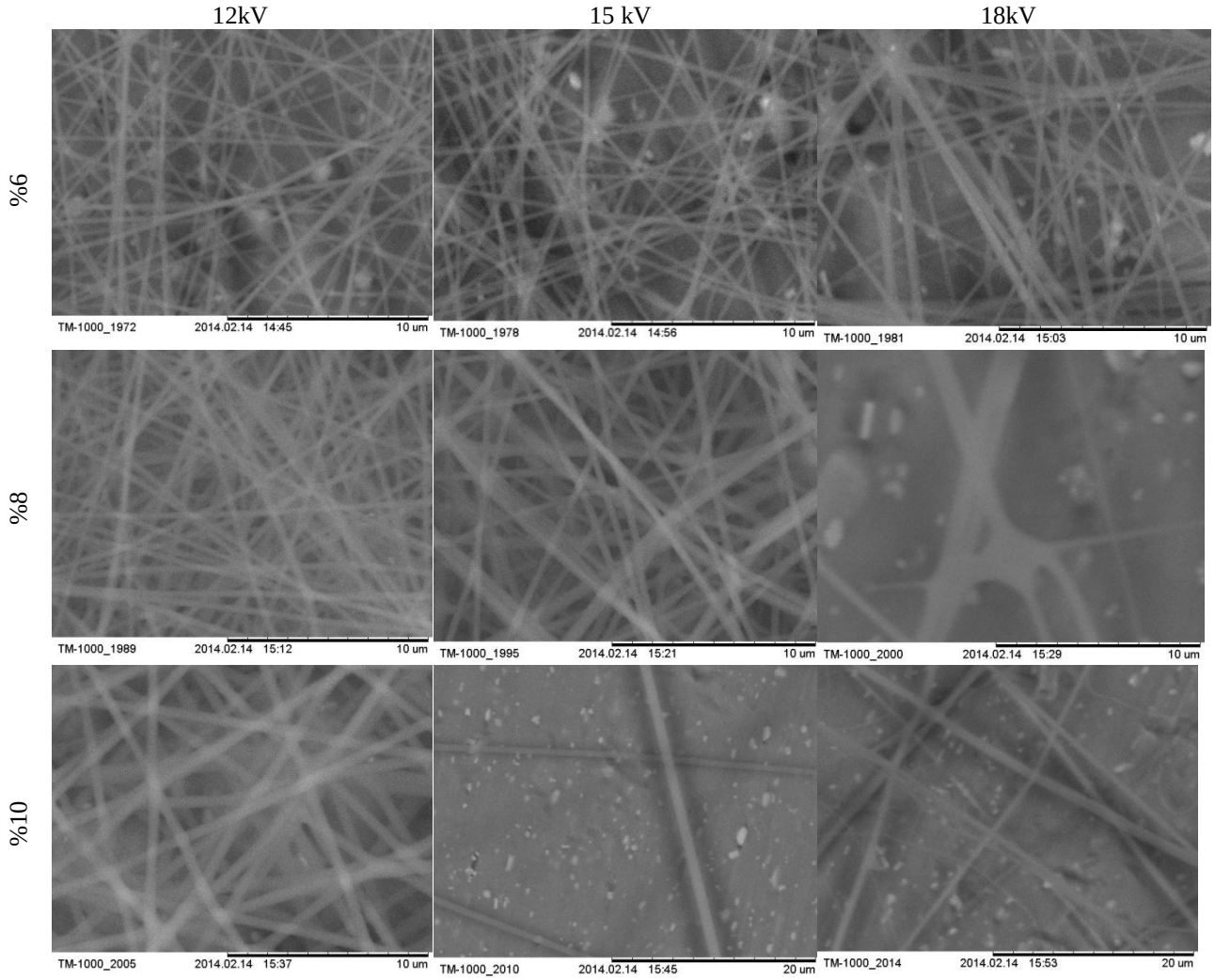


Figure 4 Images of average molecular weight of 146,000-186,000 at concentrations of 8-10 and 12% at 15 cm tip to collection distance with 0.5 ml/h feeding rate

In case of PVA with a molecular weight of 146,000-186,000 g/mol (Figure 4), 6, 8, and 10% of polymer concentrations was selected. Over 10% of polymer concentration, it was too high to pump the solution from spinneret due to very high viscosity and accordingly the images 6% of polymer concentration was favorable for uniform fibers. Confirming the effect of applied voltage for the aforementioned PVA's, at 6% polymer concentration of PVA with the molecular weight of 146,000-186,000 g/mol the average diameter of the measured fibers was increased with increasing voltage. On the other hand, especially at 10% polymer concentration, PVA solution was too viscous and over 12 kV, it was not possible to achive a continuous jet. Thicker fibres and very loose structures were observed. Considering the applied voltage as 12 kV, as the concentration was increased, resultant fibers became thicker from 248,12 nm to 542,42 nm. Finest and most easily spinnable nanofibers were electrospun from 6% PVA (146,000-186,000 g/mol) at an applied voltage of 12 kV.

Table 2. Mean Diameter, Std. Error of Mean, Std. Deviation, Range Minimum and Maximum values of electrospun PVA nanofibers

Mw 89.000-98.000									
	8%			10%			12%		
	12 kV	15 kV	18 kV	12 kV	15 kV	18 kV	12 kV	15 kV	18 kV
Mean Diameter	Beads: 556.21 Fibers: 184.69	Beads: 695.19 Fibers: 112.39	243.69	Beads: 787.92 Fibers: 159.77	218.55	172.08	426.30	303.95	239.63
Std. Error of Mean	46.40	69.56	14.64	47.88	14.31	5.71	15.82	13.42	6.89
Std. Deviation	207.49	311.07	80.20	283.24	78.39	33.29	75.89	80.55	34.47
Range	626.34	823.94	263.10	1001.06	355.86	142.18	237.91	286.41	129.37
Minimum	81.41	71.19	125.00	79.26	90.36	99.21	314.03	196.24	194.45
Maximum	707.75	895.12	388.10	1080.31	446.22	241.40	551.95	482.65	323.82
Mw ~125.000									
	8%			10%			12%		
	12 kV	15 kV	18 kV	12 kV	15 kV	18 kV	12 kV	15 kV	18 kV
Mean Diameter	157.10	175.83	182.43	242.81	254.98	263.52	403.03	421.14	438.00
Std. Error of Mean	6.32	5.80	10.88	9.39	9.89	5.38	11.04	9.05	8.75
Std. Deviation	30.98	33.79	70.50	50.57	60.14	33.14	60.45	49.54	51.03
Range	127.85	188.73	331.63	224.08	242.57	187.73	252.99	204.74	203.51
Minimum	116.23	107.05	104.97	144.10	168.83	199.72	286.48	305.16	347.31
Maximum	244.08	295.78	436.60	368.17	411.41	387.44	539.47	509.90	550.82
Mw 146.000-186.000									
	6%			8%			10%		
	12 kV	15 kV	18 kV	12 kV	15 kV	18 kV	12 kV	15 kV	18 kV
Mean Diameter	248.12	264.17	288.25	357.02	392.13	916.78	542.42	735.69	796.38
Std. Error of Mean	9.10	8.11	14.37	7.28	13.62	119.24	8.98	59.75	60.40
Std. Deviation	52.29	44.43	78.69	39.85	74.62	337.25	49.21	179.25	200.31
Range	241.77	218.26	364.05	178.65	395.26	937.80	190.94	671.76	692.96
Minimum	154.59	158.74	182.03	269.21	270.42	586.70	460.98	490.21	476.68
Maximum	396.36	377.00	546.08	447.87	665.67	1524.50	651.92	1161.97	1169.64

The average fiber diameter is plotted as a function of molecular weight and concentration in Figure 5. The average fiber diameter is generally between 175.83 to 735.69 nm and increases with concentration at a given molecular weight. Increase in the molecular weight of PVA increased the resultant fiber diameter due to higher number of chain entanglements and increased viscosity. Also, Koski et al. [3] concluded that the elongation tendency of polymeric chains during electrospinning becomes more difficult as the molecular weight increases, which decreases the splitting and splaying of the jet. This effect leads to increase in fibre diameter.

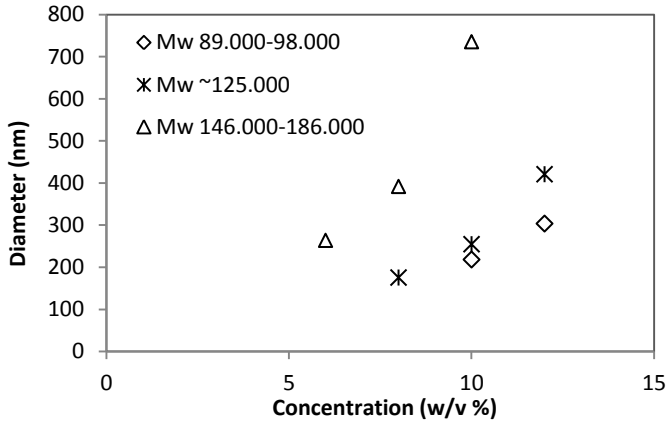


Figure 5 Average fiber diameter as a function of concentration and molecular weight. Mw 89.000-98.000, Mw~125.000 and Mw146.000-186.000 (g/mol) at applied voltage of 15 kV

4. CONCLUSIONS

The properties of the PVA polymer solution have the most significant influence in the electrospinning process and the resultant fiber morphology. One of the factors that affect the resultant fiber morphology is the molecular weight of the PVA. Higher molecular weight resulted higher viscosity and higher number of chain entanglements which means thicker fibers. Another way to increase the viscosity of the solution is to increase the polymer concentration. At each molecular weight, as polymer concentration increases, average fiber diameters increased Another important factor that affecting the fiber morphology was applied voltage, there was a slightly increase in average fiber diameter with increasing applied voltage.

5. REFERENCES

[1] MARTEN, F., Vol.8:Vinyl Alcohol Polymers, In Encyclopedia Of Polymer Science and Technology, Edited by MARK, H.F., John Wiley & Sons, 2004, ISBN: 978-0-471-27507-7.
[2] SHAO, C., KIM, H., GONG, J., LEE, D., and PARK, S., Fiber mats of poly(vinyl alcohol)/silica composite via electrospinning, Materials Letters,2003, vol. 57, pp. 1579-1584.
[3] KOSKI, A., YIM, K. and SHIVKUMAR, S., Effect of molecular weight on fibrous PVA produced by electrospinning, Materials Letters, 2004, vol. 58, pp 493–497.
[4] LEE, J.S., CHOI, K.H., GHIM, H.D., KIM, S.S., CHUN, D.H., KIM, H.Y. and LYOO,W.S., Role of Molecular Weight of Atactic Poly(vinyl alcohol) (PVA) in the Structure and Properties of PVA Nanofabric Prepared by Electrospinning, Journal of Applied Polymer Science, 2003, vol. 93, pp.1638–1646.
[5] TANG, X. and ALAVI, S., Recent advances in starch, polyvinyl alcohol based polymer blends, nanocomposites and their biodegradability, Carbohydrate Polymers,2011, vol. 85, no.1, pp. 7-16.
[6] LINH, N.T.B. and LEE, B., Electrospinning of polyvinyl alcohol/gelatin nanofiber composites and cross-linking for bone tissue engineering application, Journal of Biomaterials Applications, 2012, vol. 27 no.3, pp. 255-266.
[7] RAHMAN, W.A.W.A., SIN, L.T., RAHMAT, A.R. and SAMAD, A.A., Thermal behaviour and interactions of cassava starch filled with glycerol plasticized polyvinyl alcohol blends. Carbohydrate Polymers,2010, vol. 81, no.4, pp. 805-810.
[8] COOK J.G., Handbook of textile fibre-II manmade fibres, Merrow publishing co. ltd.1984

[9] CAY, A. and MIRAFTAB, M., Properties of Electrospun Poly(vinyl alcohol) Hydrogel Nanofibers Crosslinked with 1,2,3,4-Butanetetracarboxylic Acid, Journal of Applied Polymer Science, 2013, vol.129, no.6, 3140-3149
[10] RATANAVARAPORN, J., RANGKUPAN, R., JEERATAWATCHAI, H., KANOKPANONT, S. and DAMRONGSAKKUL, S., Influences of physical and chemical crosslinking techniques on electrospun type A and B gelatin fiber mats, International journal of biological macromolecules, 2010, vol.47, no.4, pp. 431-438.
[11] HOFFMAN, A.S., Hydrogels for biomedical applications, Advanced Drug Delivery Reviews, 2002, vol. 54, no.1, pp. 3-12.
[12] DRURY, J.L. and MOONEY, D.J., Hydrogels for tissue engineering: scaffold design variables and applications, Biomaterials, 2003, vol.24, no.24, pp. 4337–4351.
[13] QIN, X. and WANG, S., Filtration properties of electrospinning nanofibers, Journal of Applied Polymer Science, 2006, vol. 102, no.2, pp.1285-1290
[14] LIU, Y., WANG, R:, MA, H., HSIAO, B.S. and CHU, B., High-flux microfiltration filters based on electrospun polyvinylalcohol nanofibrous membranes, Polymer, 2013, vol.54, pp. 548-556.
[15] HONG, K.H., PARK, J.Y., SUL, I.H.,YOUK, J.H. and KANG, T.J., Preparation of Antimicrobial Poly(vinyl alcohol) Nanofibers Containing Silver Nanoparticles Journal of Polymer Science: Part B: Polymer Physics, 2006, vol. 44, pp. 2468–2474.
[16] KENAWY, E., ABDEL-HAY, F.I., EL-NEWEHY, M.H. and WNEK, G.E., Controlled release of ketoprofen from electrospun poly(vinyl alcohol) nanofibers, Materials Science and Engineering, 2007, vol. 459, pp. 390–396
[17] MIKOLAJCZYK, T., RABIEJ, S., BOGUN, M., SZPARAGA, G. and DRACZYNSKI, Z., Nanocomposite polyvinyl alcohol fibers for medical applications, Journal of Applied Polymer Science, 2011, vol. 120, no.2, pp.1234-1244.
[18] JIA, Y., GONG, J., GU, X., KIM, H., DONG, J. and SHEN, X., Fabrication and characterization of poly (vinyl alcohol)/chitosan blend nanofibers produced by electrospinning method, Carbohydrate Polymers, 2007, vol. 67, pp. 403-409.
[19] REN, G., XU, X., LIU, Q., CHENG, J., YUAN, X. and WAN, L.W.Y., Electrospun poly(vinyl alcohol)/glucose oxidase biocomposite membranes for biosensor applications, Reactive & Functional Polymers, 2006, vol. 66, pp. 1559–1564.