Effect of Voltage on Morphology of Electrospun Nanofibers

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Abstract

Factors affecting on properties of nanofibers fabricated by electrospinning have especially been favored due to fact that electrospun nanofibers are used readily in many areas with different objectives. In this study, effects of applied voltage on morphologies of electrospun nanofibers containing polyvinylalcohol and sodium alginate were investigated. A constant volume of the feeding solutions was delivered to the needle at a flow rate of 3 ml/h and high potentials in the range of 28 kV-45 kV were applied as they exit the needle. The electrospun fibers were collected on the aluminum foil connected to the ground. The electrical conductivity measurements of feeding solutions were performed at room temperature. The morphology of electrospun fibers was investigated by the scanning electron microscopy (SEM) analysis. The broken nanofibers were obtained at 28 kV, whereas increasing the voltage to 35 kV or higher nanofibers appeared to be continuous without any significant change in diameters. As a result junctions of fibers decreased with voltage while the size of the beads increased with it. There was no clear correlation between the applied voltage and diameters of fibers, suggesting the effect of voltage may depend on other parameters such as gap distance and eventually the shape of the electric field.

1. Introduction

Electrospinning is an effective process to make submicron-diameter polymer fibers. In electrospinning, mechanical forces are used to extrude a viscous polymer fluid to produce fibers with diameters in the range of 10-500 μm. In the process electrostatic forces are used. Typically the polymer solution is taken in a capillary and a high voltage power source is connected to generate an electric field between the tip of the capillary and a grounded collector. The drop is held at the tip of the capillary because of surface tension. As the voltage is increased, the viscoelastic forces are overcome by electric forces due to fact that the droplet gets distorted. Finally, above a critical voltage a jet is ejected from the apex of a conical surface, known as "Taylor" cone. The repulsive forces from the increased charge density on the surface of the jet due to stretching cause the jet to split. The smaller jets then split and splay as their diameter is reduced further. The fibers are collected on the collector randomly forming a nonwoven web like structure. Usually, the solvent evaporates in the air before reaching the collector or evaporates after deposition on the collector [1].

Electrospun fibers have high surface area to volume or mass ratio, small inter-fibrous pore size with high porosity and almost limitless possibilities for surface functionalization [2]. Electrospun nanofibers have been investigated for wide range applications such as filtration membranes, nanofiber composites, electrically conductive fibers, wound dressing, biocatalyst, tissue scaffolding and drug delivery systems. In order to improve applications of the electrospinning process many studies are being conducted to understand the effect of process parameters [1].

The electrospinning process can be manipulated by a number of variables. These can be classified as solution properties, controlling variables and ambient parameters. As conductivity is one of the solution parameters, the electric field strength is one of the controlling parameters [2]. The electric field strength during electrospinning process depends on the applied voltage which may affect morphology of electrospun fibers. Applied voltage provides the surface charge on the electrospinning jet. Instability and stretching of the jet therefore increase with applied voltage leading generally to smaller fiber diameters. It is interesting to note that this electric-field-attenuated change in fiber diameter is generally much smaller than that obtained by controlling the concentration of the spinning solution. In addition, sometimes no significant effect of the applied voltage or a linear increase in fiber diameter with the applied voltage has also been reported in the related literature [3], [4]. This discrepancy in experimental observations suggests that the effects of applied voltage on fiber diameter need to be considered together with other parameters, particularly the feed rate and the gap distance [3].

So far, more than 50 different polymers have been successfully electrospun. Synthetic polymers are relatively easy to dissolved in an organic solvent, while in cases where they are water-soluble such as polyinylalcohol (PVA), they can also be electrospun from aqueous solutions. Biopolymers are usually soluble in aqueous solutions, however, electrospinning themselves alone from aqueous solutions seems difficult, and in fact their electrospinning from aqueous solutions has been achieved in polymer blend form by blending with a non-toxic, non-ionic and biocompatible synthetic polymer PVA, which improves their processability while maintaining their biocompatibility [5]. PVA is highly hydrophilic, has an inherent fibre- and film-forming ability, and can be easily cross-linked [6].

Alginate, which is obtained from marine brown algae, is a naturally occurring polysaccharide. It is a water-soluble polymer and has some unique properties such as non-toxicity, biocompatibility, biodegradability, hydrophilicity and relatively low cost. It is an important biopolymer in biomedical applications such as wound dressing, tissue engineering scaffold

and drug delivery carrier [6]. The fabrication of alginate nanofibers by electrospinning is challenging. This is because the gelation of alginate solution starts to occur at very low polymer concentrations (e.g., 2 wt % for alginate in deionized water). At such a low concentration, the solution contains insufficient material to generate fibrous structures, and rather, sprayed droplets or a structure with short fibers embedded with beads is obtained. At slightly higher polymer concentrations, the solution becomes so viscous that it cannot be injected. One way to solve this problem is to incorporate a fraction of copolymer, and to apply surfactants or/and cosolvents to the alginate solution [7], [8]. In the literature has been reported that polyethylene oxide (PEO) or PVA have been used for increasing the spinnability of alginate [5], [7], [9], [10].

The objective of this study was to investigate the effect of applied voltage on the morphology of electrospun nanofibers from the alginate-PVA blend. As far as we know, no literature data available for the effect of applied voltage on the morphology of electrospun nanofibers containing alginate-PVA blends. The outcomes of this study may give the opportunity to tailor nanofibers with desirable properties for specific applications in different fields including medicine, pharmaceuticals and foods.

2. Materials and Methods

Polyvinylalcohol (PVA) was purchased from Bereket Kimya (Istanbul) and sodium alginate (SA) was kindly provided by Rotel İç ve Dış Tic. A.Ş. (İstanbul). PVA and SA were dissolved separately in tap water under continuous stirring at room temperature until completely dissolved (checked by visual appearance). After preparing PVA at 6% (w/w) and SA at 3% (w/w), they were blended at the volume ratio of 60:40, respectively.

2.1. Electrospinning

The electrospinning equipment (NE 100, Istanbul) is given in Fig 1. The setup consisted of a metal needle connected to a high voltage power supply. The needle is fed with feed solutions containing PVA and SA from a syringe mounted on a programmable syringe pump. An aluminum foil wrapped on a flat surface was used as the grounded collector. The electric field generated between the needle and the collector was shielded from surrounding materials by having a box around the tip and the collector setup. The collector was placed vertically up from the needle. A syringe pump was used to control the flow rate at 3 ml/hr. A constant tip to collector distance 9 cm was maintained in all the experiments. Electrospinning was performed by applying variable voltages at 28, 35, 40 and 45 kV. All the solutions and fiber samples were stored at room temperature. The diameter and morphology of the fibers collected were determined using a scanning electron microscope (SEM). The electrical conductivity measurements of feed solutions were performed using a digital conductivity meter (WTW 8120, Germany) at room temperature. The measurements were conducted in duplicates and the mean values were reported with the standard deviations.

Fig. 1. The electrospinning equipment (NE100, İstanbul)

3. Results

The electrical conductivities of PVA (6%, w/w), SA (3%, w/w) and blend of these solutions at 60:40 (v/v), respectively are given in Table 1. The electrical conductivity of the SA solution was very high comparing to the PVA solution. As a result, the electrical conductivity of the blend (1.84± 0.00 mS/cm) increased from that of the primary PVA solution, which was the 60% of the blend (v/v).

Table 1. Electrical conductivities of polymer solutions and their blend

Material	Electrical conductivity (mS/cm)
PVA (6%, w/w)	0.66 ± 0.00
SA (3%, w/w)	5.06 ± 0.04
PVA(6%):SA(3%) 60:40 (v/v)	1.84± 0.00

Specifically, to form fibers, the applied voltage should be sufficient to overcome the surface tension at the tip of the Taylor cone, to initiate the ejection of the charged jet [11]. In this study, the primary solutions of PVA and SA and their blend were electrospun under the applied voltages of 28, 35, 40 and 45 kV over a tip-to-target distance of 9 cm. The fibers were obtained from the PVA solution under 28 kV, whereas no fiber deposition was seen from the SA solution at the same voltage. The other voltages have not tried for the primary solutions. Their blend at 60:40 (v/v) resulted in nanofiber deposition on the collector plate under the applied voltages of 28, 35, 40 and 45 kV. The SEM images of electrospun nanofibers obtained from the blend are given in Fig 2.

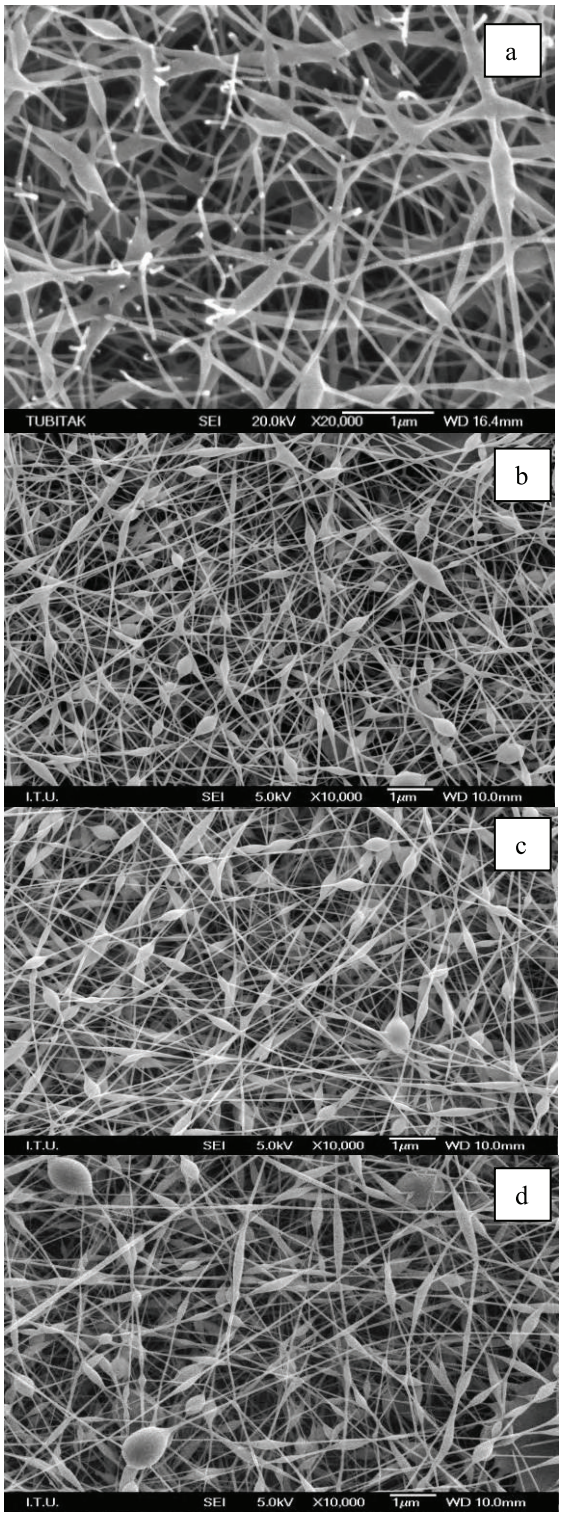


Fig. 2. SEM images of nanofibers obtained from the blend, electrospun at a) 28 kV, b) 35 kV, c) 40 kV and d) 45 kV. The bar scales are 1 μm. In the picture (a), the magnification is different (x20000).

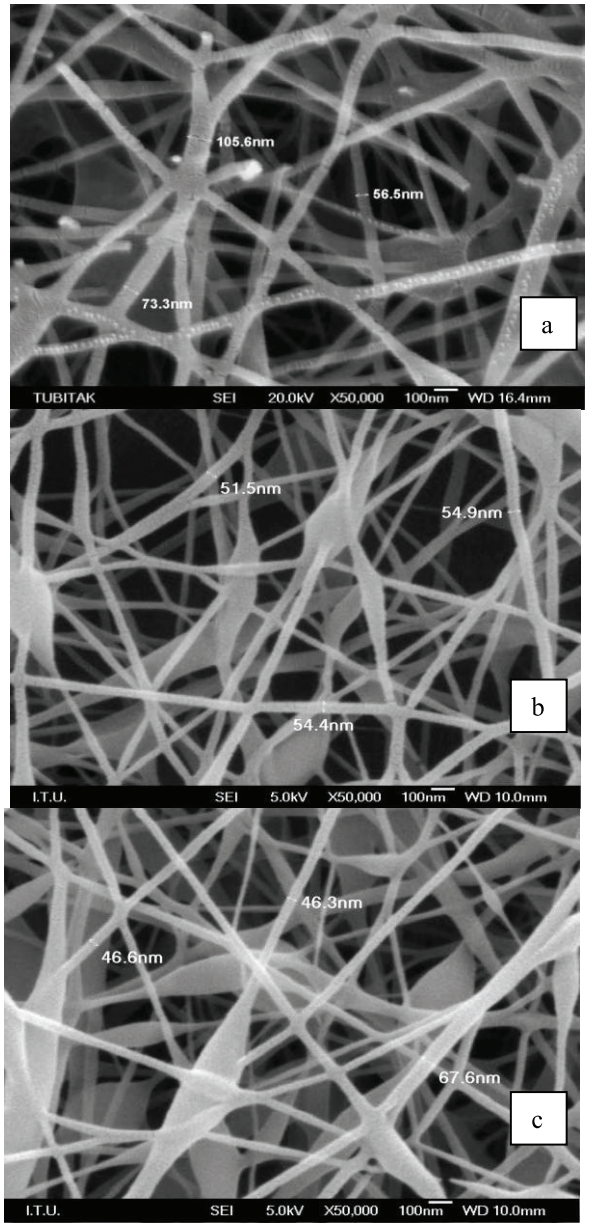
It can be seen that nanofibers obtained from the blend have beads at any given applied voltage (Fig 2). The fibers obtained at 45 kV had bigger beads comparing to the other fibers. It seems that there is no drastic effect of increasing voltage on the morphology of nanofibers. The fibers obtained at 28 kV appear broken whereas the fibers obtained at 35, 40 and 45 kV are continuous. It can be concluded that the applied voltage of 28 kV was not enough to produce continuous nanofibers from the solution at the given concentration. In case a more dilute solution, the lower voltage may carry the molecules to the collector plate as continuous nanofibers.

In Fig. 3, the same fibers are seen with more magnification than Fig 2. The general distributions of beads are almost same for the fibers obtained at 35, 40 and 45 kV. In Fig 3a, the broken fibers are seen in contrast to other fibers. In Fig 3, the diameters of fibers are also given. Even though there is no clear correlation, it may be concluded that diameter of fibers decreases with increasing voltage when comparing to Fig 3a to Fig 3b and Fig 3c. In Fig 3d, diameters of fibers almost similar with fibers obtained at 35 kV. There is no uniform distribution of diameter for all samples. The diameters of fibers change in between 46-106 nm. In [12], it was reported that bimodal diameter distribution of the fibers was the result of splitting of the electrospinning jets during fiber production. Accordingly, the non-uniform diameter distribution in this study may result from the splitting of the jets during electrospinning. In Fig 2 and 3, some fibers have junctions which lead to tip-to-collector distance was not appropriate for evaporation of water [12]. Polymer concentration is a key factor that affects the final fiber morphology. Generally, extremely high polymer concentration may lead to the electrospinning process impossible due to high viscosity, whereas low concentration results in fibers with beads. On the other hand, electric current during electrospinning also affects the fiber morphology due to fact that the shape of Taylor cone is affected by the applied voltage [12]. It has been reported that when jet current is in the range of 7-10 kV, the Taylor cone has still has a part out of the nozzle and the fibers are the most uniform fibers. When the voltage increased from 10 to 15 kV, the spinning process stooped and jet current was unstable [13]. As the voltage is increased, the volume of the drop at the tip decreases thus causing the Taylor cone to narrow down. The jet originates from the liquid surface within the tip and more beads can be observed. As the voltage is increased further, the jet eventually moves around the edges of the tip with no visible Taylor cone; at these conditions, the presence of many beads is observed [14]. In our study increasing voltage did not affect the electrospinnability of the blend, but at lower voltage (28 kv) the fibers were broken, which improved with the increasing voltage. In addition, increasing voltage during electrospinning somewhat decreased number of junctions, while increased the size of beads. In [15], the diameter of PVA nanofibers decreased with voltage; however they reported that the patterns did not appear to be linear. Therefore, they investigated variations in voltage and distance together which affects the electric field and its shape. They reported that the smallest fiber diameters were observed with the most intensive electric fields, which were more easily achieved with short distance. In our study, the slight tendency of decreasing diameters of nanofibers as apllied voltage at constant distance may be related to increased electric field.

4. Conclusions

Electrospinning process and the factors affecting properties of electrospun nanofibers have taken more attention from

different fields lately. Applied voltage is one of the affecting parameters during electrospinning. In this study, broken fibers improved with the increasing voltage from 28 kV to 35 kV. The nanofibers became continous. It may also be concluded that increasing voltage decrease junctions of fibers, which is desirable for uniform fiber distribution. The size of the beads increased with the applied voltage. However, we have not found a clear correlation between the applied voltage and diameters of fibers; and the applied voltage and number of beads. The applied voltage also affects the electrical field during the spinning process. The electrical field depends on applied voltage and the distance between the tip and the collector. In this study this distance was constant and our results showed that junctions may be related with the inadequate distance. Both distance and applied voltage affect the charge density on the solution during process. It seems that more research needs to be conducted on the affect of applied voltage together with the distance between tip to the collector and electrical conductivity of the solution.



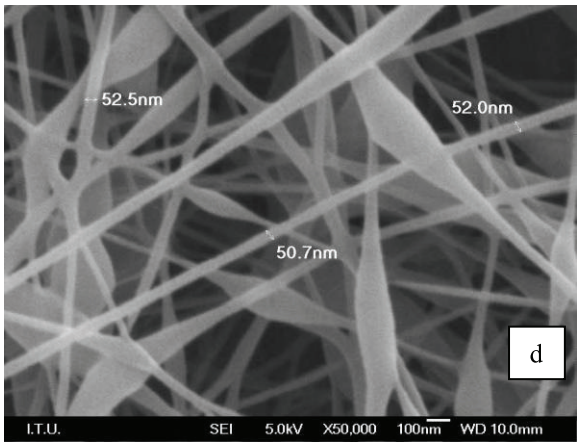


Fig. 3. SEM images of nanofibers electrospun at a) 28 kV, b) 35 kV, c) 40 kV and d) 45 kV. The bar scales are 100 nm.

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