

EXPERIMENTAL INVESTIGATION OF SALT EFFECT ON ELECTROSPINNING PARAMETERS AND NANOFIBER MORPHOLOGY

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Abstract

Dependent parameters such as throughput, throughput/jet, current, current/jet, number of jets, spinning area on the roller and distance between jets were studied for selected polymer solution forming high quality nanofibers via needleless electrospinning. The density of fiber-forming jets is controlled by conductivity of polymer solution. Conductivity affect the fiber morphology and diameter. The objective of research was to obtain finer and non-fibrous fiber morphologies with appropriate productivity, via controllable solution property for further applications.

Keywords: Needleless electrospinning, PEO, throughput, current

1. INTRODUCTION

Nanofibers gain big interest last decades due to their unique and specific properties. The aimed application area of electrospun fibers include tissue engineering scaffolds¹, wound dressing²⁻³, blood vessels⁴, drug delivery and release control⁵⁻⁶, filters⁷⁻⁸, catalyst⁹ and enzyme carriers¹⁰, sensors¹¹⁻¹², etc. Electrospinning is one of the most popular method to produce nanofibers for forming fibers with submicron-scale diameters through the action of electrostatic forces. Interest in the electrospinning process has increased in recent years. The process of the basic needle electrospinning is well described in many papers¹³⁻¹⁴.

Various production methods have been developed recently for higher productivity. Lin et al.¹⁵ divided these methods in two groups such as downward multi-jet electrospinning and upward needleless electrospinning. In this work an upward needleless electrospinning is used. This technology is known as roller electrospinning system with the trade name Nanospider. The basic elements of electrospinning are simple to implement and explained in previous study¹⁶. Roller electrospinning system is suitable for production in industrial scale.

As a consequence of both commercial and scientific interest in electrospinning and nanofibers, much effort has been made to understand and control the process and system parameters. The purpose of the current work is to look systematically at the effects of process parameters on the structure and morphology of electrospun polyethylene oxide (PEO) fibers. It was found that significant changes in fiber diameter, size distribution, morphology and productivity accompany changes in these variables.

2. MATERIAL AND METHODS

PEO was purchased from Sigma Aldrich. The weight average molecule weight (Mw) of PEO was 400.000. This material was dissolved in distilled water. 5% wt. of PEO solutions was prepared in various content of lithium chloride (LiCl) salts. LiCl salts were prepared according to molar ratio as 0, 0.024 and 0.062 and 0.124 mol/L. Conductivity (Radelkis OK-102/1), viscosity (HaakeRotoVisco 1 at 23 C°), surface tension

(Krüss K9) tests were done. Polymer solution was spun by using roller electrospinning system as nominated in Fig. 1.

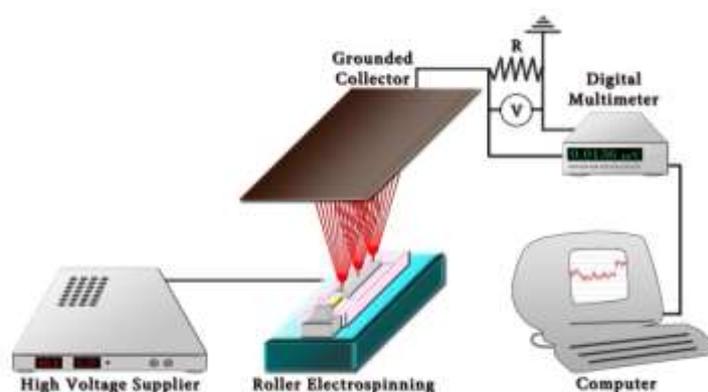


Fig. 1. Image of roller electrospinning system.

Spinning conditions of PEO with and without salt content are shown in Table 1.

Sample	Distance between electrodes	Applied voltage	Rotating roller speed	Roller diameter	Temperature	Humidity
0	150 mm	42 kV	1.5 rpm	20 mm	25±1 °C	25±1 %
0.024	150mm	42 kV	1.5 rpm	20 mm	25±1 °C	25±1 %
0.062	150mm	42 kV	1.5 rpm	20 mm	25±1 °C	25±1 %
0.124	150mm	42 kV	1.5 rpm	20 mm	25±1 °C	25±1 %

The polymer throughput of the roller electrospinning process was calculated from the area weight and width of the nanofiber layer and from the velocity of the backing material, using formula¹⁶. The density of jets was calculated by using digital camera (Sony Full HD NEX-VG10E Handy cam). Distance between jets was calculated according to formula¹⁷. The voltage is measured by a 33401 A digital multimeter produced by Agilent and stored on a computer and has a resistance R is equal to 9811Ω. Current was calculated by using Ohm's law.

3. RESULTS AND DISCUSSION

PEO solutions were electrospun in order to investigate the effects of process parameters of electrospinning. It was found that solution properties are the main factors influencing the diameter and spinning performance^{14,16}. Surface tension, conductivity and viscosity of solution are tabulated in Table 2. Table 2 shows that adding salt influence only conductivity of solution. In this work the only solution parameter which has effective role on spinning result is conductivity.

Table 2. Solution properties of PEO with and without salt.

5%PEO+salt	Viscosity (Pa.s)	Conductivity (mS/cm)	Surface tension (mN/m)
0	0.167±0,1	0.158±0,1	59.2±2
0.024	0.184±0,1	3.027±0,1	60.8±2
0.062	0.155±0,1	5.928±0,1	62.2±2
0.124	0.162±0,1	10.944±0,1	61.5±2

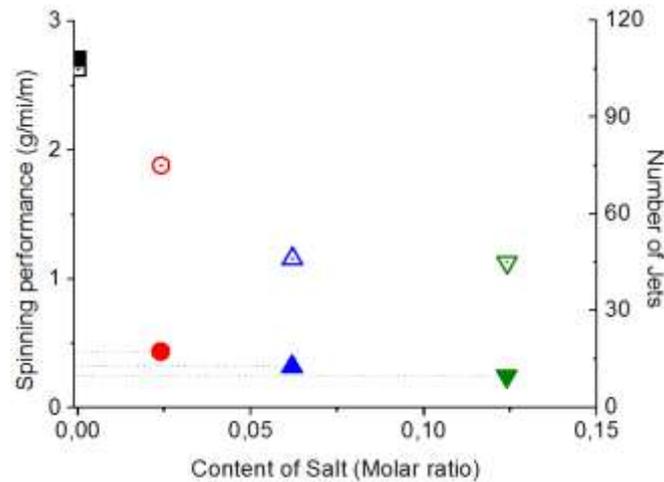


Fig. 2. Spinning performance and number of jets vs. content of salt (filled symbols indicate spinning performance, empty symbols indicate number of jets)

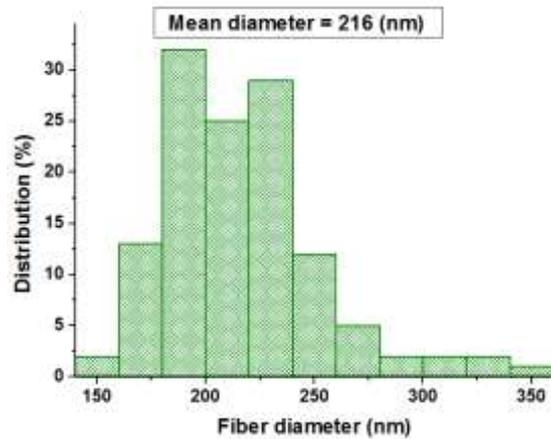
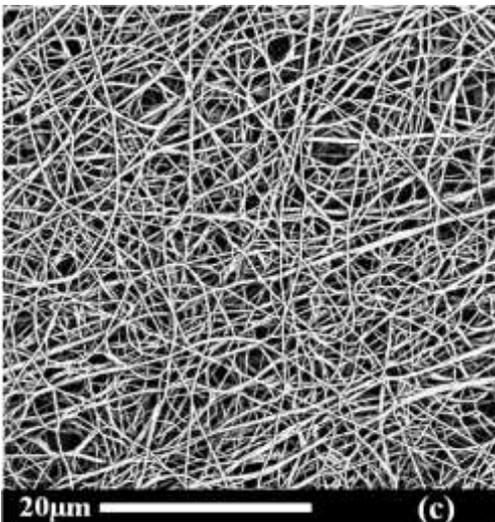
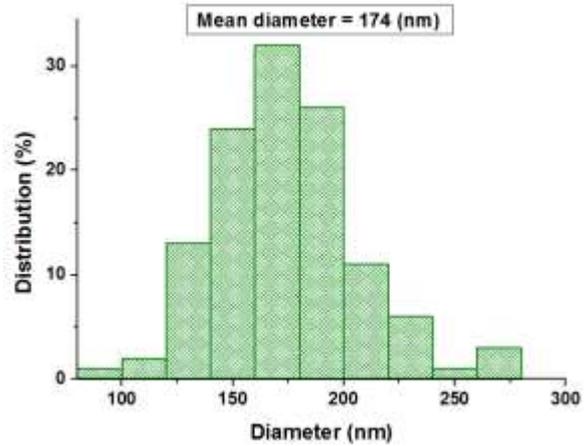
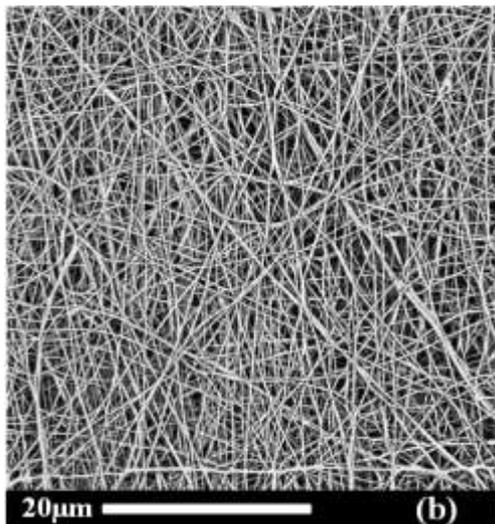
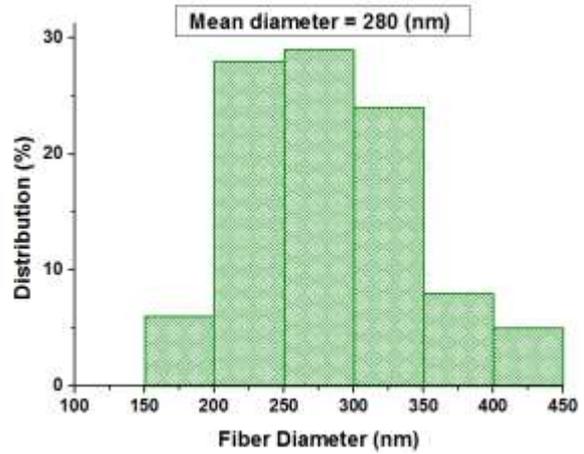
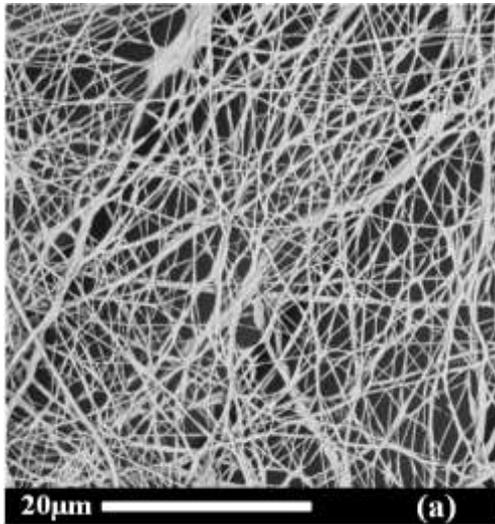
Fig.2 shows that spinning performance is decreasing with content of salts. Number of jets shows the same tendency as spinning performance. It means that number of jets decrease and it effects the productivity. This case can be explained by the leaky dielectric model which was first proposed by Melcher and Taylor¹⁸. It is important to know that if the changes in conductivity resulting from salt additions are large enough to alter the behavior of the fluid from that of a leaky dielectric to that resembling a conductor, then the tangential component of the electrical stress that accelerates the fluid is likely to diminish and the flow process be stopped. In this limit the electrical stress will be balanced by the alteration of the shape of the interface and surface tension only¹⁹. Herein, we can assume that high conductivity of PEO solutions shows a behavior as conductor under the electrical field. The other process parameters such as current, current/jet, spinning area, distance between jets and spinning performance/jet is tabulated in Table 3.

Table 3. Effect of salt on dependent parameters of PEO electrospun fibers.

5%PEO +salt	Number of jets	Current (μA)	Current/jet (μA)	Spinning Area $\times 10^3$ (m^2)	Distance between jets $\times 10^3$ (m)	Spinning performance/jet (g/h)
0	105	48	0.457	1.177	3.348304	0.2245
0.024	75	110	1.467	1.177	3.961766	0.0508
0.062	46	120	2.609	1.121	4.936804	0.0466
0.124	45	160	3.556	1.177	5.114618	0.0475

Current per one jet increased with salt content. It shows number of ions which are transported with jet increases due to increase in conductivity. As a result total current increase. On the other hand spinning area did not change with salt content, distance between jets increase. It could be because of highly charged jet repulse each other and distance between jets increases. Spinning performance per one jet for 5%PEO without any additive is extremely high. PEO without any salt has very high spinning performance and number of jets. However, only polymer solution is transported to collector with forming few fibers. 5% PEO (without any salt) electrospun web shows a surface with non-fibrous area around 90%. Non-fibrous area means there is no fiber only polymer droplets are forming. Adding salt helps to create thinner jet and highly splitting jet. As a result fibers are forming by adding salt and non-fibrous area is eliminated. The fibers and diameter distribution is shown in Fig. 3. In case of 5% PEO without any additives, samples were prepared from non-fibrous area to compare diameter of fibers with salt solution.

This work shows that adding salt has positive effect to produce thin nanofibers and better surface of web. On the other hand, salt content decrease spinning performance.



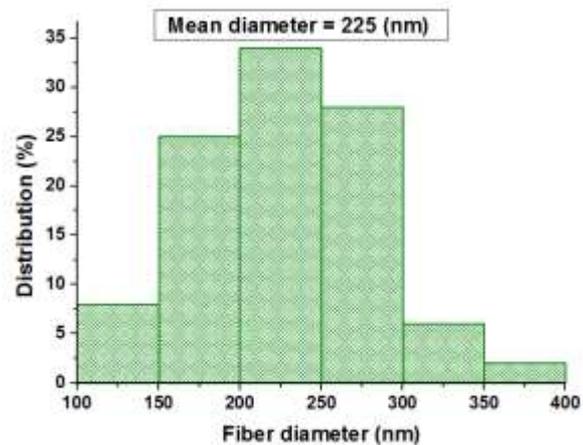
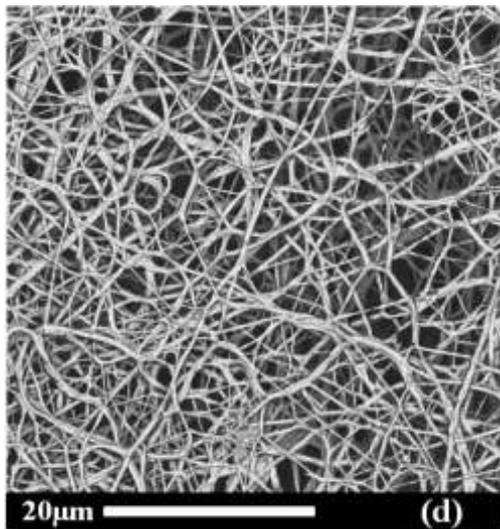


Fig.3. PEO electrospun nanofibers and fiber diameter distribution (a) 5%PEO, (b) 5%PEO+0.024M LiCl, (c) 5%PEO+0.062M LiCl, (d) 5%PEO+0.124M LiCl.

CONCLUSION

Ultrafine PEO fibers without non-fibrous area were obtained from electrospinning. Above a certain content of salt, fibers without non-fibrous area are electrospun and thinner fibers are obtained from a polymer solution with higher net charge density. Increase conductivity favors the formation of fibers without non-fibrous area. At high content of salt as Fig.3 (d), diameter of fibers increase and productivity decrease. It is necessary to arrange content of salt in a desired amount to control fiber diameter, non-fibrous area and spinning performance. This work shows that even at very low content of salt (0.024M \approx 0.1% wt.) shows low fiber diameter and good web surface. The content of LiCl salt can be adjustable according to desired properties web.

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REFERENCES

- [1] LI, W. J., LAURENCIN, C. T., CATERSON, E. J., TUAN, R. S., KO, F. K., Electrospun nanofibrous structure: A novel scaffold for tissue engineering, *Journal of Biomedical Materials Research*, Vol. 60, Issue 4, pp. 613-21, 2002.
- [2] RUJITANAROJ, P., PIMPFA, N., SUPAPHOL, P., Wound-dressing materials with antibacterial activity from electrospun gelatin fiber mats containing silver nanoparticles, *Polymer*, Vol. 49, issue 21, pp. 4723–4732, 2008.
- [3] VACANTI, J.P., LANGER, R., UPTON, J., MARLER, J.J., Transplantation of cells in matrixes for tissue regeneration. *Advanced Drug Delivery Reviews*, Vol.33, No.1,2, pp 165-182, 1998.
- [4] MCCLURE, M. J., SELL, S. A., AYRES, C. E., SIMPSON, D. G., BOWLIN, G. L., Electrospinning-aligned and random polydioxanone-polycaprolactone-silk fibroin-blended scaffolds: geometry for a vascular matrix, *Biomedical Materials*, Vol. 4, issue 5, 2009.
- [5] ZENG, J., XU, X., CHEN, X., LIANG, Q., BIAN, X., YANG, L., JING, X., Biodegradable electrospun fibers for drug delivery, *Journal of Controlled Release*, Vol.92, No.3, pp 227-231, 2003.

- [6] ZONG, X., KIM, K., FANG, D., RAN, S., HSIAO, B.S., CHU, B., Structure and process relationship of electrospun bioabsorbable nanofiber membranes, *POLYMER*, Vol.43, No.16, pp 4403-12, 2002.
- [7] GRAHAM, K., OUYANG, M., RAETHER, T., GRAFE, T., MCDONALD, B., KNAUF, P., Polymeric Nanofibers in Air Filtration Applications, *Fifteenth Annual Technical Conference & Expo of the American Filtration & Separations Society*, Galveston, Texas, April 9-12, 2002.
- [8] THAVASI, G. SINGH, S. RAMAKRISHNA, Electrospun nanofibers in energy and environmental applications: tools and resources, *Energy Environmental Science*, Vol.1, pp. 205–221, 2008
- [9] DEMIR, M.M., GULGUN, M.A., MENCELOGLU, Y.Z., ERMAN, B., ABRAMCHUK, S.S., MAKHAEVA, E.E., KHOKHLOV, A.R., MATVEEVA, V.G., SULMAN, M.G., Palladium nanoparticles by electrospinning from poly(acrylonitrile-co-acrylic acid)-PdCl₂ solutions. Relations between preparation conditions, particle size, and catalytic activity. *Macromolecules*, Vol.37, No.5, pp 1787-1792, 2004.
- [10] JIA, H., ZHU, G., VUGRINOVICH, B., KATAPHINAN, W., RENEKER, D.H., WANG, P., Enzyme- carrying polymeric nanofibers prepared via electrospinning for use as unique biocatalysts, *Biotechnology Progress*, Vol.18, No.5, pp 1027-1032, 2002.
- [11] DENG, C., GONG, P., HE, Q., CHENG, J., HE, C., SHI, L., ZHU, D., LIN, T., Highly fluorescent TPA-PBPV nanofibers with amplified sensory response to TNT, *Chemical Physics Letters*, Vol.483, No.4-6, pp 219-223, 2009.
- [12] WANG, X., LEE, S., DREW, C., SENECA, K.J., KUMAR, J., SAMUELSON, L.A., Electrospun nanofibrous membranes for optical sensing, *Polymeric Materials Science and Engineering*, Vol.85, 617-618, 2001.
- [13] DOSHI, J., RENEKER, D. H., Electrospinning process and applications of electrospun fibers, *Journal of Electrostatics*, vol. 35, no. 2-3, pp. 151–160, 1995.
- [14] YENER, F., JIRSAK, O., GEMCI, R., Using A Range of PVB Spinning Solution to Acquire Diverse Morphology for Electrospun Nanofibres, *Iranian Journal of Chemistry & Chemical Engineering-International English Edition*, Vol.31, issue 4, 2012.
- [15] LIN, T., WANG, X. G., Recent Developments in Electrospinning of Nanofibers and Nano fiber Yarns, *Proceedings of the Second International Conference on Advanced Textile Materials&Manufacturing Technology*, pp. 560-563, 2010.
- [16] YENER, F., JIRSAK, O., Effect of Nonsolvent on Electrospinning Performance and Nanofiber Properties, *Nanocon 4th International Conference*, pp. 471-475, 2012.
- [17] YENER, F., YALCINKAYA, B., JIRSAK, O., On the Measured Current in Needle- and Needleless Electrospinning, *Journal of Nanoscience and Nanotechnology*, Vol. 13, issue 7, 2013.
- [18] MELCHER, J.R., TAYLOR, G.I., Electrohydrodynamics: A review of role of interfacial shear stresses, *Annual Review of Fluid Mechanics*, Vol. 1, pp. 111-146, 1969.
- [19] Bhattacharjee, P.K., Rutledge, G.C., Electrospinning and polymer nanofibers: process fundamentals, *Comprehensive Biomaterials*, Vol. 1, pp. 497-512, 2011.