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Fiber Diameter Dependency of Electrospun Polysulfone/SiO_2/TiO_2 Nanocomposite Membranes on the Solution Properties

Mohammad Mahdi Teymuri Sangari, Elham Bagherzadeh, Seyed Mojtaba Zebarjad*

Department of Materials Science and Engineering, School of Engineering, Shiraz University, Shiraz, Iran.

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**Corresponding author email: mojtabazebarjad@shirazu.ac.ir*

ABSTRACT

Polysulfone (PSU) is one of the most frequently used polymers in membranes technology, and it can be electrospun to form nonwoven fibers. However, its hydrophilicity should be improved for water purification purposes. The fiber diameter in electrospun membranes can affect the physical properties of the product. The electrospinning parameters can largely control the average fiber diameter in electrospun membranes. In this study, PSU/SiO_2/TiO_2 nanocomposite membranes were fabricated via the electrospinning method, and the effect of the introduced nanoparticles on the properties of the primary solutions and hence the average fiber diameter has been investigated. Silica and Titania nanoparticles (0, 0.5, 1wt%) were added to 20 wt.% PSU solution and were electrospun at a constant voltage and feed rate of 15.5 kV and 2 ml/h, respectively. The conductivity of the prepared solutions and the surface tension was measured. In addition, the rheological behavior of the solutions was evaluated using rheometric measurements. Finally, scanning electron microscopy (SEM) was used to study the morphology of the membranes and estimate the average fiber diameter. The obtained results showed that increasing titania nanoparticles at a constant SiO_2 content has decreased the average diameter from 959 to 712 nm, which can be attributed to the higher conductivity and lower surface tension of solutions with a higher TiO_2 amount leading to facilitated fiber stretching during electrospinning. On the other hand, introducing silica nanoparticles to a certain extent can decrease the fiber diameter due to the predominant effect of improved conductivity. However, beyond this extent, the significant increase in the solution viscosity at 1wt.% caused the formation of thicker fibers with an average diameter of about 1160 nm. These findings emphasize the importance of solution properties for designing an efficient water membrane by controlling its fiber diameter and specific surface area.

KEYWORDS: *Silica nanoparticles, Titania nanoparticles, Polysulfone, Electrospun membranes, Solution parameters.*

1. Introduction

Nowadays, many health problems have occurred worldwide due to the lack of enough drinking water [1]. Since water consumption is very high and resources are limited, developing a low-energy and low-cost water purification method is needed [2]. Due to simplicity and continuous process as well as the ability to fabricate 2D and 3D structures with size-dependent structural behaviours, electrospinning is a perfect choice for producing fibers [1,3]. The conventional chemical water purification method is costly and may cause corrosion and further contamination [4]. Considering easy fabrication methods for preparing water purification membranes, the cost-effective membrane technology could be an excellent choice to solve these problems [5].

Polysulfone (PSU) is a popular thermoplastic polymer for microfiltration membrane processes, and it has become an interesting subject for

researchers all over the world. The stability in a vast range of pH, high thermal resistance, and mechanical strength are some of the crucial properties of PSU membranes [6-8]. PSU membranes are mostly fabricated by the phase inversion method; however, the provided porosity in this method is limited to 10-20%. To enhance the porosity of the membrane, other methods such as electrospinning are considered for membranes fabrication [9-13]. Electrospinning is a promising method capable of producing fibers with high porosity, interconnected pores, and a large specific surface area which can be used in treatment and pre-treatment water purification stages [14]. However, PSU membranes can form a gel layer and block the pores due to their hydrophobic nature leading to a flux decline and a short lifetime of the membrane. To solve such problems, adding nanoparticles is known as an effective way to improve the membrane properties [14]. Introducing silica, titania, alumina, and zeolite nanoparticles to polymeric membranes had shown improvement in the hydrophilicity, mechanical and thermal stability, and flux of water membranes [6]. The antibacterial effect of titania is well-known due to its photocatalytic nature. In addition, it can improve the UV resistance and hydrophilicity of the membrane. Titania is crystallized in three different crystal structures, namely, anatase, brookite, and rutile and provides a variety of advantages [14]. Silica can improve the anti-fouling properties and increase the pore size of the polymer membrane and thus improve PSU properties [15]. In recent years, fabrication and improvement of PSU membranes via electrospinning was a subject of study. Gopal et al. has developed a membrane in a certain electrospinning condition and investigated its properties [16]. Almasi et al. investigated the distribution of nano titania in PSU fibrous mats [17]. Obaid et al. studied the effect of adding porous silica to PSU on the fiber diameter and mechanical properties of PSU membranes [15].

Diameter is a critical issue in fibers that is directly affected by electrospinning parameters. By altering the diameter of a fibrous membrane, many properties can be properly controlled. In this paper, PSU/TiO_2/SiO_2 nanocomposites were fabricated via electrospinning, and the effects of titania and silica nanoparticles on the electrospun fiber diameters have been investigated. To understand the underlying mechanisms for changes in the fiber diameter, solution parameters including conductivity, surface tension, and viscosity of solutions have been measured.

2. Experimental details

2.1. Solutions preparation

To prepare 20 wt.% polymer solution, 0.708 g PSU pellets (BASF, Germany), were dissolved in 3 ml N,N-dimethylformamide (MERCK, Germany). To prepare composite solutions, proper amounts of titania and silica nanoparticles (both TECNAN, Spain) were added to the polymer solution according to Table 1 and followed by 24 h stirring at room temperature. In order to prevent agglomeration, solutions were ultrasonicated for 2 h prior to electrospinning. The solution was then transferred to a 5 ml syringe, and electrospinning was conducted using a Nanozama electrospinning instrument (Full Option Lab 2ES II-I, NanoazmaCo., Iran). The distance from the needle tip to the collector was set to 15 cm, and electrospinning was done at a constant voltage (15.5 kV) and feed rate (2 ml/h) for all solutions. Then fibers were collected on an aluminum foil and heat-treated at 185 °C for 2 h (Memmert 30-1060, Germany).

2.2. Characterization

The morphology of fibers was observed using a Scanning Electron Microscope (TESCAN_Vega3JK, Czech Republic). In order to estimate the average fiber diameter, 100 measurements were performed on the SEM images of each sample using Image J software. To assess the solutions behavior, viscosity, electrical conductivity, and surface tension of the solutions were measured at room temperature. The viscosity of solutions was measured by a rheometer (MCR-302, Anton Paar, Austria). The surface tension test was performed using a CAG-10 contact angle goniometer and tensiometer (JICAN, Iran), and electrical conductivity was measured by an AZ86505 Probe.

3. Results and discussion

The SEM images of the electrospun samples are shown in Fig. 1. A little titania nanoparticles agglomeration has been observed in S3 and S5 samples. However, the obtained images show almost bead-free fibers with a homogenous structure.

Table 1- Percentage of nanoparticles in polymer solutions

Sample code	Silica NPs (wt.%)	Titania NPs (wt.%)
S1	0.5	0
S2	0.5	0.5
S3	0.5	1
S4	0	0.5
S5	1	0.5

To understand the fiber diameter distribution of each fibrous mat, the histograms of all samples are illustrated in Fig. 2. As can be observed in Fig. 2, all composites have a relatively normal distribution of fiber diameters.

The average fiber diameter of the electrospun

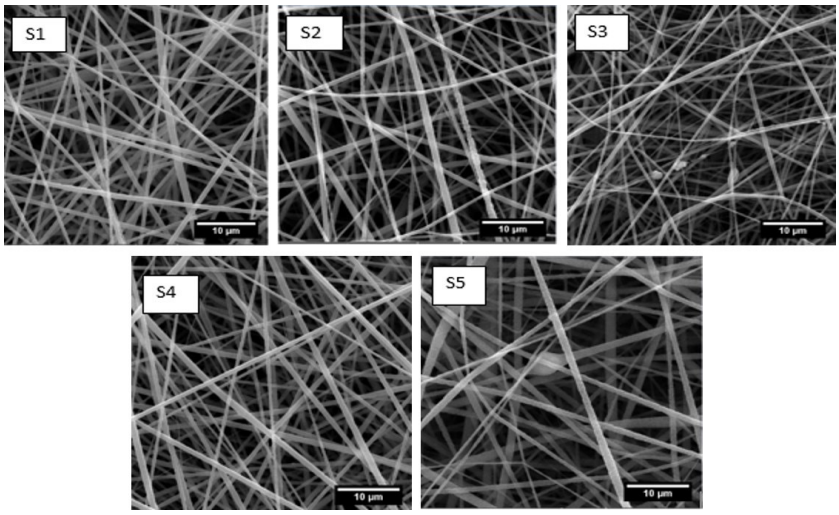

Fig. 1- SEM images of electrospun fibers.

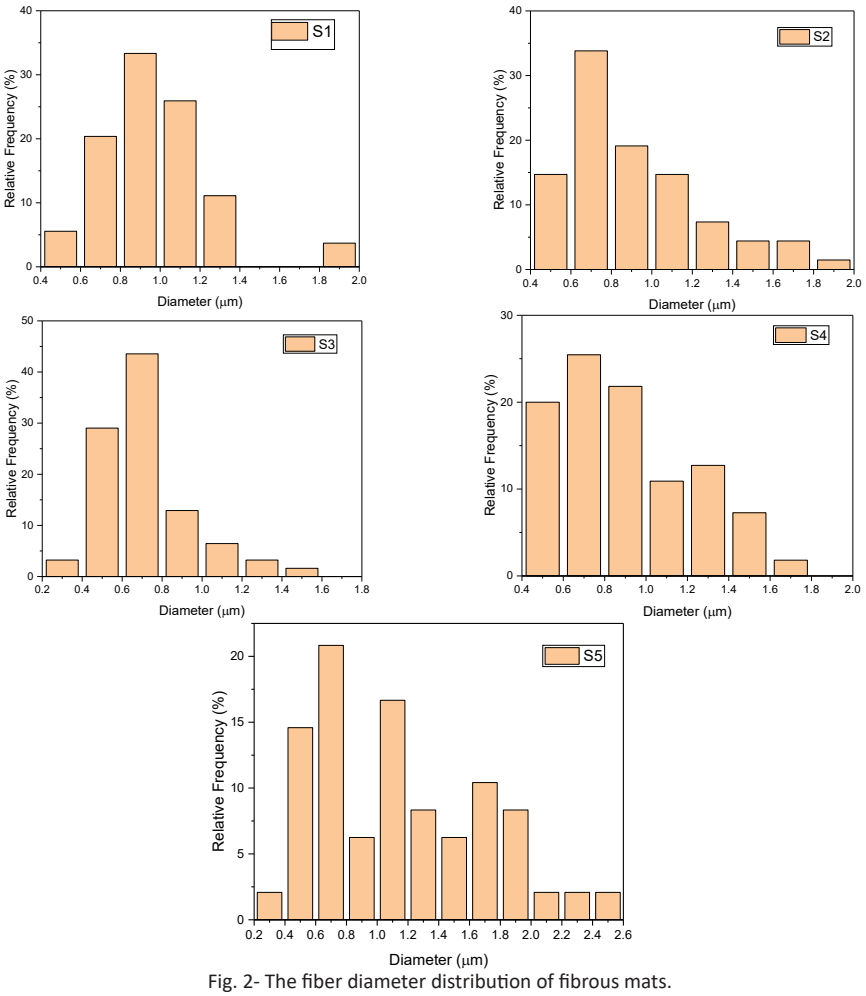

Fig. 2- The fiber diameter distribution of fibrous mats.

fibers was calculated, and its variations with silica and titania content are plotted in Fig. 3. It should be noted that in these plots, the amount of the other nanoparticles was kept constant at 0.5 wt.%. According to Fig. 3, when the amount of titania nanoparticles increased, the average fiber diameter at a constant silica content decreased from 959 to 712 nm. On the other hand, when the amount of silica nanoparticles increased, the average fiber diameter at a constant titania weight percent first decreased from 914 to 883 nm, and then followed by a sharp increase beyond a certain silica percentage and reached 1160 nm.

To assess the reasons for this phenomenon, the properties of the composite solutions were studied. Fig. 4 and 5 indicate the variations of the electrical conductivity and surface tension of solutions with titania and silica wt%. at a constant amount of the

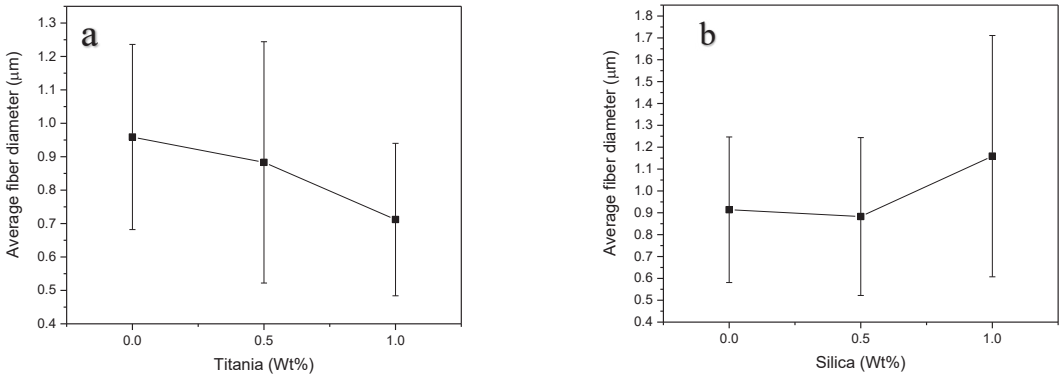

Fig. 3- Average fiber diameter of electrospun fibers at constant amount (0.5 wt%) of a) silica and b) titania.

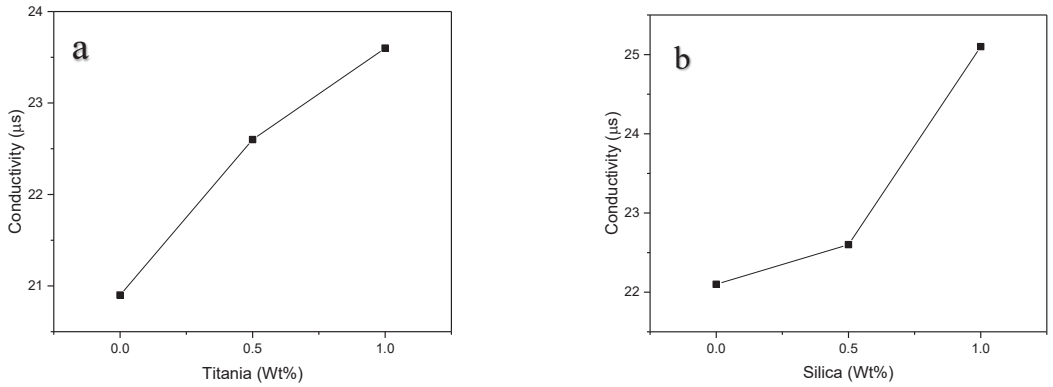

Fig. 4- Conductivity of composite polymer solutions at constant amount (0.5 wt%) of a) silica and b) titania.

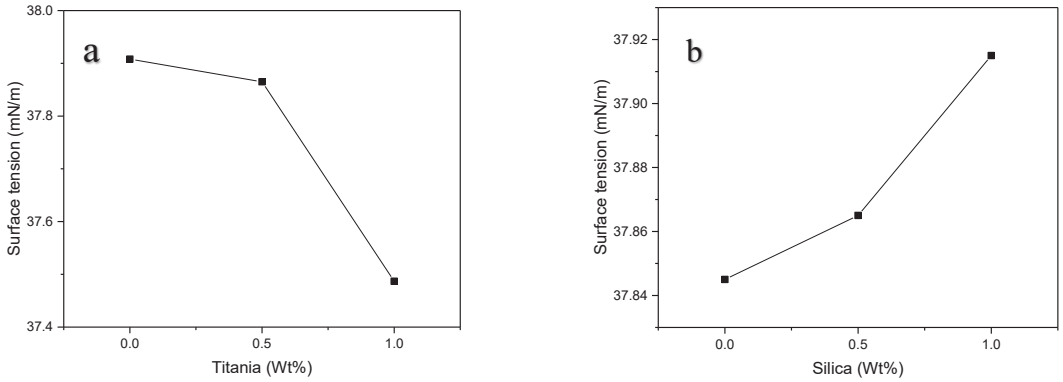

Fig. 5- Surface tension of composite polymer solutions at constant amount (0.5 wt%) of a) silica and b) titania.

other nanoparticle, respectively.

As can be observed in Fig. 4, both nanoparticles have enhanced the electrical conductivity of the polymer solution. Increasing the electrical conductivity will increase the driving force on the polymer jet for stretching and thus leads to a smaller fiber diameter. Moreover, higher electrical conductivity causes more bending instability of the electrospinning jet and prolongs the path taken by the fibers from the needle tip to the collector. Hence, there would be more time for solvent evaporation, which leads to smaller fiber diameters. On the other hand, the surface tension resists fiber stretching, and its increase would require a higher driving force for the formation of the polymer jet and fiber stretching. In other words, solutions with higher surface tension tend to form thicker fibers. As a result, when other electrospinning parameters, including voltage, feed rate, and distance are fixed, increasing the surface tension would increase the fiber diameter.

Fig. 4a shows that increasing titania at a constant amount of silica, has increased the electrical conductivity of composite polymer solution from 20.9 to 23.6 µS/cm. The same trend has happened for silica at a constant amount of titania, leading to an increase from 22.1 to 25.1 µS/cm. Fig. 5 shows that increasing titania at a constant amount of silica has decreased the surface tension of the polymer solution from 37.91 to 37.48 mN/m. However, introducing higher amounts of silica nanoparticles to PSU solution at a constant amount of titania has increased its surface tension from 37.84 to 37.92 mN/m. Based on these solution properties, increasing titania content is expected to decrease the fiber diameter from both aspects of providing higher solution conductivity and lower surface tension.

Fig. 6 illustrates the viscosity of the composite polymer solutions at a constant amount (0.5 wt%) of a) silica and b) titania. Increasing the viscosity causes more resistance to polymer jet stretching during electrospinning and thus increasing the fiber diameter. The results showed that the solution containing equal amounts of silica and titania (S2) had the lowest viscosity, which is in favor of thinning the fibers. Regardless of the nanoparticle type, solutions with the highest nanoparticle content were highly viscose.

The obtained results confirm that solution properties play a significant role in determining the fiber diameter of PSU fibers which is an important physical feature in membrane performance. The obtained results showed that at a constant amount of silica nanoparticles, the variations of both electrical conductivity and surface tension tend to decrease the fiber diameter. Therefore, their combined effect is dominant over the solutions viscosity, and a declining trend is observed in the fiber diameter by increasing titania content. In contrast, at a constant amount of titania, higher silica contents tend to thicken the fibers due to the increased surface tension. This factor amplifies the viscosity trend beyond 0.5 wt.% silica leading to a sharp increase in the average fiber diameter. On the contrary, in the 0 to 0.5 wt.% silica range, the variations of the solution conductivity and viscosity are in the same direction, tending to produce thinner fibers.

4. Conclusions

In the present study, the effects of titania and silica nanoparticles on the average fiber diameters in electrospun PSU-based composite membranes at constant voltage, feed rate, and polymer concentration were investigated. The results indicated that titania had decreased the average fiber

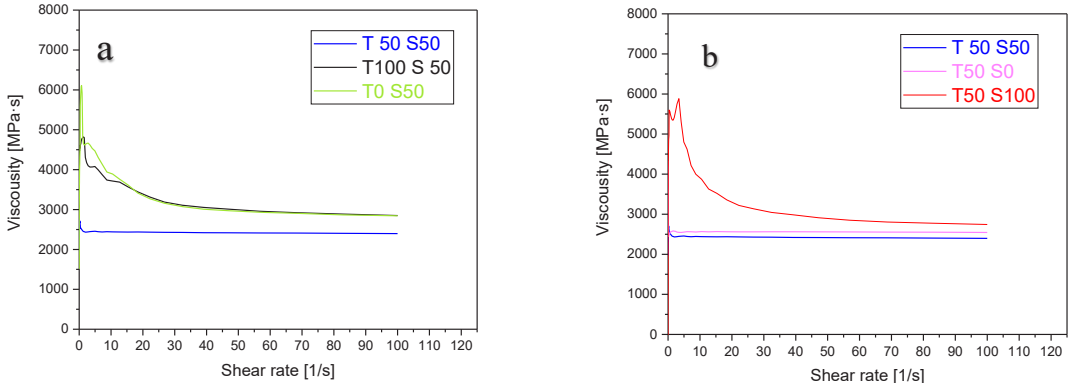

Fig. 6- Viscosity of composite polymer solutions at constant amount (0.5 wt.%) of a) silica and b) titania.

diameter at a certain amount of silica (0.5 wt.%). However, increasing silica created an optimum in the average fiber diameter variations at a constant amount of titania (0.5 wt.%). The obtained results on the solution properties, including conductivity, surface tension, and viscosity, showed that thinner fibers are produced at higher solution conductivity, smaller surface tension, and lower viscosity values. The present findings emphasize the importance of in-depth knowledge of the solution properties to determine the physical feature, hence the performance of PSU membranes.

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