Structure and Process Parameter Relations of Electrospun Nanofibers

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Abstract

Electrospinning has been a process of great interest due to its versatility and potential to be used in a wide range of applications. It is possible to produce nanofibers with diameters ranging between a few nanometers to micrometers thanks to the latest developments in electrospinning. Electrospun nanofibers promise diverse applications including biotechnology, drug delivery, wound healing, tissue engineering, microelectronics, environmental protection, energy harvest and storage due to their very large surface area to volume ratio, flexibility in surface functionalities and superior mechanical performance. This paper focuses on electrospinning process principles and relation of process parameters with electrospun polyurethane (PU) nanofiber structural properties. The electrospun PU nanofibers have been used as coating on textile fabric.

Keywords

Electrospinning, Electrospun Nanofibers, Polyurethane, Electrospinning process parameters, Nanofibers Structure

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INTRODUCTION

Electrospinning is a simple and versatile technique that produces continuous micro and nano diameter polymeric fibers. Electrospun nanofibers promise diverse applications including biotechnology,drug delivery, wound healing, tissue engineering, microelectronics, environmental protection, energy harvest and storage due to their very large surface area to volume ratio, flexibility in surface functionalities and superior mechanical performance [1-3]. There is also the advantage to control nanofiber composition and electrospinning parameters to achieve the desired property and functionality [4]. The ideal targets in electrospinning a polymer into nanofiber are that the fiber diameters must be consistent and controllable, uniformity of fiber diameter must be achieved, the fiber surface must be defect-free and continuos single nanofibers must be collectable.

The characteristics of electrospun nanofibers are determined by electrospinning parameters and as they effect fiber morphologies, it is very important to understand these working parameters. It is much easier and more possible to obtain desired fiber diameters and morphologies through control of these parameters.

The parameters governing electrospinning process are given in Figure 1. The effect of these parameters have been investigated widely. Sukigara et al have suggested that an optimum solution concentration must be obtained, as at very low concentrations beads are formed, whereas at very high concentrations continuous fiber cannot be obtained due to inability to maintain the flow of the solution [5]. Fong et al showed that higher polymer concentrations led to a structure with less beads [6]. Koshi et al have investigated the structure of nanofibers at various molecular weights and they found that keeping the concentration constant, using a polymer with too low molecular weight leads to formation of beads rather than fibers,whereas a very high molecular weight will result in very large nanofiber diameters [7]. The effect of applied voltage has been extensively studied and there are different arguments. Reneker et al have shown that applied voltage does not have a significant effect on the nanofiber diameter in electrospinning of polyethylene oxide [8], while other researchers observed that increase in applied voltage favoured the narrowing of fiber diameter and they showed that fiber diameter decreased with increasing voltage due to the increase in electrostatic repulsive force on the charged jet and bead formation increased [9, 10]. Thompson et al have determined material and operating parametersby varying the parameter values in an electrospinning theoretical model and showed that volumetric charge density,distance from nozzle to collector initial jet/orifice radius, relaxation time and viscosity have the most significant effect on fiber diameter [11].

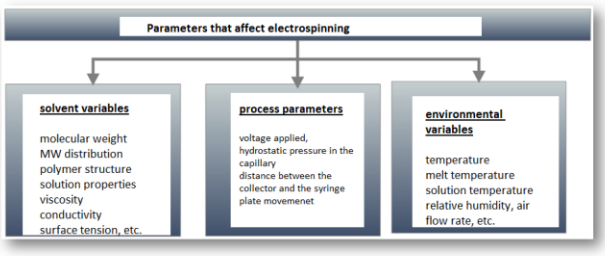


Figure 1. Electrospinning process parameters

Polyurethanes (PU) are segmented polymers built up from soft and hard segments. They have a highly elastomeric behavior, abrasion and chemical resistance, clarity and tensile strength [12, 13].

This paper reviews electrospinning process principles, process parameters and structure and process parameters relations of electrospun nanofibers from polyurethane, by changing tip to collector distance and applied voltage. The effect of polymer solution was published elsewhere [14]. The electrospun nanofibers have been deposited on textile fabric substrate as coating.

1. METHOD

1.1 Electrospinning Process

Electrospinning makes use of electrostatic forces to stretch the solution or melt as it solidifies. The fiber mat is collected as a distribution of continuous nanofibers. A typical electrospinning set-up, as shown in Figure 2, consists of mainly three components :

1. A syringe with a metal spinneret
2. A high voltage supplier
3. A rotating collector

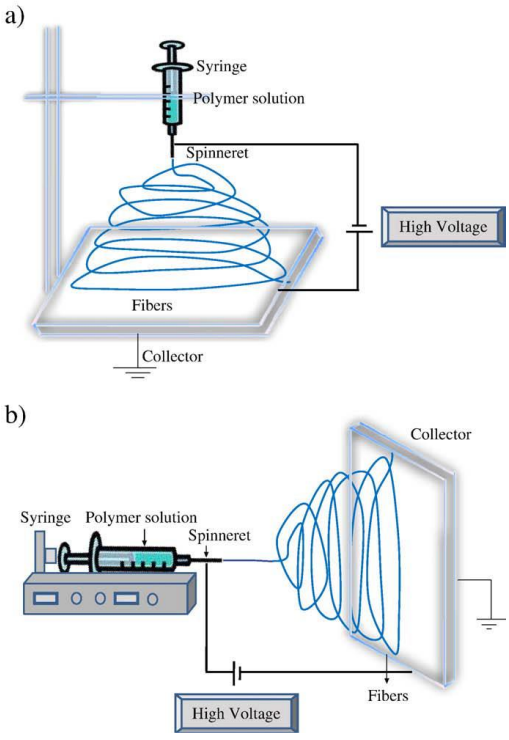


Figure 2. Schematic diagram of set-up of electrospinning a)typical vertical set-up, b) horizontal set up [4]

A high voltage is applied to create an electrically charged jet of polymer solution or melt. The jet undergoes stretching before it reaches the collector and it solidifies on the collector in the form of nanofibers by the evaporation of the solvent [3, 15]. The process principle involves subjecting a polymer solution or melt held at its surface tension at the end of a capillary to an electric field. As the intensity of the electric field is increased, the hemispherical surface of the solution at the tip of the capillary elongates and forms a conical shape known as the Taylor cone. The electric field reaches a critical value where the repulsive electric force overcomes the surface tension force. At this critical value, a charged jet of the solution is ejected from the tip of the Taylor cone. The solvent evaporates as the jet travels in air. The charged polymer fiber is randomly deposited on a collector [16]. A number of theories and simulated modeling techniques were used to explain the electrospinning process. Generally, it is agreed that there are four different regions within electrospinning process [17, 18] :

1. The base region : the charged surface of the solution at the nozzle end,
2. The jet region : where the solution travels along a straight line,
3. The splay region : where the jet splits into many nanofibers,
4. The collector region : where nanofibers eventually settle.

1.2 Materials

Thermoplastic polyurethane adhesive elastomer was supplied with a standard viscosity of about 2000 cps at 25^{0}C from Coim Company. The advantages of this type of polyurethane are high adhesive strength and good flexibility, high adhesion to a range of synthetic and natural materials and good thermal resistance.
PU was dissolved in Dimethylformamid (DMF, $(CH_3)_2NC(O)H$, Riedel-de Haen, analytical). All of the chemicals were used as received.

1.2 Preparation and characterization of nanofibers

For preparing electrospinning solutions, PU was dissolved in in DMF. The effect of process variables were studied and analyzed by using DMF as the solvent. The electrospinning set-up at Istanbul Technical University Polymer Science and Technology laboratory (Figure 3).
The set-up consists of a syringe pump (Ne-500 model, New Era Pump Systems In., USA) with a feeding rate from 5.5 μL/h to 400 mL/h, a high-voltage direct current (DV) power supplier generating positive DC voltage up to 30 kV (ES30 model, Gamma Hiigh Voltage Inc., USA). The electrospun nanofibrous web obtained was collected on a grounded collector, covered with aluminium foil. The solution was loaded into a syringe, having a needle outer diameter of 0.8 mm. A positive electrode was clipped onto the syringre needle. The feeding rate of the polymer solution was controlled by the syringe pump and the PU polymer solutions were electrospun on the collector. The electrospinning process was carried out at room temperature.

The process parameters were changed in order to see their effect on the fiber diameter, fiber diameter distribution and fiber morphology [19].

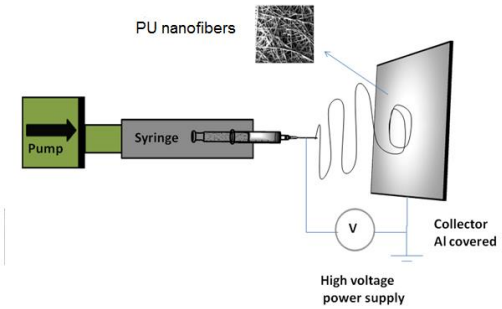
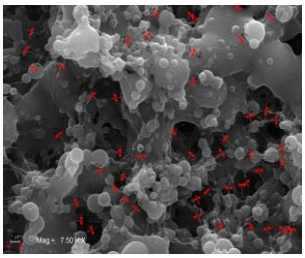


Figure 3. Schematic illustration of the nanofiber electrospinning process

Nanofiber images were taken by ZEISS, EVO MA10 model SEM. The morphology was observed with these SEM images.

2. RESULTS AND DISCUSSION

Electrospinning of PU nanofibers obtained by PU/DMF solution resulted in lower nanofiber diameter. The effect of process variables were studied and analyzed by using DMF as the solvent. SEM photographs of electrospun nanofbers obtained from different polymer concentration solutions, keeping other process and material parameters constant, are given in Figure 4. (Voltage 15 kV, tip to collector distance 15 cm, flow rate 0.5 mL/h). The fibers were analyzed for their diameter and morphology and the results were published elsewhere [14].



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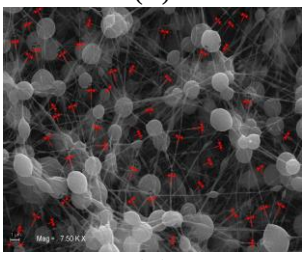

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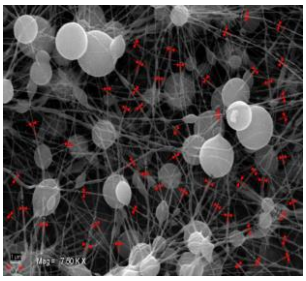

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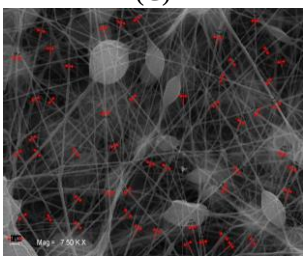

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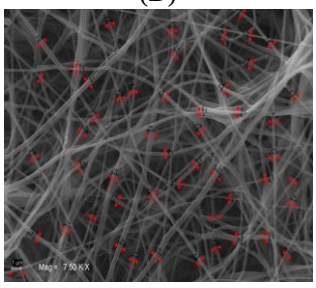

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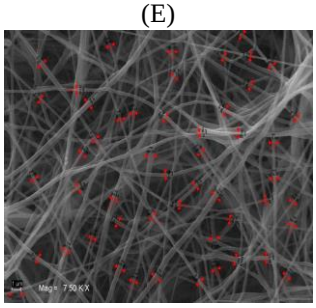
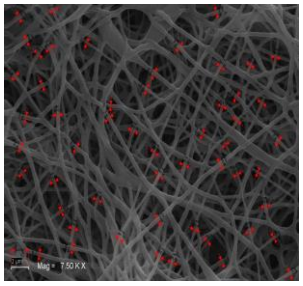


(F)

Figure 4. SEM image of nanofibers obtained from different polymer concentrations (A) 4 wt% PU, (B) 6 wt% PU, (C) 8 WT% PU (D) 9 wt% PU, (E) 10 wt% PU, (F) 12 wt% PU

It can be observed that at very low polymer concentration, it was impossible to obtain nanofiber. As the concentration was gradually increased, nanofibers were obtained, however the bead structure was predominant in the obtained web. The number of the beads decreased as the polymer concentration was further increased, and finally a more uniform electrospun nanofiber web could be obtained at higher polymer concentration [14].

Tip to collector distance has a significant effect on the fiber diameter and morphology. Figure 5 shows the SEM images and Figure 6 shows the fiber diameter distribution of electrospun PU nanofibers at various distances.



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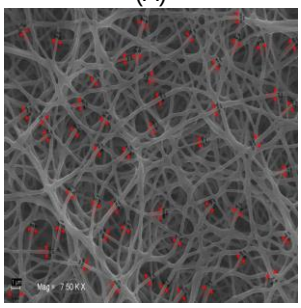

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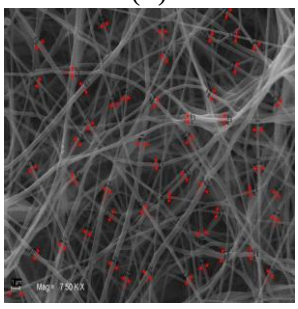

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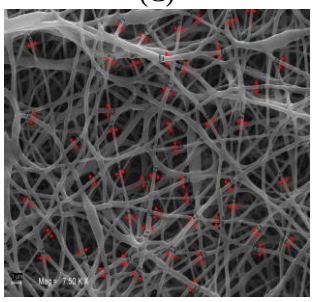

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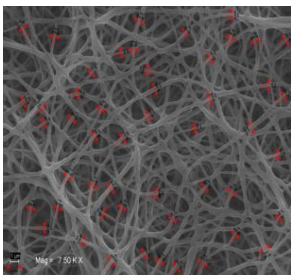

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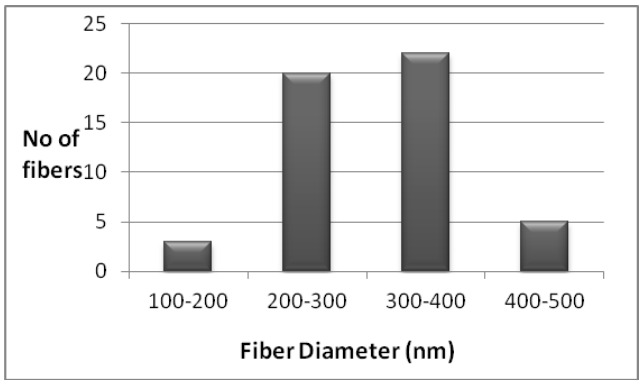
Figure 5. SEM image of nanofibers obtained from different tip to collector distances (A) 10 cm, (B) 12,5 cm (C) 15 cm (D) 17,5 cm (E) 20 cm



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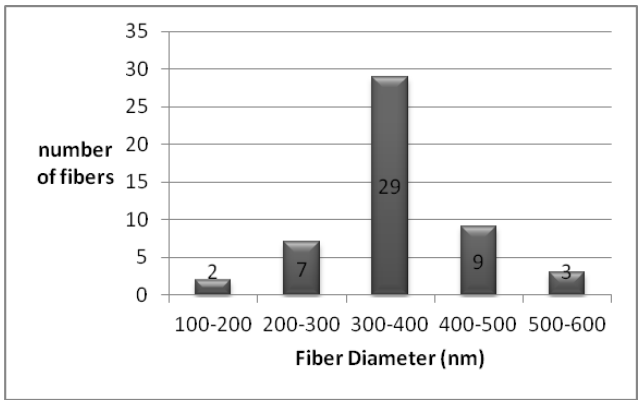

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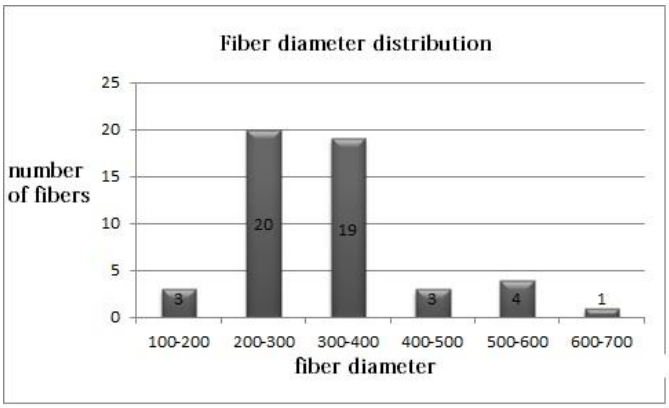

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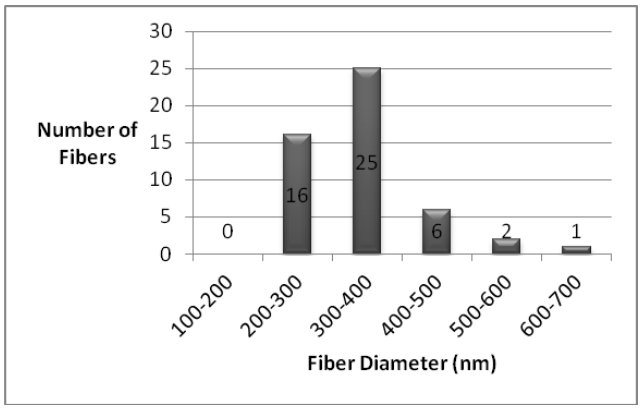

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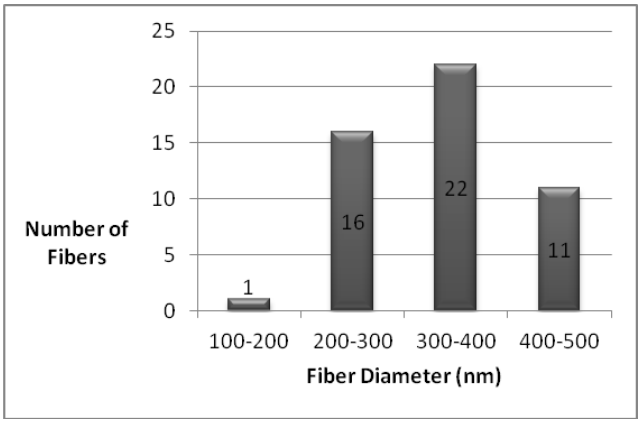
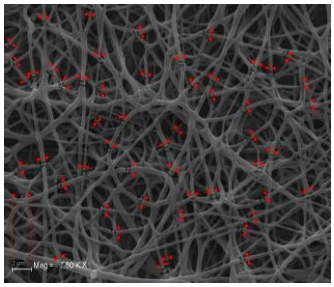


(E)

Figure 6. Fiber diameter distribution of nanofibers obtained from different tip to collector distances (A) 10 cm, (B) 12,5 cm (C) 15 cm (D) 17,5 cm (E) 20 cm

SEM results and fiber diameter distributions showed that there is a slight decrease in fiber diameter with an increase in the number of beads. Formation of beads is an undesired ccharacteristic in nanofibers, though decrease in fiber diameter with increase in tip to colector dictance may favor some applications, where lower diameters are required. The effect of applied voltage as also studied to observe the change in nanofiber characteristics. The process parameters were kept at 10 wt% polymer solution, 15 cm tip to colector distance and 0.5 mL/h feed rate. The SEM results are given in Figure 7.



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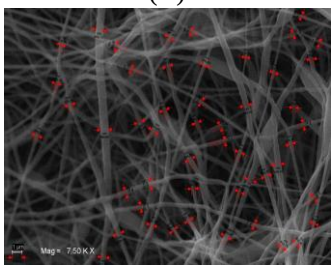

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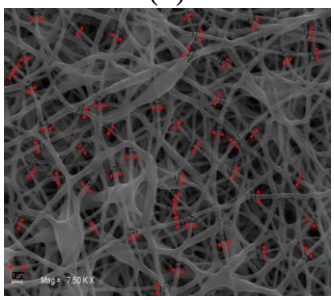

(C)

Figure 7. SEM image of nanofibers obtained from different applied voltages(A) 10 kV, (B) 15 kV (C) 20 kV

The diameter range was between 221.2 nm and 506.15 nm during these trials. The average fiber diameter was 364.48 nm. Further increase in applied voltage led to a slight decrease in fiber diameter and a structure without beads. As the voltage was finally increased to 20 kV, the fiber diameter decreased, whereas a structure with beads was formed.

In order to investigate the applicability of electrospun PU nanofibers on textile fabric, the nanofibers have also been deposited on textile fabric (Figure 8 and Figure 9). The electrospinning conditions were selected as 10 wt% polymer solution concentration, 17.5 cm tip to collector distance 10 kV applied voltage, 0.5 ml/h solution flow rate.

Figure 8. Deposition of PU nanofibers on denim fabric surface

Figure 9. PU nanofiber coated denim fabric

3. CONCLUSION

This paper focused on electrospinning process and the parameters effective on the obtained nanofiber diameter and fibar diameter distribution. PU nanofibers were electrospun and effective parameters were determined. Fiber diameters at various tip to collector distances were measured and SEM images were analyzed. Process parameters were selected to try the deposition of PU nanofibers on fabric surface. The electrospinning process was carried out at these parameters and PU was electrospun on denim fabric for coating.

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