

Polyurethane Nanofibers Obtained By Electrospinning Process

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Abstract—Electrospinning is a broadly used technology to obtain polymeric nanofibers ranging from several micrometers down to several hundred nanometers for a wide range of applications. It offers unique capabilities to produce nanofibers with controllable porous structure. With smaller pores and higher surface area than regular fibers, electrospun fibers have been successfully applied in various fields, such as, nanocatalysis, tissue engineering scaffolds, protective clothing, filtration, biomedical, pharmaceutical, optical electronics, healthcare, biotechnology, defense and security, and environmental engineering. In this study, polyurethane nanofibers were obtained under different electrospinning parameters. Fiber morphology and diameter distribution were investigated in order to understand them as a function of process parameters.

Keywords—Electrospinning, polyurethane, nanofibers.

I. INTRODUCTION

ELECTROSPINNING is a broadly used technology to obtain polymeric nanofibers ranging from several micrometers down to several hundred nanometers for a wide range of applications. It offers unique capabilities to produce nanofibers with controllable porous structure. With smaller pores and higher surface area than regular fibers, electrospun fibers have been successfully applied in various fields, such as, nanocatalysis, tissue engineering scaffolds, protective clothing, filtration, biomedical, pharmaceutical, optical electronics, healthcare, biotechnology, defense and security, and environmental engineering. This technique involves stretching a polymer fluid under a strong electric field into fine filaments. A strong electrostatic field is applied and the high voltage induces electric charge to the solution. After electric force overcomes the solution surface tension, fibers are deposited randomly to form nonwoven fiber mats [1-3].

Solution, process and ambient parameters govern the electrospinning process. Viscosity, conductivity, molecular weight and surface tension are among the solution parameters. Process parameters include applied electric field, the distance between the tip and the collector and feeding rate, while surrounding air temperature and humidity are the most important ambient parameters [4]. A good understanding of the effect of these parameters is very important in order to obtain nanofibers with the desired morphology and diameter distribution.

Polyurethanes (PU) are versatile materials used in a wide variety of application areas. Thermoplastic polyurethanes are well established in various applications because these materials combine the processability of thermoplastics with rubber like elastic properties. Some of the advantages of TPU are excellent tensile strength, anti- abrasion, wear and flexibility at room temperature [5]. Polyurethanes can be used in the textile industry, medicine, environmental fields and so on [6]. Polyurethane has also been applied to waterproof-breathable fabric, synthetic leather, antishrink wool, military textiles, adhesives and fine chemicals [7]. Furthermore, combining ordinary fabrics with semi-conductive polyurethane films can lead to the development of a type of smart textiles.

Although it has been shown in a recent review by Huang and co-workers [8] that various aspects of electrospun fibers have been intensely explored and reported in the open literature in the past, a number of fundamental aspects of the process for different polymer-solvent systems are still worthy of further investigation in order to gain a thorough understanding of the process.

The purpose of this study was to determine the effects of these parameters on the morphology of the nanofibers produced from the utilized specific polymer, which was a thermoplastic polyurethane and to determine the optimal amount of these parameters among the tested samples.

The effects of solution conditions on the morphological appearance and the average diameter of electro-spun fibers were investigated by scanning electron microscopy (SEM) technique. It was observed that the electrospinning properties (i.e. solution concentration, nozzle-collector distance, applied voltage and the solution flow rate) were important factors in the final fiber diameter and fiber morphology. Among these properties, solution concentration was found to have the strongest and the solution flow rate to have the weakest effect.

II. MATERIALS AND METHODS

A. PU Nanofiber Production

PU nanofibers were obtained by electrospinning apparatus at Istanbul Technical University Polymer Science and Department laboratory. The schematic illustration of the apparatus is shown in Fig. 1. The apparatus consists of a syringe pump, a high-voltage direct current (DC) power supplier that generates DC voltage upto 30 kV and a grounded collector covered with aluminum foil. The solution was loaded into a syringe and a positive electrode was clipped onto the syringe needle, having an outer diameter of 0.8 mm.

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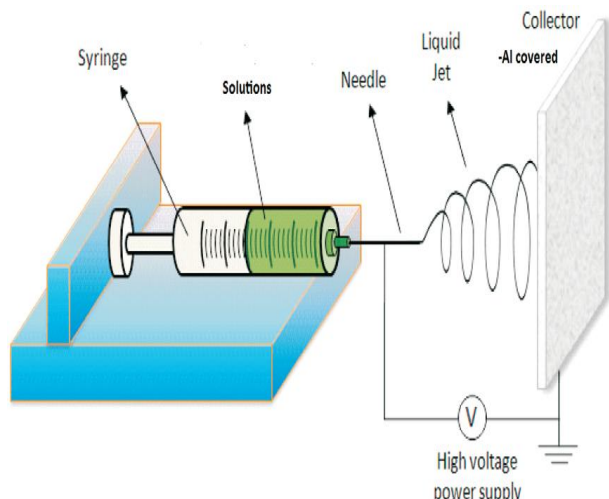


Fig. 1 The schematic illustration of the electrospinning apparatus

The glass syringe has a capacity of 2 ml. The metering pump was from New Era Pump System Inc and its model was NE-300 (Volts/Hz=12VDC and Amperage of 0.75). A Gamma High Voltage Research ES50P power supply was used to charge the spinning PU solutions by connecting the emitting electrode of positive polarity to the nozzle and the grounding electrode to the collective screen. A piece of thick aluminium (Al) sheet was used as a collective screen.

The utilized polymer was thermoplastic polyurethane 1660 LARICOL from Coim Company. The polymer solution was fed at a controlled rate through the syringe pump and the electrospinning process was carried out by electrospinning of the solutions onto the collector.

To investigate the effect of parameters on the morphology of the fibers, samples with the same parameters were made in a way that in each sample, one of the parameters was variable and all the other ones were remained constant. For instance, in one group of the samples, all the other parameters (like nozzle-collector distance, applied voltage, flow rate, etc.) were constant numbers and just the solution concentration differed among the samples of this group. To increase the accuracy of the results, three samples were pDMF (Dimethylformamide) and THF (Tetrahydrofuran) were used as the solvents in the electrospinning process. TPU (thermoplastic polyurethane) was dissolved by using these solvents.

All solution preparations and electrospinning studies were carried out at room temperature. Electrospun nanofibers were obtained by changing process and solution parameters. The diameter measurements were tested using TA Q800 Model Dynamic Mechanical Analyzer.

III. RESULTS AND DISCUSSION

The first electrospinning trials were made using THF and DMF mixture as the solvent to dissolve PU. However, there were difficulties in keeping the solution concentration constant due to high evaporation rate of THF. Also, the fibers

obtained by PU and THF solution were not satisfactory, as the fiber diameter was high (above 1 micron). Fig. 2 shows the nanofibers obtained by using 45wt% THF and 45wt% DMF 10wt% of the polymer (10gr polyurethane, 45gr DMF, 45gr THF). The voltage was 10kv, needle-collector distance 15 cm and the flow rate amount 0.5 ml/hr during these trials. The results of the mixed solvent (THF/DMF) showed that the average fiber diameter was 940.32 nm.

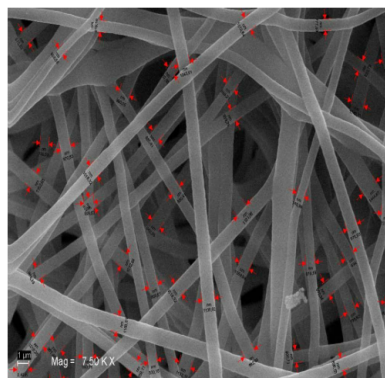


Fig. 2 SEM photo and diameter measurements of nanofibers obtained by 10wt%Pu, 45wt% THF, 45wt% DMF

Table I shows the parameters changed in order to see their effect on fiber diameter and morphology.

TABLE I
SAMPLE PLAN

Sample	Concentration	Voltage	Tip to Collector Distance, cm	Flow rate, ml/hour
1	4wt%	15kV	15	0,5
2	6wt%	15kV	15	0,5
3	7wt%	15kV	15	0,5
4	8wt%	15kV	15	0,5
5	9wt%	15kV	15	0,5
6	10wt%	15kV	15	0,5
7	12wt%	15kV	15	0,5
8	10wt%	10kV	15	0,5
9	10wt%	15kV	15	0,5
10	10wt%	20kV	15	0,5
11	10wt%	15kV	10	0,5
12	10wt%	15kV	12,5	0,5
13	10wt%	15kV	15	0,5
14	10wt%	15kV	17,5	0,5
15	10wt%	15kV	20	0,5

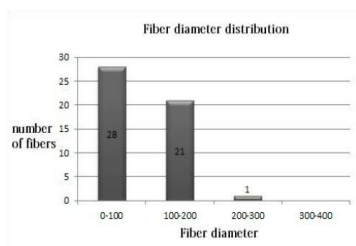
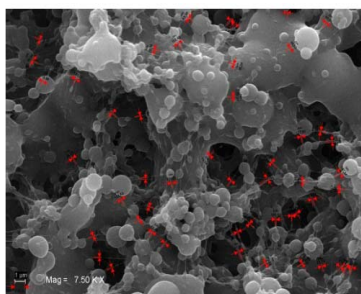


Fig. 3 4wt% PU, 15cm nozzle-collector distance, 15KV applied voltage, 0.5 ml/hr polymer flow rate

The sample prepared by using the process conditions of 8wt% PU/DMF concentration, the applied voltage 15kv, the nozzle-collector distance 15cm and the polymer solution flow rate was 0.5ml/hr gave the average diameter of 180.99 Nm and the fiber diameter range was between 62.71 nm to 414.23 nm (Fig. 4). Although the fiber diameters are acceptable and fine enough, the number of beads created was still high and due to this high number of beads, this sample was not acceptable.

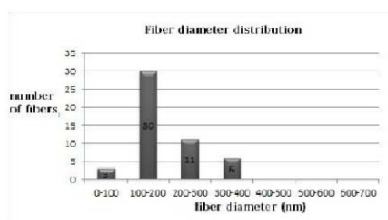
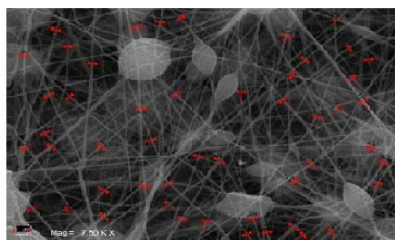


Fig. 4 SEM micrograph of Sample 5 (9wt%PU, 15kV, 15cm distance, 0.5ml/hr flow rate)

In the nanofiber production with 10wt% PU/DMF concentration was used, the applied voltage was 15kv, the nozzle-collector distance was 15cm and the polymer solution flow rate was 0.5ml/hr (sample 6). The fiber diameters were between 156.79 and 621.24 nm and the average fiber diameter was 329.57 nm (Fig. 5). Although this trial had fine enough fibers, no beads appeared, and it was acceptable.

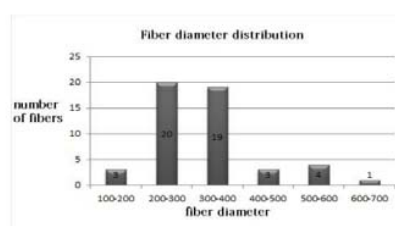
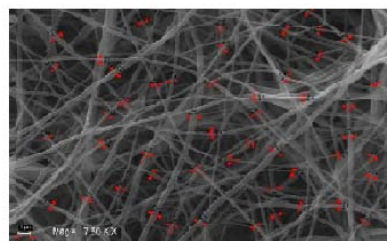


Fig. 5 Sample 6 (10wt% PU) fiber diameter distribution

In 10wt% concentration sample incredibly the beads almost vanished and the diameters of the fibers were fine enough to be considered as nanofibers (Average 329.57 nm). In 12wt% sample although there were no beads in the fibers structure and the diameters of the fibers were still fine enough (Average 519.60 nm), the diameters of the fibers which had been produced with 10wt% concentration were better due to their delicacy. After the determination of the best concentration, the other parameters (nozzle-collector distance, applying voltage and the solution flow rate) were individually examined.

Comparing 10cm to 12.5cm Nozzle-Collector distance SEM result, it was observed that the fiber diameters are decreasing slightly with the increase in the Nozzle-Collector distance. This is also in accordance with the findings in the literature. The longer path length between the nozzle tip and the collector means that there will be a higher probability for the jet segment to thin down as a result of the Coulombic repulsion.

In order to see the effect of applied voltage, 10wt% PU/DMF solution concentration, 15cm Nozzle-Collector distance, 0.5ml/hr solution flow rate was used and the applied voltage was selected as 10KV to determine the best electrical field for electrospinning the used polyurethane. The achieved fibers in this study had diameters between 225.05 nm and 548.24 nm, and the average fiber diameter was 391.64 nm.

IV. CONCLUSION

The effects of solution conditions on the morphological appearance and the average diameter of electro-spun fibers

were investigated by scanning electron microscopy (SEM) technique. It was observed that the electrospinning properties (i.e. solution concentration, nozzle-collector distance, applied voltage and the solution flow rate) were important factors in the final fiber diameter and fiber morphology. Among these properties, solution concentration was found to have the strongest and the solution flow rate to have the weakest effect.

REFERENCES

- [1] H. Zhuo, J. Hu, Shaojun Chen, L. Yeung, "Preparation of polyurethane nanofibers by electrospinning", *Journal of Applied Polymer Science*, Volume 109, Issue 1, pages 406–411, 5 July 2008.
- [2] M. M. Demir, I. Yilgör, E. Yilgör, B. Erman, "Electrospinning of polyurethane fibers", *Polymer*, 43, 3303-3309, 2002.
- [3] N. Bhardwaj, S.C. Kundu, "Electrospinning: A Fascinating Fiber Fabrication Technique", *Biotechnology Advances*, 28, 325-347, 2010.
- [4] E.J. Chong, T.T. Phan, IJ Lim, Y.Z. Zhang, B.H. Bay, S. Ramakrishna S. "Evaluation of electrospun PCL/gelatin nanofibrous scaffold for wound healing and layered dermal reconstitution" *Acta Mater*; 3:321–30, 2007.
- [5] A. Voda, K.T.S. Beck K, M. Adler, "Investigation of soft segments of thermoplastic polyurethane by NMR, differential scanning calorimetry" *Polymer Testing*, 25, 203-213, 2006.
- [6] Ding XM, Hu JL, Tao XM, "Preparation of Temperature-Sensitive Polyurethanes for Smart Textiles" *Textile Research Journal*, 76, 406, 2006.
- [7] H. Tsai, P. Hong, M. Yen, "Preparation and Physical Properties of MDEA-based Polyurethane Cationomers and their Application to Textile Coatings" *Textile Research Journal*, 77(9), 710-720, 2007.
- [8] Z.M. Huang, Y.Z. Zhang, M. Kotaki, S. Ramakrishna, "A review on polymer nanofibers by electrospinning and their applications in nanocomposites" *Compos Sci Technol*, 63:2223–53, 2003.