ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

EFFECT OF SOLUTION PROPERTIES ON FIBER DIAMETERS OF POLYVINYL ALCOHOL NANOFIBROUS MATS

KOC Muhammed Zahid [1], KESKIN Reyhan [2]

[1] Pamukkale University, Graduate School of Natural and Applied Sciences, Textile Engineering, Denizli, TURKEY, E-mail: mzahidkoc87@gmail.com

[2] Pamukkale University, Engineering Faculty, Dept. of Textile Engineering, Kinikli, 20070, Denizli, TURKEY, E-mail: reyhank@pau.edu.tr

Corresponding author: Keskin, Reyhan, E-mail: reyhank@pau.edu.tr

Abstract: *In this study, PVA (polyvinyl alcohol) solutions with different concentrations (8, 10, 12, 14, 16 and 18 wt %) were prepared and nanofibers were produced with changing system parameters via electrospinning. Image analysis was performed after FESEM analysis using Image J programme. Prior to electrospinning, properties of solutions were measured, nanofiber diameter distributions were calculated and relationship between electrical conductivity and nanofiber average diameters was evaluated. In this study, we aimed to assess relation between solution properties and fiber diameter of produced nanofibrous mats. We obtained increased viscosity with increased solution concentration in our study; on the other hand there was not a proportional increase either in electrical conductivity or in surface tension of the solutions. Increasing solution viscosity gives higher nanofiber diameter; in our study we observed a general increase tendency in diameter; however, a diameter decrease from 14 wt % to 16 wt % increase in solution concentration is observed as well. We obtained 145.9 nm thickenesses in 16 wt % solutions and they were thinner than nanofibers produced from 14 wt % and 18 wt % solutions. Our fiber diameter averages show a tendency of being indirectly proportional with the exponential of electrical conductivity (*$\mathbf{1 / \tau_e^{0.1}}$*) compared to the mathematical formulation relationship stated in a previous literature study conducted by An et al.*

Key words: *Nanofibrous mats, polyvinyl alcohol, viscosity, electrical conductivity, surface tension.*

1. INTRODUCTION

During electrospinning Taylor cone forms and propagates jet formation followed by nanofiber production. There are many parameters affecting nanofiber structure in electrospinning such as voltage, flow rate, solution concentration, viscosity, distance between needle and collector, polymer and its molecular weight, solvent type, additives and surfactants added to solution [1-7].

Surface tension is an important factor affecting jet formation during electrospinning [1]. Zhang et al observed that increasing voltages caused increases in fiber diameters; also, they concluded that distance between needle and collector did not have a strong effect on morphology of nanofibers produced [2]. Koski et al found that increasing molecular weight causes increases in nanofiber diameters [3]. Tsai studied which concentrations are suitable for electrospinning with PVA (polyvinyl alcohol) polymers and suggested 9-17 wt % solutions for PVA polymers at 50 000-85 000 g/mol range [4]. In literature, there are several studies on the effects of parameters on nanofibers showing either similar or conflicting tendencies to previous studies [5-7]. As Subbiah et al reviewed, an era for mathematical formulations on electrospun nanofibers started in 1914 with Zeleny's study on the fluid behavior to electrostatic forces [8]. In this study, we aimed to assess relation between solution properties and fiber diameter of produced nanofibrous mats.

2. EXPERIMENTAL APPROACH

2.1 Materials and Method

With partially hydrolyzed polyvinylalcohol (PVA) with a molecular weight of 70 000 g/mol (Merck) and distilled water solutions were stirred using specific weights of PVA and water, Table 1, at $80^{o}C$ in 3 hours at 600 rpm; and were kept at 200 rpm until production. The viscosities and electrical conductivities were measured respectively with Brookfield DV50 viscometer and ADWA brand AD32 conductivity meter. Surface tension measurements were done using the droplet method using Pasteur pipettes. Table 2 lists measured properties of PVA solutions used in the study.

The production of pure PVA nanofibrous mats was done on a laboratory scale one-nozzled electrospinning machine (Inovenso, model Ne 100) using 23-28 kV voltage ranges. FESEM (Field Emission Scanning Electron Microscopy) analysis was conducted at backscattering mode on a Zeiss Supra 40 VP model. Figure 1 shows image of nanofiber produced with 8 wt % solution. Fiber diameter distributions were obtained by Image J software using around 100 fibers on FESEM image. Table 3 gives properties of nanofibrous mats produced in the study.

Table 1: *The parameters of PVA solutions used in the study*

Solution	PVA wt%	water (g)	PVA (g)
A	8 wt %	92	8
B	10 wt %	90	10
C	12 wt %	88	12
D	14 wt %	86	14
E	16 wt %	84	16
F	18 wt %	82	18

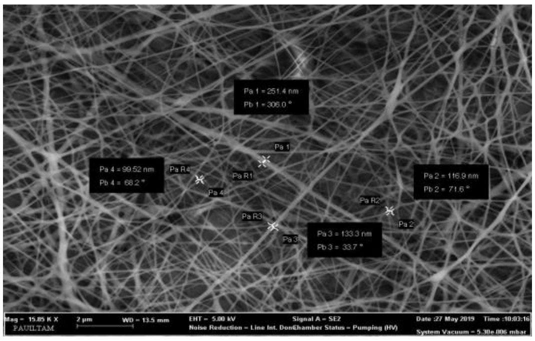

Fig. 1: *8 wt% PVA solution. 28 kV voltage, 10 cm distance, 0.1 ml/h flow rate (sample A)*

An et al (2014) studied the effects of viscosity, electrical conductivity and surface tension of solution on droplet formation during direct electrohydrodynamic printing which forms a Taylor cone as well and experimented that droplet formation was not giving directly proportional results to neither viscosity nor surface tension and electrical conductivity and found that the number of droplets formed in a time interval has a limitation to have Taylor cone formation. Researchers devised a dimensionless coefficient `$C_u$` ,given in Formula 1, to show relations of droplet formation and viscosity, surface tension and electrical conductivity besides other affecting factors [9].

***Table 2:** Viscosities, electrical conductivities and surface tensions of PVA solutions used in the study*

Solution	PVA wt%	viscosity (cP)	Electrical conductivity (μS/cm)	Surface tension (dyne/cm)
A	8 wt %	84	0.85	61.12
B	10 wt %	137.6	0.87	59.97
C	12 wt %	221	0.88	58.17
D	14 wt %	244	0.89	56.77
E	16 wt %	404	1.05	55.77
F	18 wt %	913.3	0.91	62.44

***Table 3:** Properties of nanofibrous mats produced in the study*

Sample	Voltage (kV)	distance (cm)	Flow rate (ml/h)	Nanofiber diameter (nm)	Standard Deviation
A	28	10	0.1	139.7	0.600
B	23	10	0.1	142.4	0.539
C	24	10	0.1	154.5	0.580
D	24	10	0.1	202	0.857
E	27	10	0.1	145.9	0.538
F	24	10	0.1	213.2	0.103

***Table 4:** Calculations for electrical conductivity of PVA solutions*

Sample	$\tau_e^{0.1}$	$1 / \tau_e^{0.1}$
A	0.983	1.017
B	0.986	1.014
C	0.987	1.013
D	0.988	1.012
E	1.0049	0.995
F	0.99	1.010

$$C_u = Re^{10} \times We \times N_e \times \frac{\tau_f}{\tau_e^{0.1}} = \frac{(\rho u D)^{11}}{2} \left(\frac{V}{\sigma}\right)^2 \frac{K^{0.1} \varepsilon^{0.9}}{\mu^{10}} \qquad \textbf{(1)}$$

Where:
Re: is the Reynolds number (about viscosity),
We: is the Weber number (about surface tension) and
τ_e: is the electrical conductivity

We decided to compare our results with the calculations of electrical conductivity factor in the formula of An et al. The calculations for electrical conductivity values of our study are given in Table 4. Our results show similarity with the formulation suggested by An et al. Our fiber diameter averages show a tendency of being indirectly proportional with the mathematical relation suggested for electrical conductivity as an exponential of electrical conductivity (**$1 / \tau_e^{0.1}$**) formulated; however, researchers stated that drop generation will become unstable if electrical conductivity is increased and when there is decreased viscosity and decreased surface tension [9].

2.2 Results

In the equation given in Formula 1, viscosity has a high effect while electrical conductivity has a small effect. The formula suggested by An et al is suitable for our nanofiber diameters as the electrical conductivity increased in `solution E` leads to thinner nanofibers compared to nnaofibers producedfrom solution D and solution F.

3. CONCLUSIONS

We obtained increased viscosity with increased solution concentration in our study; on the other hand there was not a proportional increase either in electrical conductivity or in surface tension of the solutions. Increasing solution viscosity gives higher nanofiber diameter [2]; in our study we observed a diameter decrease from 14 wt % to 16 wt % increase in solution concentration. We obtained 145.9 nm thickenesses in 16 wt % solutions and they were thinner than nanofibers produced from 14 wt % and 18 wt % solutions. Our fiber diameter averages show a tendency of being indirectly proportional with the mathematical relation suggested for electrical conductivity as an exponential of electrical conductivity ($\mathbf{1 / \tau_e^{0.1}}$) formulated by An et al [9].

ACKNOWLEDGEMENT

This research was supported by Pamukkale University Scientific Research Projects Institute (PAUBAP) under the project number 2013FBE024.

REFERENCES

[1] J. Zhao, Z. Sun, Z. Shao, and L. Xu, "*Effect of surface-active agent on morphology and properties of electrospun PVA nanofibers*" Fibers and Polymers, vol 17, pp 896-901, 2016.

[2] C. Zhang, X. Yuan, L. Wu, Y. Han, and J. Sheng, "*Study on morphology of electrospun poly(vinly alcohol) mats*", European Polymer Journal, vol 41, pp 423-432, 2005.

[3] A. Koski, K. Yim, S. Shivkumar, *"Effect of molecular weight on fibrous PVA produced by electrospinning"*, Materials Letters, vol 58, pp 493– 497, 2004.

[4] P.P. Tsai, W. Chen and J.R. Roth, *"Investigation of meltblown microfiber and electrospun nanofiber fabrics treated with a one atmosphere uniform glow discharge plasma (OAUGDP)"*, Proceedings of the 13th International TANDEC Nonwovens Conference, pp 1-23, Knoxville, USA, 2003.

[5] C. Burger, B. S. Hsiao, and B. Chu, *"Nanofibrous Materials and Their Applications"*, Annual Review of Materials Research, vol 36, 333–368, 2006.

[6] S.Rafiei, S.Maghsoodloo, M.Saberi, S.Lotfi, V. Motaghitalab, B.Noroozi and A.K. Haghi, "*New horizons in modeling and simulation of electrospun nanofibers: A detailed review*", Cellulose Chemistry and Technology, vol. 48, pp. 401-424, 2014.

[7] D.H. Reneker, A. Yarin, E. Zussman, S. Koombhongse and W. Kataphinan, "*Nanofiber manufacturing: Toward better process control*", in Polymeric Nanofibers, H. Fong, Ed. New York, United States of America: American Chemical Society, 2009, pp 7-20, ISBN 9780841239197.

[8] T. Subbiah, G.S. Bhat, R.W. Tock, S. Parameswaran and S.S. Ramkumar, "*Electrospinning of nanofibers*", Journal of Applied Polymer Science, vol. 96, pp. 557-569, 2005.

[9] S. An, M,W, Lee, NY Kim, C Lee, SS Al-Deyab, SC James and SS Yoon, "*Effect of viscosity, electrical conductivity and surface tension on direct-current- pulsed drop-on-demand electrohydrodynamic printing frequency*", Applied Physics Letters, vol. 105, 2014.