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THE IMPACT OF SOLVENTS ON THE PROPERTIES OF ELECTROSPUN NANOFIBERS

Abstract:

Electrospun Polyurethane nanofibrous webs were produced from the solutions prepared with various volume ratios of N,N-dimethylformamide (DMF) and Tetrahydrofuran (THF). Characteristics of the blended solutions were explored in terms of viscosity and conductivity. Morphologies of nanofibrous webs were observed by SEM analysis. Experimental results exhibited that the morphologies of polyurethane nanofiber webs have been changed significantly with the solvent selection and mixing ratios of the solvents during electrospinning. Diameter of the nanofibers was ranged between 277 nm and 556 nm, respectively. Tensile strength and elongation measurements proved that mechanical properties of the nanofibrous webs were remarkably influenced by the fiber morphology and the uniformity.

Keywords:

Polyurethane, Electrospinning, Nanofiber, Solvent

JEL Classification: Z00, C90

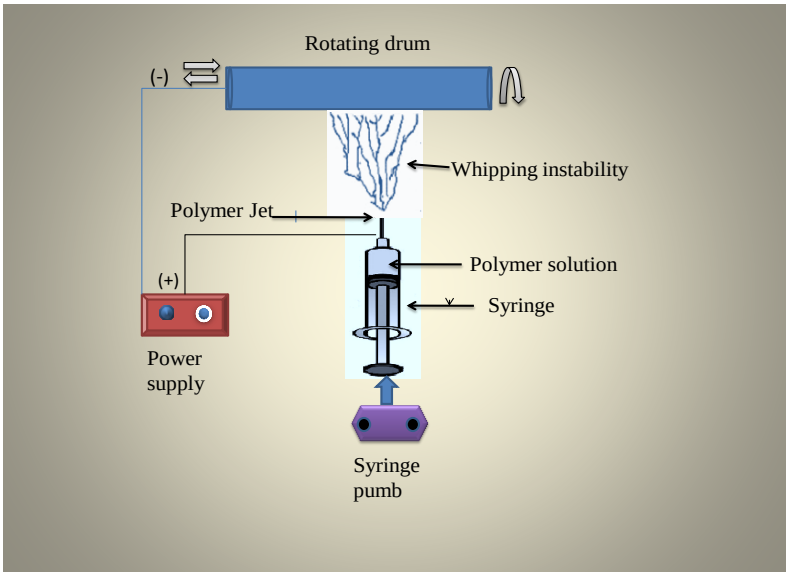
1 Introduction

There are variety of traditional techniques to manufacture them such as melt spinning, dry spinning and wet spinning in where mechanical forces are applied for the extrusion of polymer fluids (Zaibicki, 1976). Recently electrospinning technique has been announced by the researchers, which offers promising opportunities to obtain polymer nanofibers at submicron range. As a novel technology, electrospinning continues to attract the attention of both scientific world and industry because of eliminating the limitations of conventional fiber production techniques (Hong *et al*, 2005).

Electrospinning is a very simple and versatile technique which uses electrostatic forces to prepare polymer nanofibers. Briefly, an anode connected a high voltage power supply also connects to a syringe which contains polymer solution or melt. Cathode is connected to collector (rotating drum in our case) which is placed to a certain distance from the syringe capillary tip. Through this set up, an electric field is generated between the capillary tip and the collector during the electrospinning process. When the polymer solution/melt fed to the electric field, it becomes a hemispherical drop at the end of the capillary tip because of the surface tension. Increasing the applied voltage causes a distortion on the droplet due to the inducing charge on the solution surface. As the applied voltage reaches to a specific level, surface tension of the polymer solution is overcome and a single jet is emitted from a Taylor cone. Then whipping instability occurs during the single jet travelling from capillary tip to collector. At the end, single jet is split, solvent evaporates and finally nanofibers are collected on the collector (Figure 1) (Fong and Reneker, 1995; Srinivasan and Reneker, 1995; Fong, Chun, Reneker, 1999).

It is very well known that the morphology of electrospun fibers influenced by the several parameters such as the solution properties (polymer type, polymer weight, polymer concentration, solvent type, viscosity and conductivity), process variables (applied voltage, feeding rate, distance between capillary tip and collector, speed of the rotating drum etc.) and ambient conditions (temperature and relative humidity) (Reneker and Chun, 1996).

Figure 1. Schematic illustration of electrospinning process



In electrospinning process, polymer solution properties such as conductivity and evaporation rate are one of the most important factors that determine the final nanofiber characteristics (Wannatong, Sirivat, Supaphol, 2004). Therefore, solvent selection and mixing ratios of the solvents are vital matters.

In this study, PU solutions for electrospinning were prepared in a mixed solvent of Tetrahydrofuran (THF)/N,N-dimethylformamide (DMF), with the volume ratio of 100/0%, 75/25%, 50/50%, 25/75% and 0/100%. This altered the solutions characteristics as well as the nanofiber morphologies during the electrospinning process. The main purpose of this study is to explore the impact of solvent type and solvent mixing ratios on nanofiber formation and the mechanical properties of the final nanofibrous webs.

Materials and Methods

Solution Preparation

PU (8%wt.) was dissolved in Dimethylformamide (DMF)/ Tetrahydrofurane (THF) mixed solvents at various ratios of 100/0%, 75/25%, 50/50%, 25/75%, 0/100% (v/v) at 80°C for 6 hours by using laboratory type magnetic stirrer (Stuart, SB 162). The viscosities of the solutions were identified with a Brookfield Digital Viscometer by using s21 type spindle with a rotational speed of 100 rpm/min. The electrical conductivity of the blended solutions was also measured with a laboratory type conductivity meter (WTW, Cond 3110) under ambient atmosphere.

Electrospinning Process

Electrospinning was performed in the laboratory spinning unit (NS24, NanoFMG), which was designed in terms of a vertical working principle. Each solution was placed in a 4 ml syringe and sent to the drum collector (covered with aluminum foil) through a 20-gauge nozzle. The power supply (AC) was set up for a positive voltage of 29,5 kV. The flow rate of the solution was also determined by setting up the syringe pump at 2,20 ml/hr. The rotational speed of the drum collector was 35 rpm/min and its distance was set to 22 cm away from the nozzle. At the time of the experiments, relative humidity and temperature values ranged from 35-42% RH and 26-31°C.

SEM Analysis of Electrospun Nanofibers

Electrospun fibers were characterized by Scanning Electron Microscopy (SEM, JSM-5910 LV from JEOL). First of all, fibers coated with a thin gold palladium (20/80%) layer using a sputter coater from Polaron (SC7620) and the morphology of the nanofibrous webs were observed by SEM analysis at an accelerating voltage of 20 kV. The fiber diameter distribution was calculated over 50 fibers with the Image J software (Image J, 2011) from the SEM images obtained at a magnification of 1000× and 5000×.

Mechanical Measurements of ElectrospunNanofibrous Webs

In order to determine the mechanical properties of the PU based nanofibrous webs, tensile and elongation tests were carried out by using an Instron Machine (Instron 4411) in the textile laboratory at Marmara University. The mechanical properties of the blended nanofibrous webs were examined at ambient environment (22±3 °C temperature and 50±5% relative humidity). The specimens were cut into approximately 30 mm × 10 mm (length × width) in both machine direction and width direction in order to be loaded into the uni-axial testing machine. During the experiment, 50 N load cell under a cross-head speed of 10 mm/min was applied to the specimens. Three repetitions were taken for each specimen in order to calculate the tensile strength and elongation at break values.

Results and Discussion

Solution properties

For successful electrospinning, it is necessary to prevent polymer jet forming into droplets before the solvent evaporates. As a result of that polymer solution should possess have high charge density, low surface tension and proper viscosity. It is already known that greater electrical forces are needed to overcome both the surface tension and the viscoelastic forces to stretch the polymer solution into the nanofiber jets. In addition, high solvent vapor pressure (quick evaporation) is a critical factor to gain nanofibers with

uniform morphology (Herman *et al,* 1985).Table 1 presents the properties of PU solutions prepared with THF/DMF solvents. According to the table, conductivity of the PU solutions increased as the DMF content incremented. Results are consistent with the literature because DMF is defined as a dipolaraprotic solvent which has a high dielectric constant (36,7 at 25°C) and dipole moment (3,8 D) and it tends to exhibit polyelectrolyte behavior due to the dissociated positive and negative charges in the solution. On the other hand, THF contains five-membered ring structure and van der Waals attraction occurs between the molecules. Furthermore, it has a low dielectric constant (7,6 at 25°C) and dipole moment (1.7 D), consequently, it does not incline to show polyelectrolyte behavior (Wypych, 2001; Andrew et al, 1992; Son *et al,* 2004).

Table 1. Properties of solutions prepared for the electrospinning process

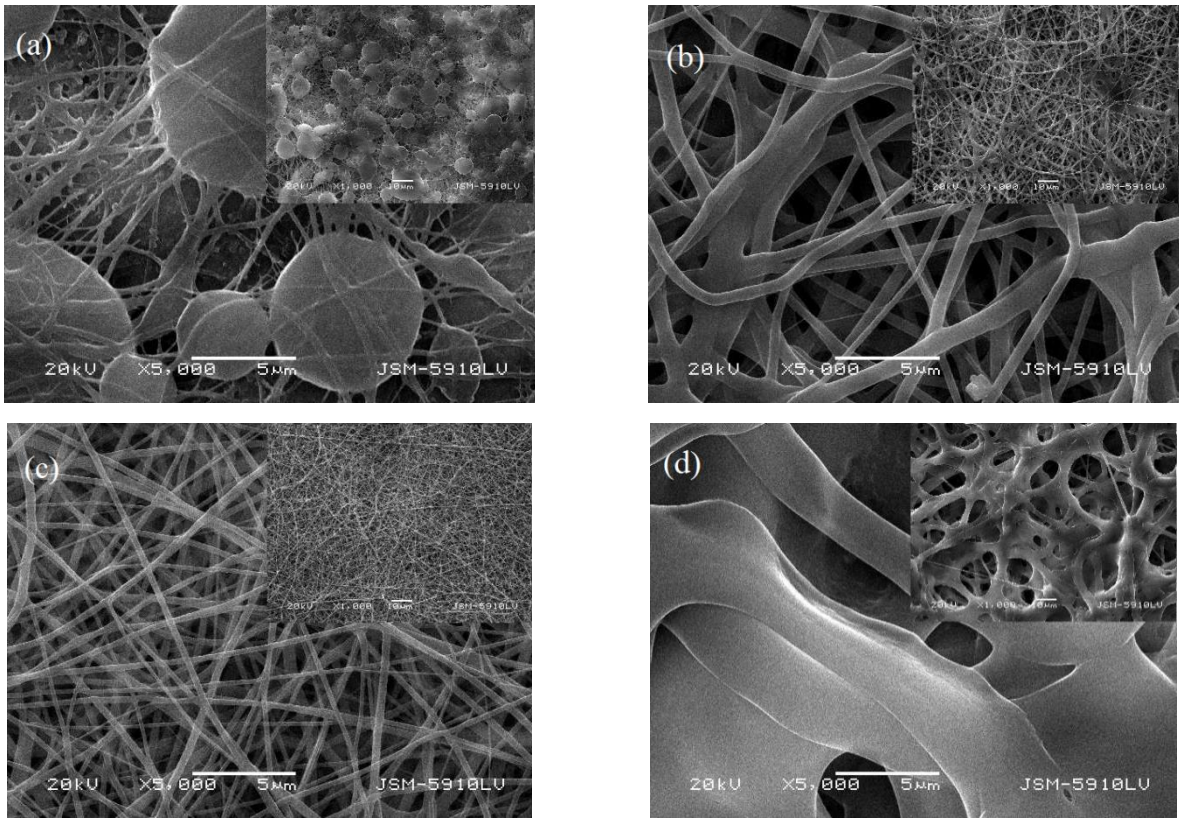
Polymer	THF/DMF (%)	Conductivity (μS/cm)	Viscosity (cP)
PU (8% wt.)	100/0	1,2	15
PU (8% wt.)	75/25	1,7	20
PU (8% wt.)	50/50	2,7	40
PU (8% wt.)	25/75	4,2	50
PU (8% wt.)	0/100	4,5	55

Morphology of PU Nanofibers

Figure 2 presents the SEM images of the electrospunnanofibrous PU based webs fabricated by various ratios of solvents. The solution concentration, voltage, and tip-to-collector distance were 8 wt%, 29,5 kV, and 22 cm, respectively.

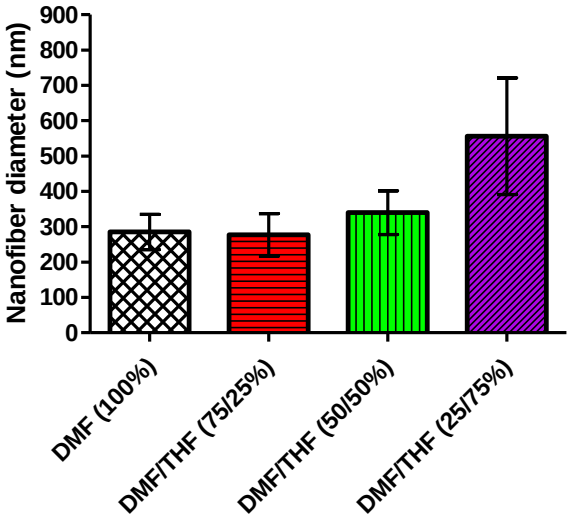
Figure 2. SEM images of electrospun PU nanofibers with various volume of solvents;

(a) 100%DMF, (b) 75/25% DMF/THF, (c) 50/50% DMF/THF, (d) 25/75% DMF/THF



The alterations in nanofiber diameters are shown in Figure 3. According to the results, by changing the solvent ratio from pure DMF to DMF/THF mixture, larger diameters were gained. The fiber diameters were recorded in the range between 277±104 nm and 556±280 nm.

Figure 3. Diameters of electrospun PU nanofibers prepared from DMF/THF (v/v) containing solutions



Mechanical Properties of the PU based Nanofibrous Webs

The mechanical behaviors of electrospun blend fibrous webs are exhibited in Figure 4 and 5. The tensile strength and elongational properties of the electrospunnanofibrous webs are dependent on the polymer type, fiber structures, geometrical arrangements of fibers and their interactions (Wei *et al,* 2009). Test measurements clearly proved that there was a strong relationship between the morphology and the mechanical behavior of electrospun fiber webs. The greatest strength value (approximately 2,4 MPa in machine direction and 1,4 MPa in width direction) was obtained for the web produced from the solution having 50/50% of DMF/THF (v/v). Elongation at break values showed similar trend with the tensile strength findings where the best results were (344% in width direction and 317% in machine direction) recorded for 50/50% DMF/THF (v/v).

Figure 4. Tensile strength of PU based electrospunnanofibrous webs prepared from various solutions with different mixing volume of DMF/THF solvents

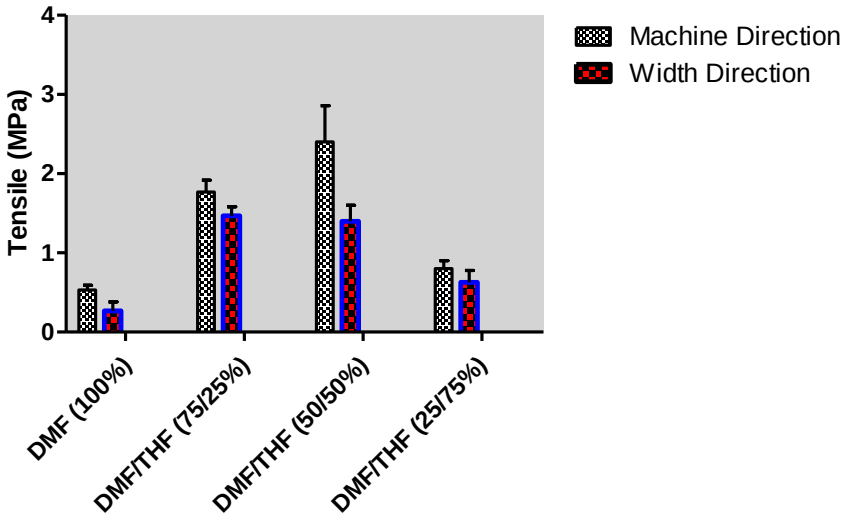
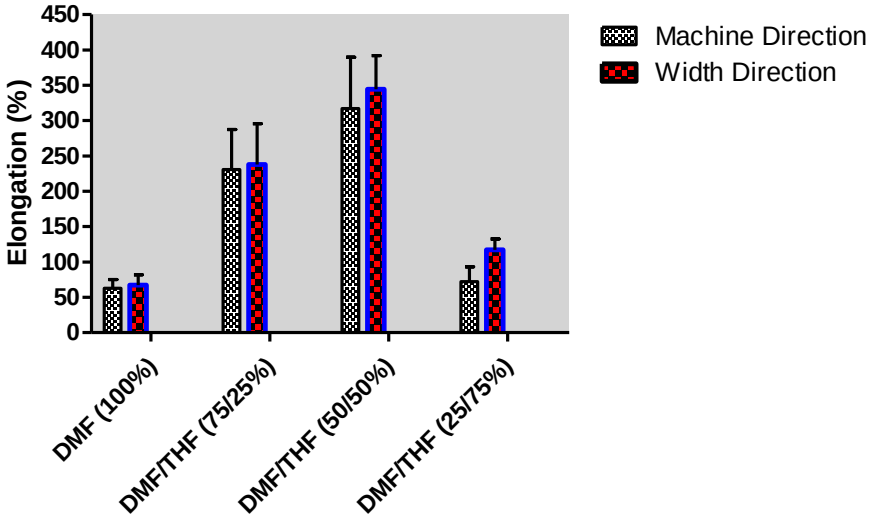


Figure 5. Elongation results of PU based electrospunnanofibrous webs prepared from various solutions with different mixing volume of DMF/THF solvents



Conclusion

Through this study, it has been established that solvent selection is one of the driving factors for controlling the morphology of the polyurethane electrospun nanofiber webs. Solution properties were affected by the solvent characteristics such as dielectric constant, dipole moment and solvent vapor pressure. Although both DMF and THF are suitable solvents to dissolve PU efficiently, only DMF showed well performance in terms

of electrospinnability. The best result of fiber morphology and mechanical characteristics were recorded for the webs electrospun from the solution containing 50/50% of DMF/THF.

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