Archives of Metallurgy and Materials

Original research

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Keywords
electrospinning, titania nanoparticles, polyacrylonitrile, electrospun membranes, fouling

Abstract
Electrospun membranes have very promising properties such as high surface area, high surface area-to-pore volume ratio, high pore interconnectivity, and uniform pore distribution. Nanoparticles are a promising alternative for improving the properties of the electrospun membranes. Titania nanoparticles which are stable, resistant, and non-toxic, have various applications including water treatment, sensors, food additive and cosmetics. Due to the high hydrophilicity of titania nanoparticles, membrane fouling is reduced in titania nanoparticles doped membranes. Titania nanoparticles doped PAN nanocomposite electrospun membranes were prepared by electrospinning method in this work. Compared to bare polyacrylonitrile PAN electrospun membranes 0.05% titania nanoparticles doped electrospun membranes have thinner nanofibers, higher hydrophilicity and almost 2 times lower bovine serum albumin adsorption, which shows lower fouling tendency.

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Titania Nanoparticles Doped Electrospun Membranes

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Abstract

Electrospun membranes have very promising properties such as high surface area, high surface area-to-pore volume ratio, high pore interconnectivity, and uniform pore distribution. Nanoparticles are a promising alternative for improving the properties of the electrospun membranes. Titania nanoparticles which are stable, resistant, and non-toxic, have various applications including water treatment, sensors, food additive and cosmetics. Due to the high hydrophilicity of titania nanoparticles, membrane fouling is reduced in titania nanoparticles doped membranes. Titania nanoparticles doped PAN nanocomposite electrospun membranes were prepared by electrospinning method in this work. Compared to bare polyacrylonitrile PAN electrospun membranes 0.05% titania nanoparticles doped electrospun membranes have thinner nanofibers, higher hydrophilicity and almost 2 times lower bovine serum albumin adsorption, which shows lower fouling tendency.

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1. Introduction

One dimensional nanocomposite fibers are used in sensors, membrane filtration, biomedical applications, energy production, etc. due to their improved electrical, optical and chemical properties [1-7]. There are various methods to produce nanofibers including drawing, templates, phase separation, self-assembly, and electrospinning [8]. Among them, electrospinning is the most practical, economical, and fast [9, 10]. Electrospinning has attracted attention since its discovery in 1934. Nanofibers prepared by electrospinning has many remarkable features such as small diameter (50 nm - 10 mm), high aspect ratio (length-to-diameter ratio), large specific surface area (ratio of surface area to volume), diversity in composition, unique physicochemical properties, flexibility in chemical / physical surface functionalization [5, 11, 12]. The properties of electro spun nanofibers can be improved by adding nanomaterials. Nanomaterials doped composite electro spun nanofibers in many fields including filtration, sensors, fuel cell and nanoelectronics.

Electrospun membranes have very promising properties such as high surface area, a high surface area-to-pore volume ratio, high pore interconnectivity, and uniform pore distribution. There are many recent researches in functionalizing electrospun nanofibers to improve their applicability in different areas. Nanoparticles are a promising alternative for improving the properties of the electrospun nanofibers. Properties like uniform pore size, narrow pore size distribution, hydrophilicity, mechanical strength, and stability can be enhanced by nanoparticle addition in the nanofiber structure [13].

Titania nanoparticles are stable, resistant, and non-toxic. Hence, they have various applications, including water treatment, sensors, food additive and cosmetics [14-16]. Due to the high hydrophilicity of titania nanoparticles, membrane fouling is reduced in titania nanoparticles doped membranes [17]. The objective of this work is to synthesize titania nanoparticles doped

polyacrylonitrile (PAN) nanocomposite electrospun membranes by electrospinning with lower fouling tendency. Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) were employed for characterizing the nanocomposite electrospun membranes. Moreover, bovine serum albumin adsorption of nanocomposite electrospun membranes was also determined.

2. Materials and Methods

Titania nanoparticles (with a diameter of less than 25 nm) and anhydrous N, N-dimethyl formamide (DMF, 99.8%) were purchased from Sigma (USA), and PAN (with a molecular weight of 150,000) from Polysciences Inc. (USA).

The dope solution for the nanofiber synthesis was prepared as follows: Initially titania nanoparticles was ultrasonicated in DMF, then PAN was dissolved. Afterwards, the solution was ultrasonicated to remove air bubbles. All nanofibers were synthesized by using the electrospinning instrument (NE100, Inovenco Co. Ltd., Turkey) represented in Fig. 1.

<Fig. 1.>

Electric field was generated between the nozzle system and a rotating collection drum. There were 4 nozzles with an inner diameter of 700 μm each. The rotation speed of the collection drum was 350 rpm. A syringe pump was used for pumping the dope solution. Nanofibers were collected on a non-woven fabric. Initially voltage applied, distance between the nozzle system and collection drum, and feed rate of the dope solutions were optimized for all solutions. Then these values (TABLE 1) were used for nanocomposite electrospun membrane synthesis.

<TABLE 1.>

A viscosimeter (Vibro, And, Japan) was used to measure the viscosities of the polymer solutions. SEM (Quanta FEG 250; FEI, USA) and FTIR (Spectrum Two, Perkin Elmer) were used for determining the surface morphologies and the structure of the nanocomposite electrospun membranes. Average fiber diameters were reported by averaging the diameters of the 20 nanofibers from each of 20 different SEM images for each membrane.

The structures of the electrospun membranes were examined by FTIR (Spectrum Two, PerkinElmer, USA), and their surface hydrophilicity was determined using a contact angle goniometer (Theta Lite, Attension, Sweden). It is calculated by averaging at least seven contact angle values measured for each membrane.

For the adsorption tests, membranes were cut into small pieces and immersed into 1 g/L BSA solution at neutral pH at room temperature for 4 h. Afterwards, the coupons were ultrasonicated in DI water for 2 min. The amount of the adsorbed BSA was directly measured using a UV-vis spectrometer (UV-VIS Spectrophotometer Shimadzu, Japan) at 280 nm. The average of at least two measurements was reported.

3. Results and Discussion

Viscosities of the polymer solutions of the electrospun membranes are given in TABLE 2. As shown in the TABLE titania nanoparticles addition increased the viscosity of the polymer solution. The increase in the viscosity in the polymer solution improved the dispersion of the nanoparticles in the polymer solution.

<TABLE 2.>

SEM images of the electrospun membranes are given in Fig. 2. SEM images show that no

beads were formed in any of the electrospun membranes. The balance between the electrostatic repulsion, surface tension, and viscoelastic forces determines the quality of the fibers in the electrospinning process. Increase in viscosity of the polymer solution results in suppression of the surface tension due to the electrostatic repulsion and viscoelastic forces. Bead free and smooth fibers were formed by the dominating viscoelastic forces [9].

<Fig. 2.>

Reported nanofiber diameters of the electrospun membranes are the average of the 20 nanofibers from 20 different SEM images for each membrane. The average of the nanofiber diameters determined is shown in Fig.3. Addition of 0.05% titania nanoparticles in the polymer solution reduced the nanofiber diameter. However, further increase in the titania nanoparticles amount resulted in increased nanofiber diameter.

<Fig. 3.>

FTIR spectra recorded in the spectral range of 4000 - 400 cm-1 of the electrospun membranes are given in Fig.4. The peak around 2250 cm^{-1} corresponds to C≡N stretching vibration [18], around 1260 cm^{-1} corresponds to weak ether peak (C–O–C) [19] of PAN. Compared to the bare PAN electrospun membrane (P/T-0) two new peaks were observed in titania nanoparticles doped PAN electrospun membranes (P/T-0.05, P/T-0.1, P/T-0.2) around 874 cm^{-1} and 972 cm^{-1} corresponding to Ti–O–Ti vibrations [18, 20], which confirmed the presence of titania nanoparticles into the nanofiber matrix.

<Fig. 4.>

Hydrophilicity of the membranes was evaluated by determining contact angles (Fig.5). Lower contact angle shows higher hydrophilicity and higher contact angle shows higher

hydrophobicity. Addition of titania nanoparticles increased the hydrophilicity of the electrospun membranes. Moreover, increasing the titania nanoparticles amount in the fiber composition increased the hydrophilicity of the electrospun membranes.

<Fig. 5.>

BSA was chosen as a model protein for determining the adsorption resistances of the electrospun membranes. BSA adsorption on electrospun membranes is shown in Fig.6. Addition of titania nanoparticles in the structure of the nanofibers of the electrospun membranes reduced the BSA adsorption almost 2 times compared to the bare membranes at neutral pH. This indicates the potential usage of titania nanoparticles for alleviating the fouling.

<Fig. 6.>

4. Conclusions

The preparation and fouling behavior of titania nanoparticles doped PAN electrospun membranes were investigated, with several conclusions subsequently drawn. These conclusions include the following.

- Titania nanoparticles doped electrospun membranes were successfully synthesized by the electrospinning method. New peak formations in FTIR analysis confirmed that titania nanoparticles successfully blended in the nanofiber structure.

- Nanofibers of the titania nanoparticles doped PAN electrospun membranes are thinner than the bare membranes.

- Titania nanoparticles doped PAN electrospun membranes are more hydrophilic than the bare electrospun PAN membranes.

- BSA adsorption on titania nanoparticles doped PAN electrospun membranes are almost 2 times lower than the bare membranes, indicating potential usage of titania nanoparticles for alleviating the fouling.

- Titania nanoparticles doped PAN electrospun membranes can be an alternative to disposable membranes like syringe filters with their reduced fouling tendency.

Acknowledgments

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Figures

Fig. 1. Schematic representation of electrospinning instrument

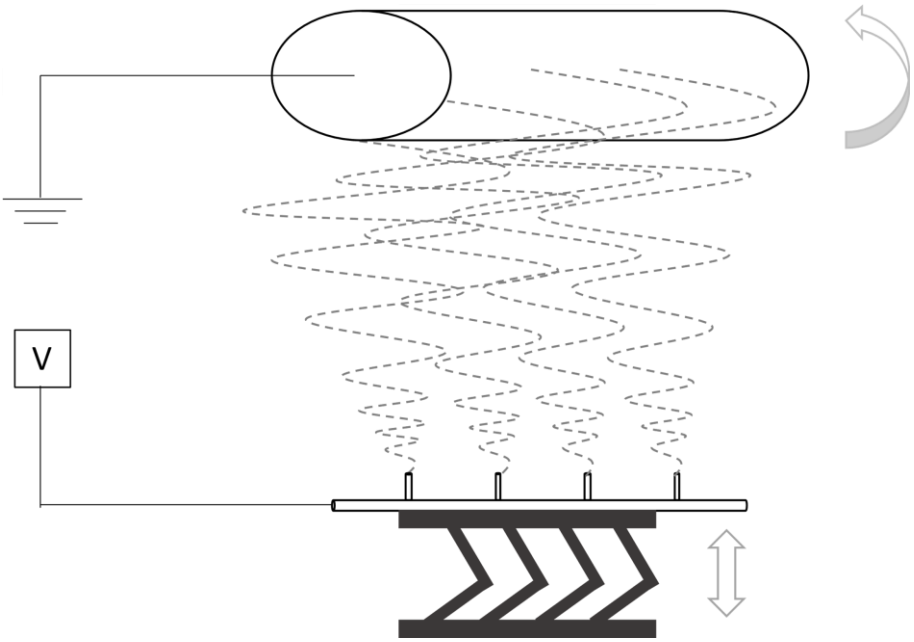
Fig. 2. SEM images of electrospun membranes at different magnifications; (a) P/T-0 at 1000x magnification, (b) P/T-0 at 10000x magnification, (c) P/T-0.05 at 1000x magnification, (d) P/T-0.05 at 10000x magnification, (e) P/T-0.1 at 1000x magnification, (f) P/T-0.1 at 10000x magnification, (g) P/T-0.2 at 1000x magnification, (h) P/T-0.2 at 10000x magnification

Fig. 3. Fiber thicknesses of the electrospun membranes

Fig. 4. FTIR spectra of electrospun membranes

Fig. 5. Contact angles of the electrospun membranes

Fig. 6. BSA adsorption on electrospun membranes



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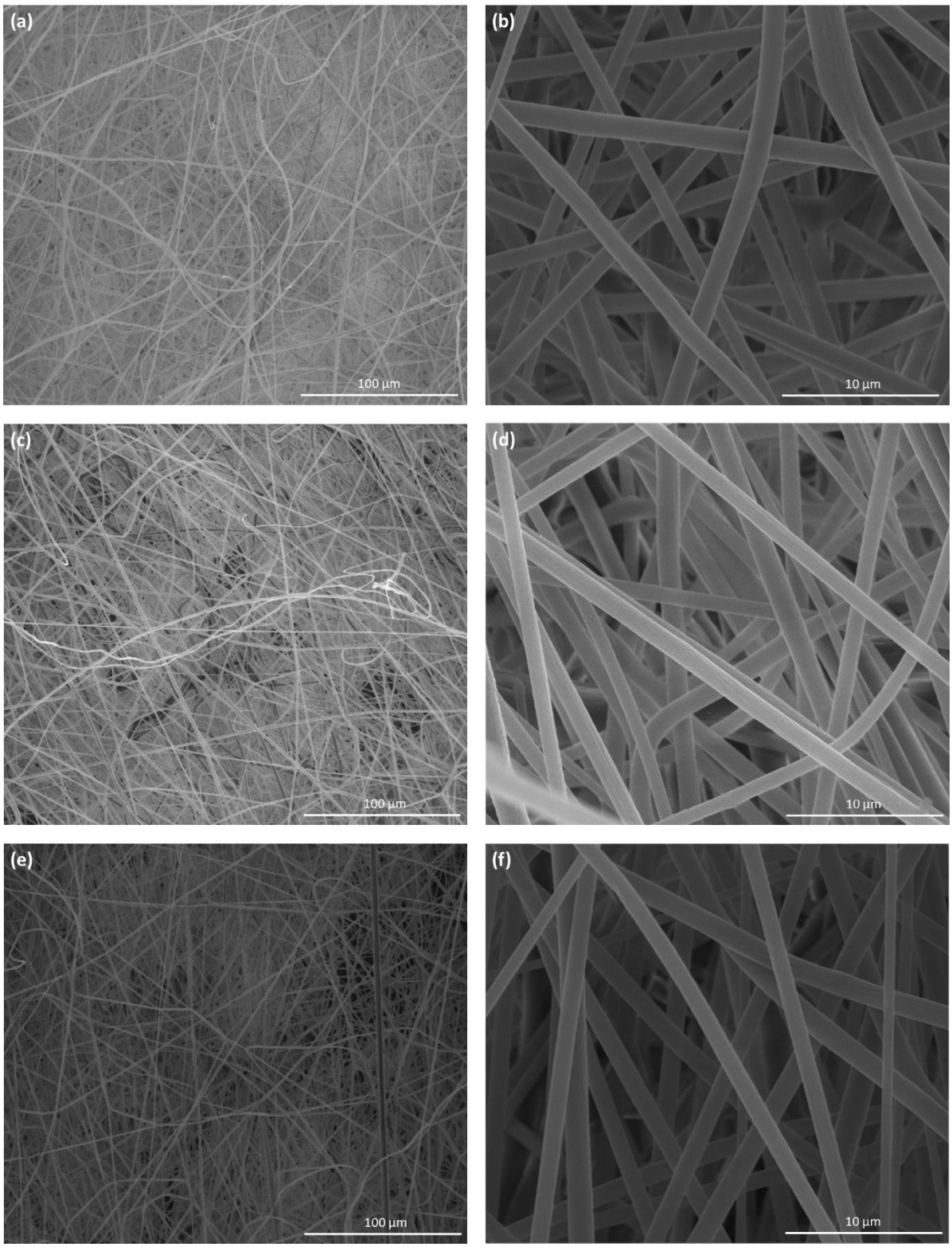
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100 µm
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(c)
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(d)
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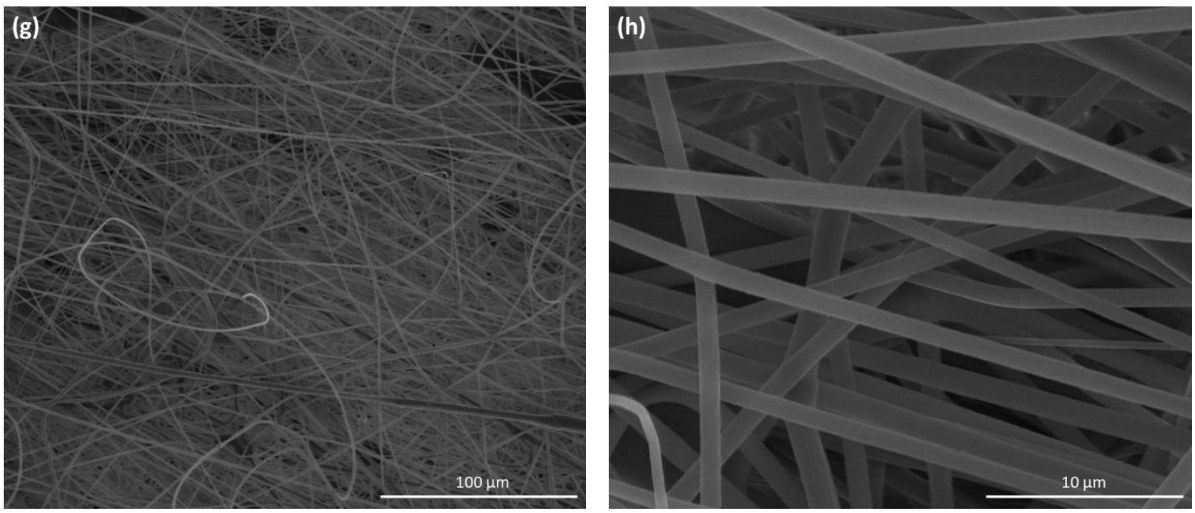
(e)
100 µm
(f)
10 µm



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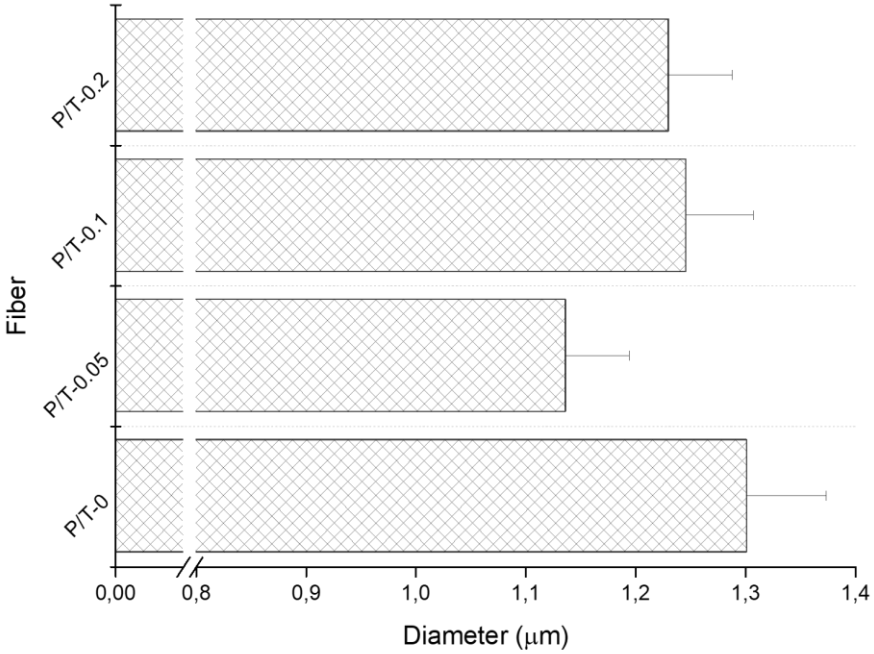

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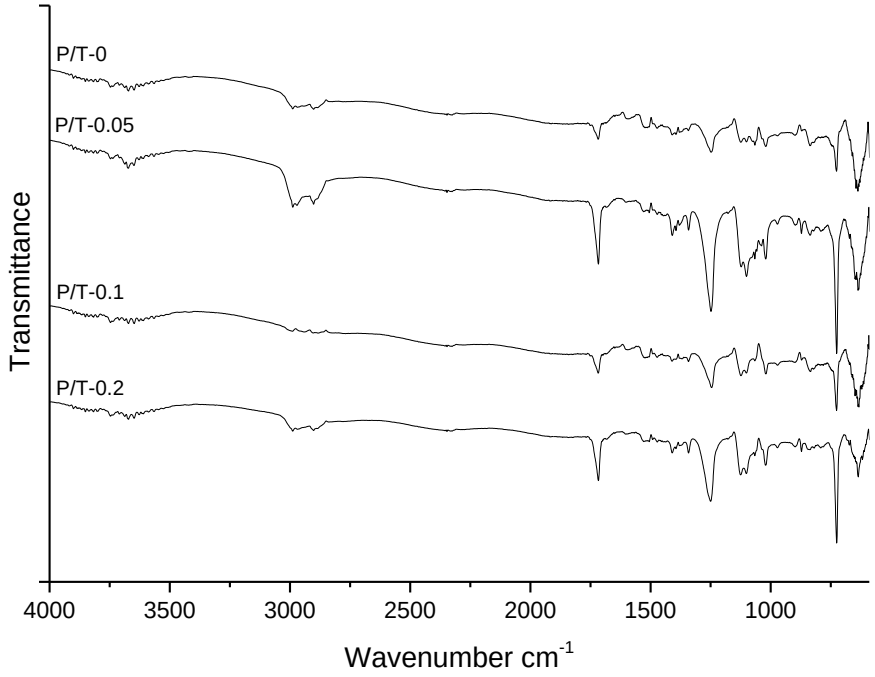


Fig. 4. FTIR spectra of electrospun membranes

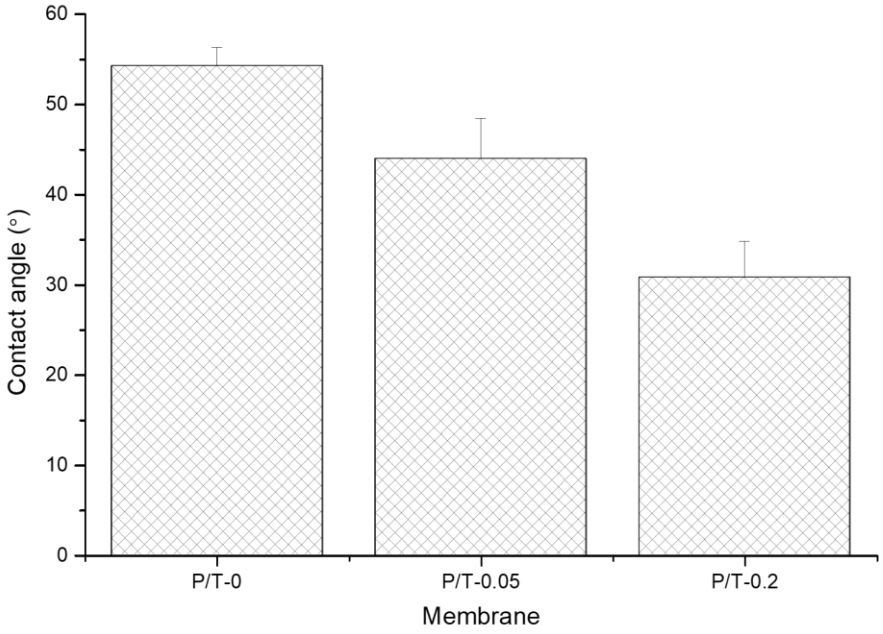
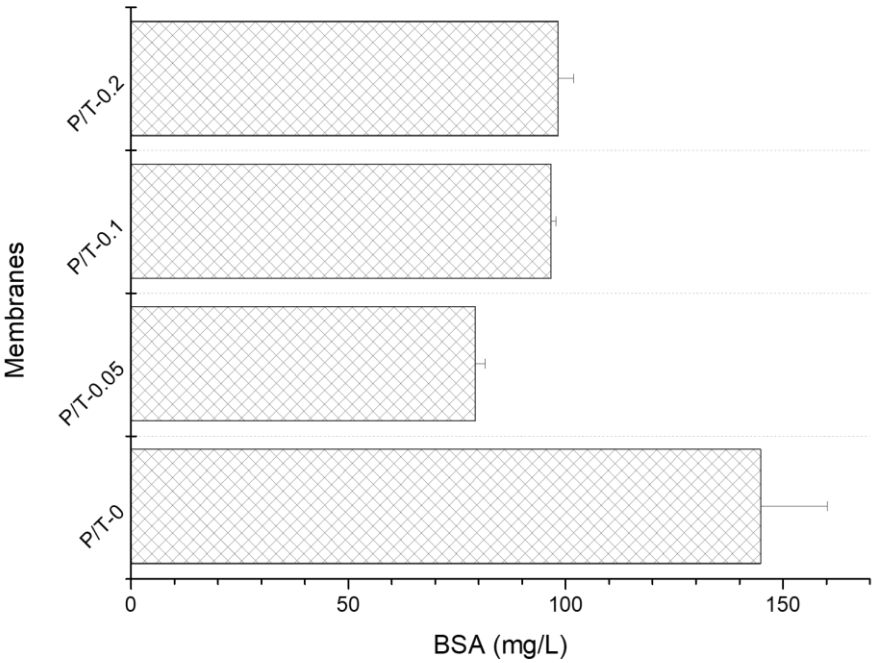


Fig. 5. Contact angles of the electrospun membranes



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228 Tables

229 TABLE 1. Electrospinning characteristics

230 TABLE 2. Viscosities of the polymer solutions

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Membrane Name	$nTiO_2$ Ratio (%)	Voltage (kV)	Feed Rate (mL/h)	Distance (cm)
P/T-0	0	35	6	16
P/T-0.05	0.05	34	12	16
P/T-0.10	0.10	34	12	16
P/T-0.20	0.20	34	10	16

TABLE 2. Viscosities of the polymer solutions

Membrane Name	Viscosity (Pa.s)	Temperature (°C)
P/T-0	3.25	21.0
P/T-0.05	4.09	20.3
P/T-0.10	3.70	20.1
P/T-0.20	3.65	20.2

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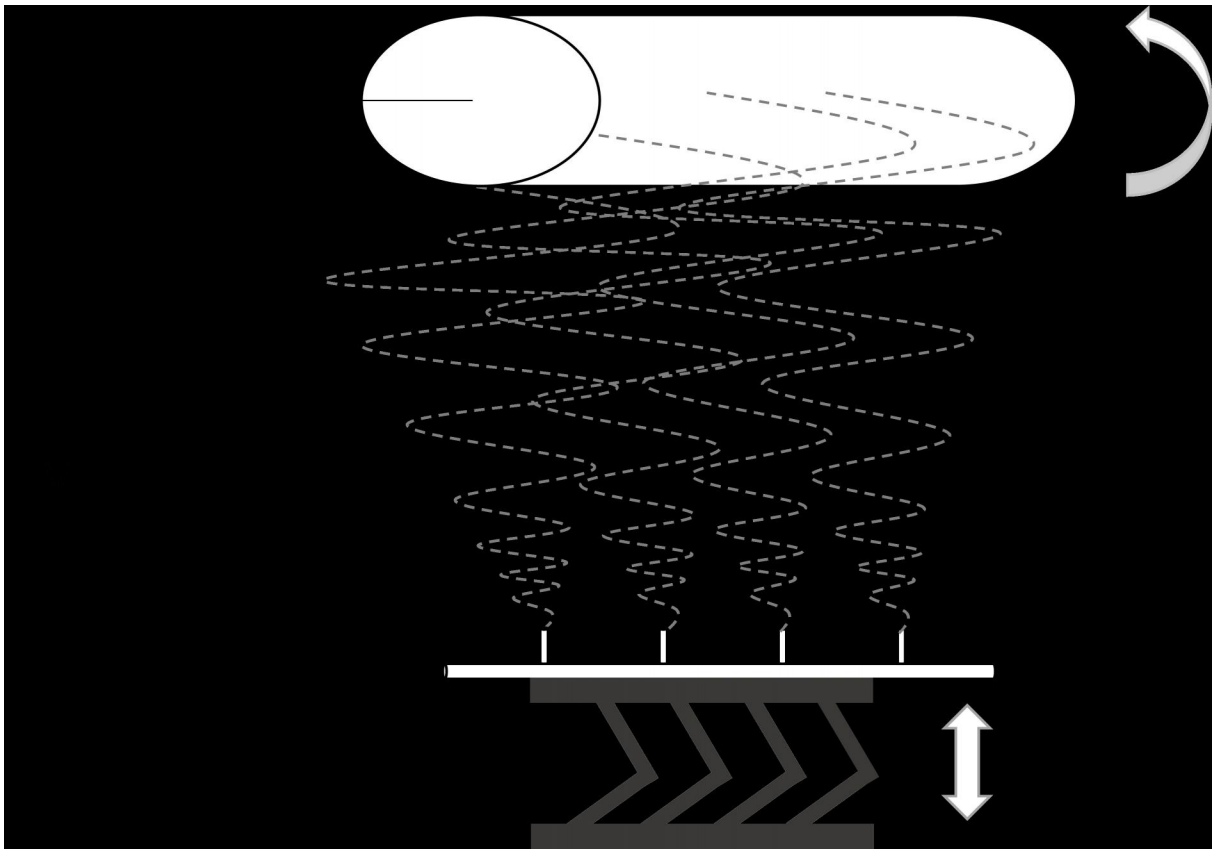

Fig. 1 Schematic representation of electrospinning instrument

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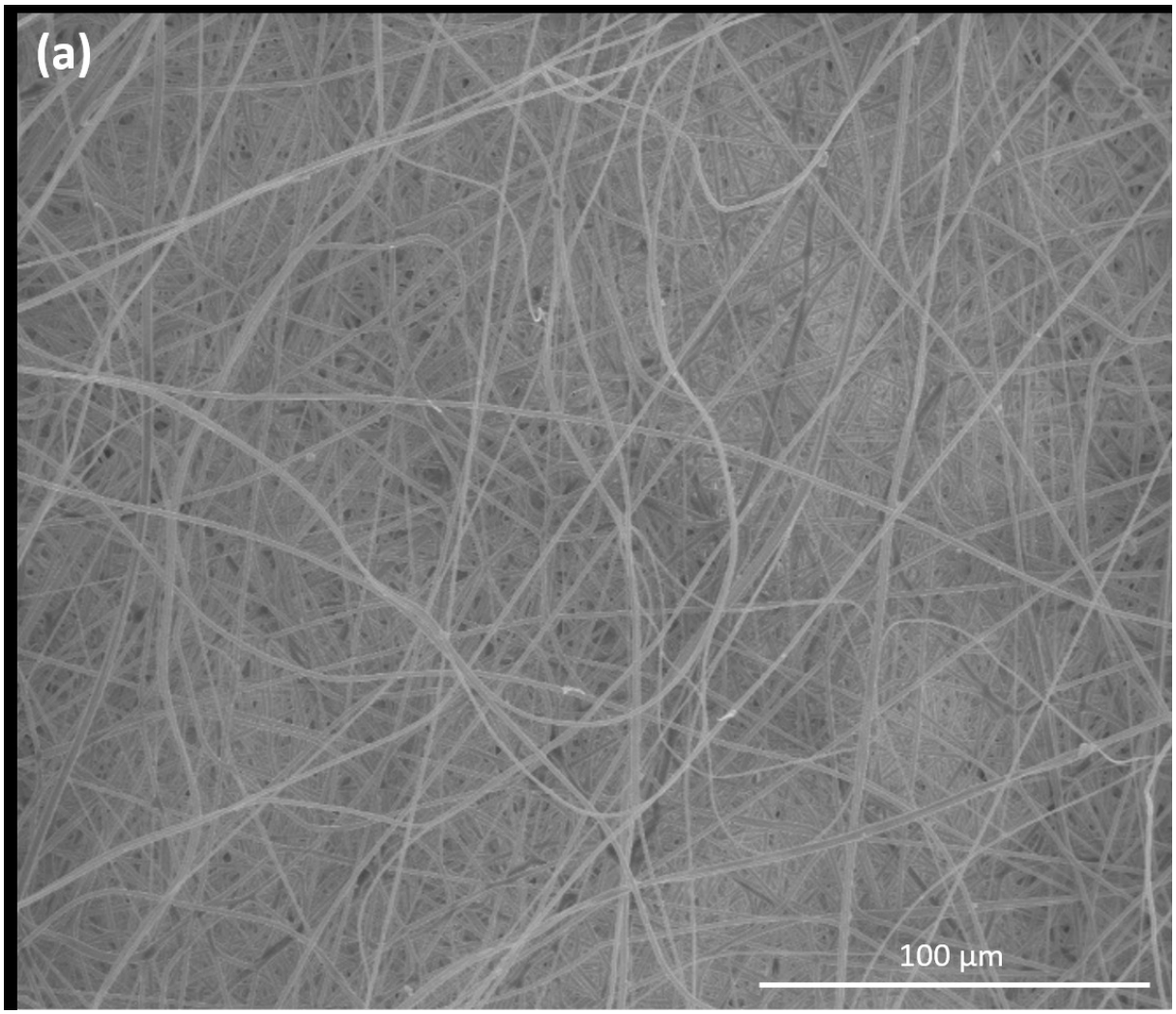

Fig. 2a. P/T-0 at 1000x magnification

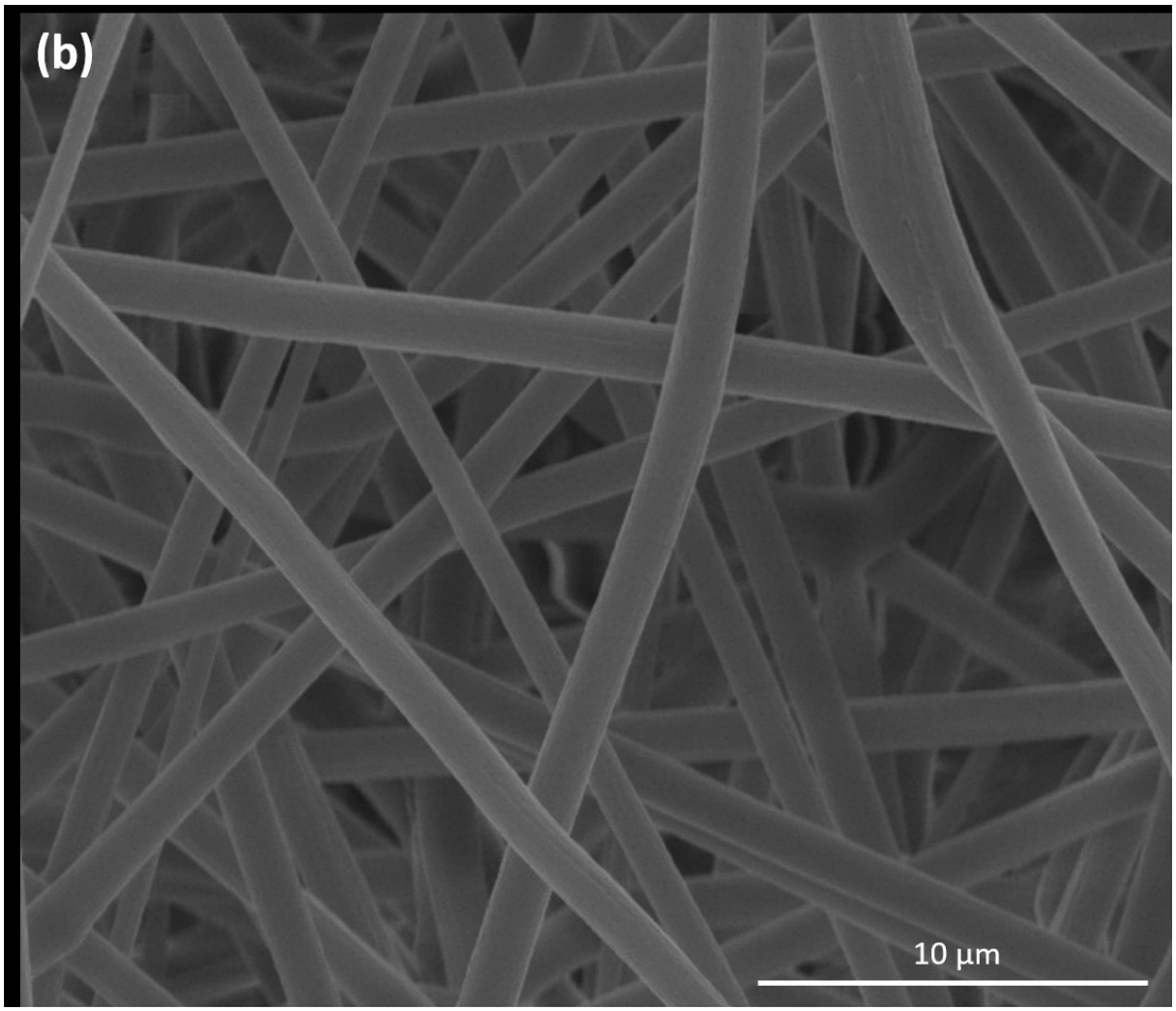

Fig. 2b. P/T-0 at 10000x magnification

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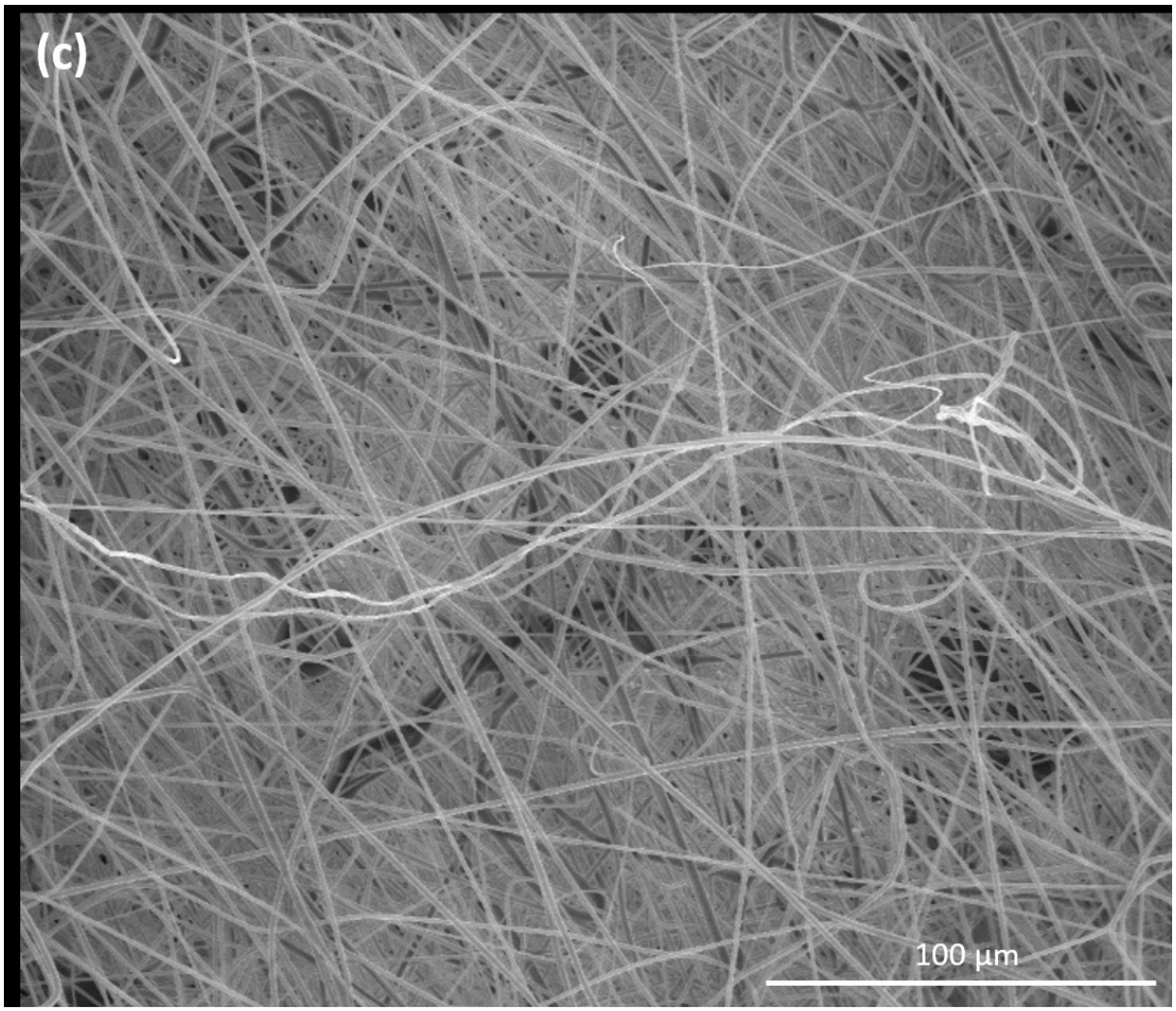

Fig. 2c. P/T-0.05 at 1000x magnification

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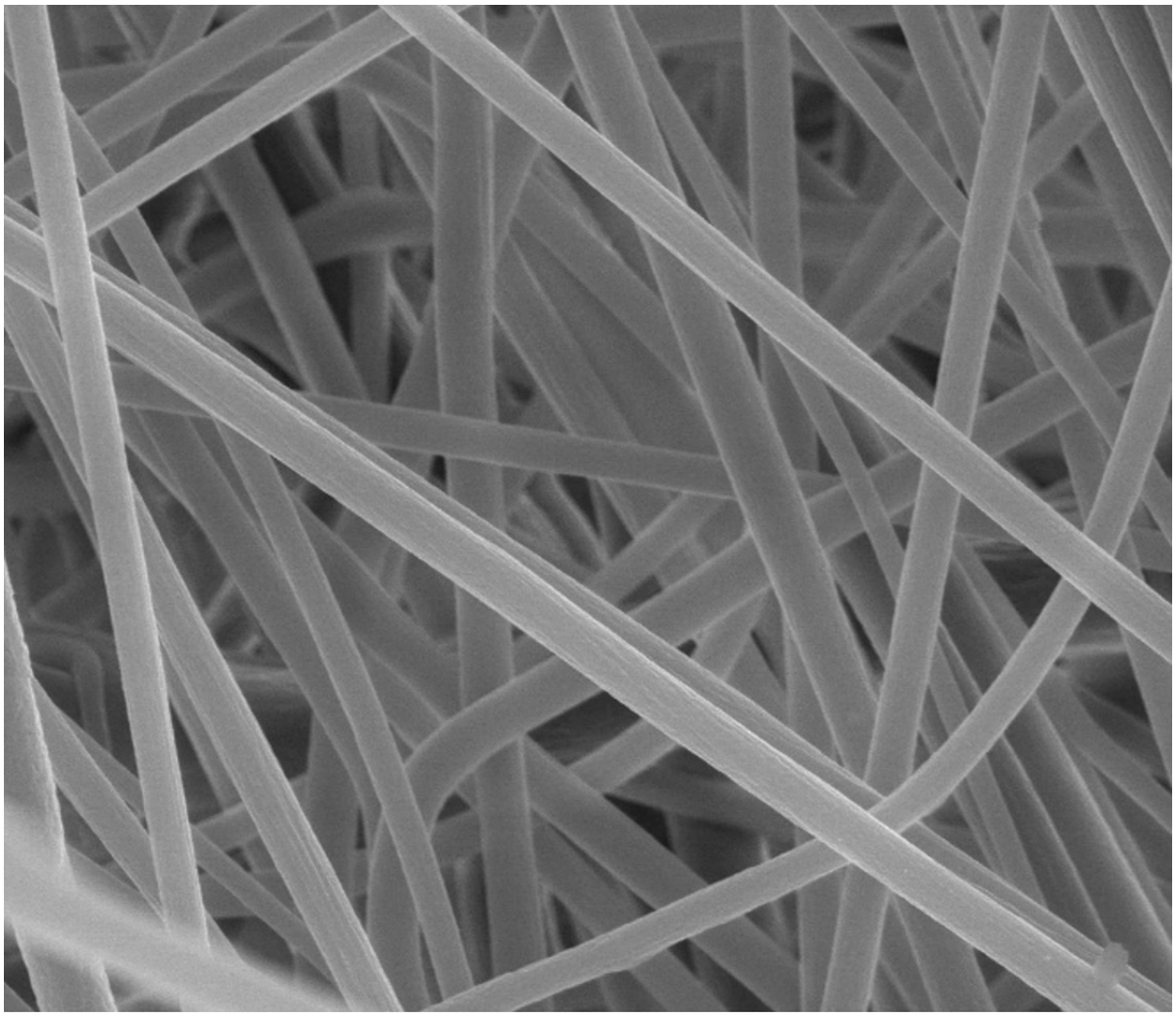


Fig. 2d. P/T-0.05 at 10000x magnification

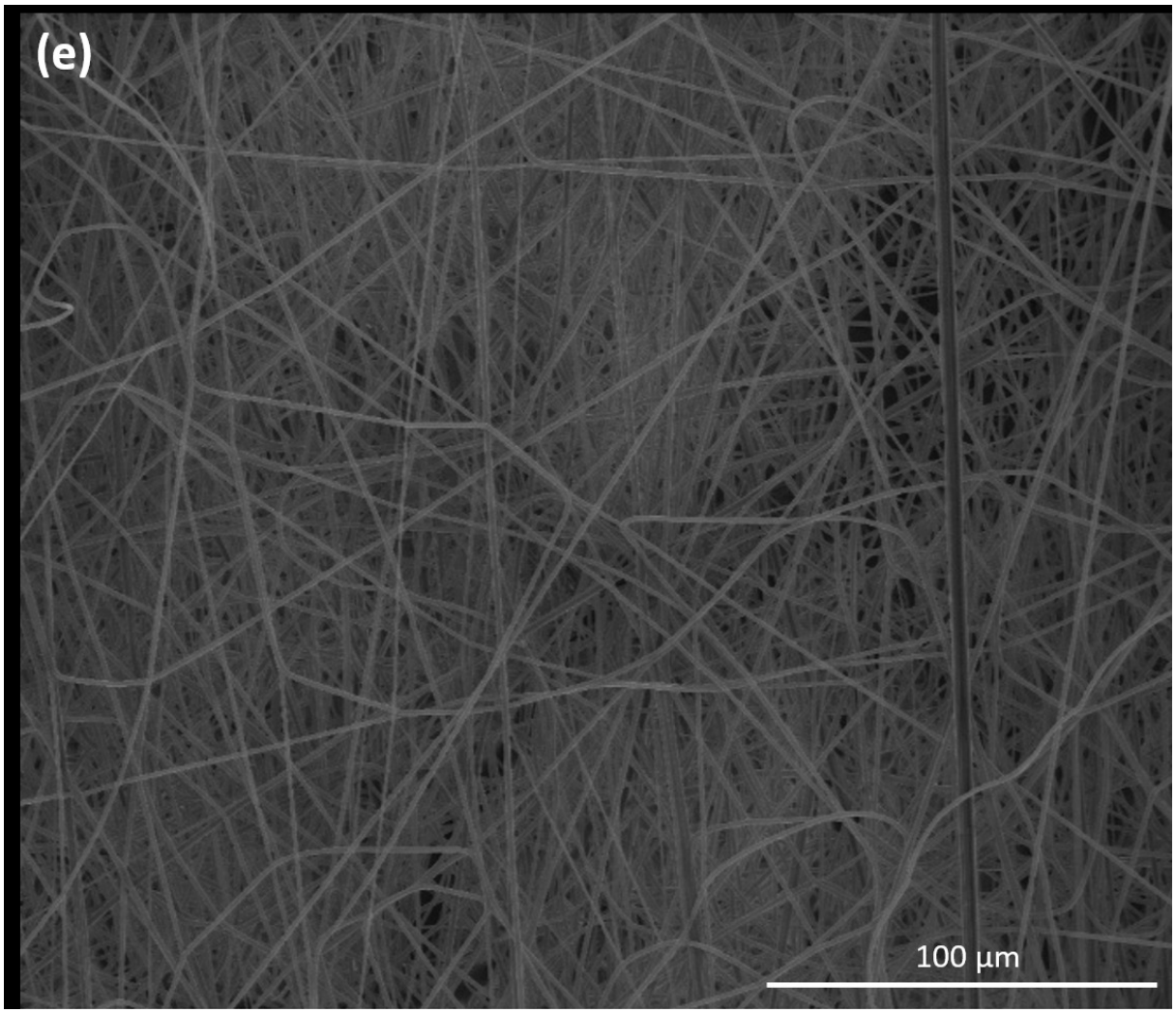
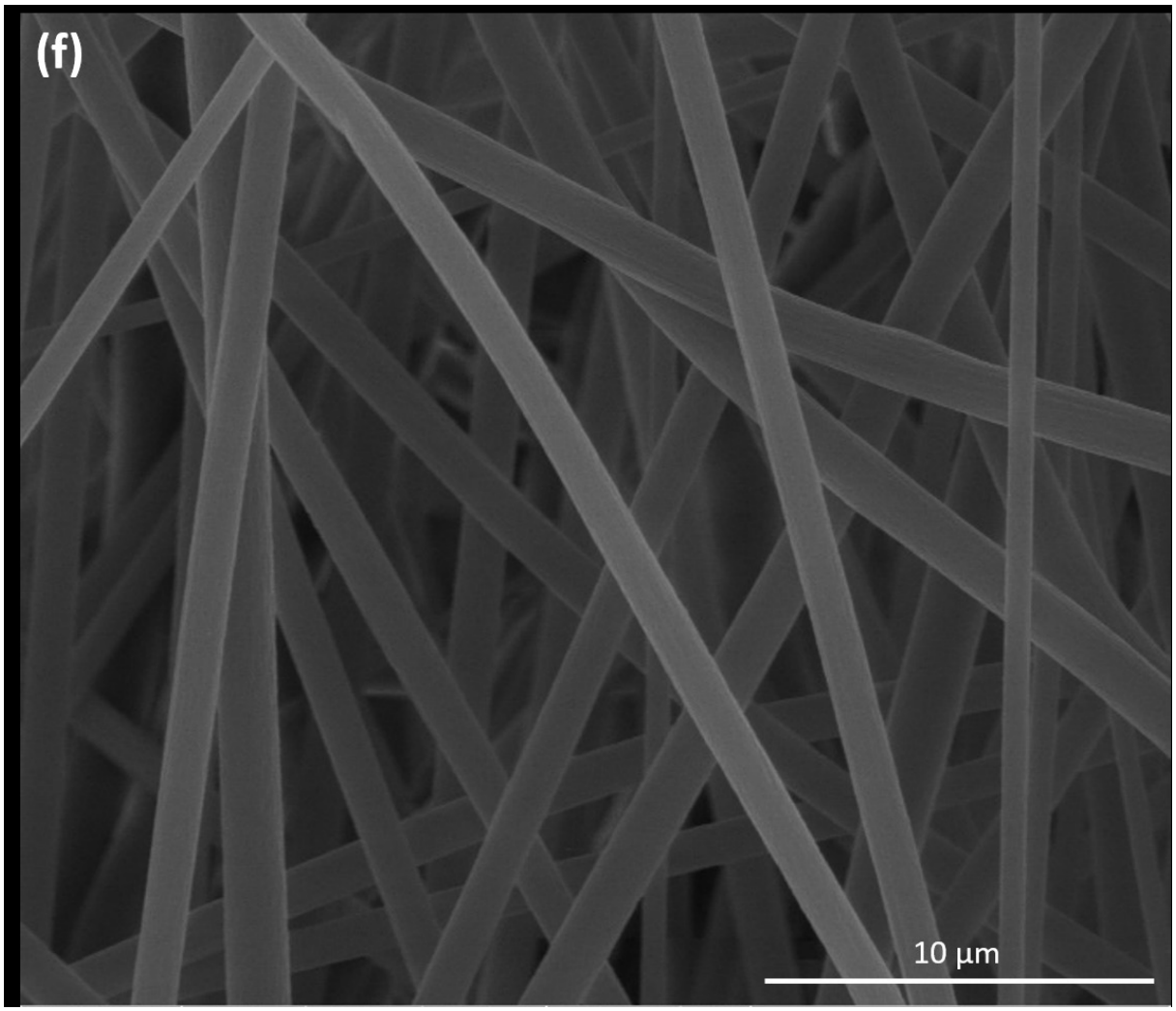


Fig. 2e. P/T-0.1 at 1000x magnification



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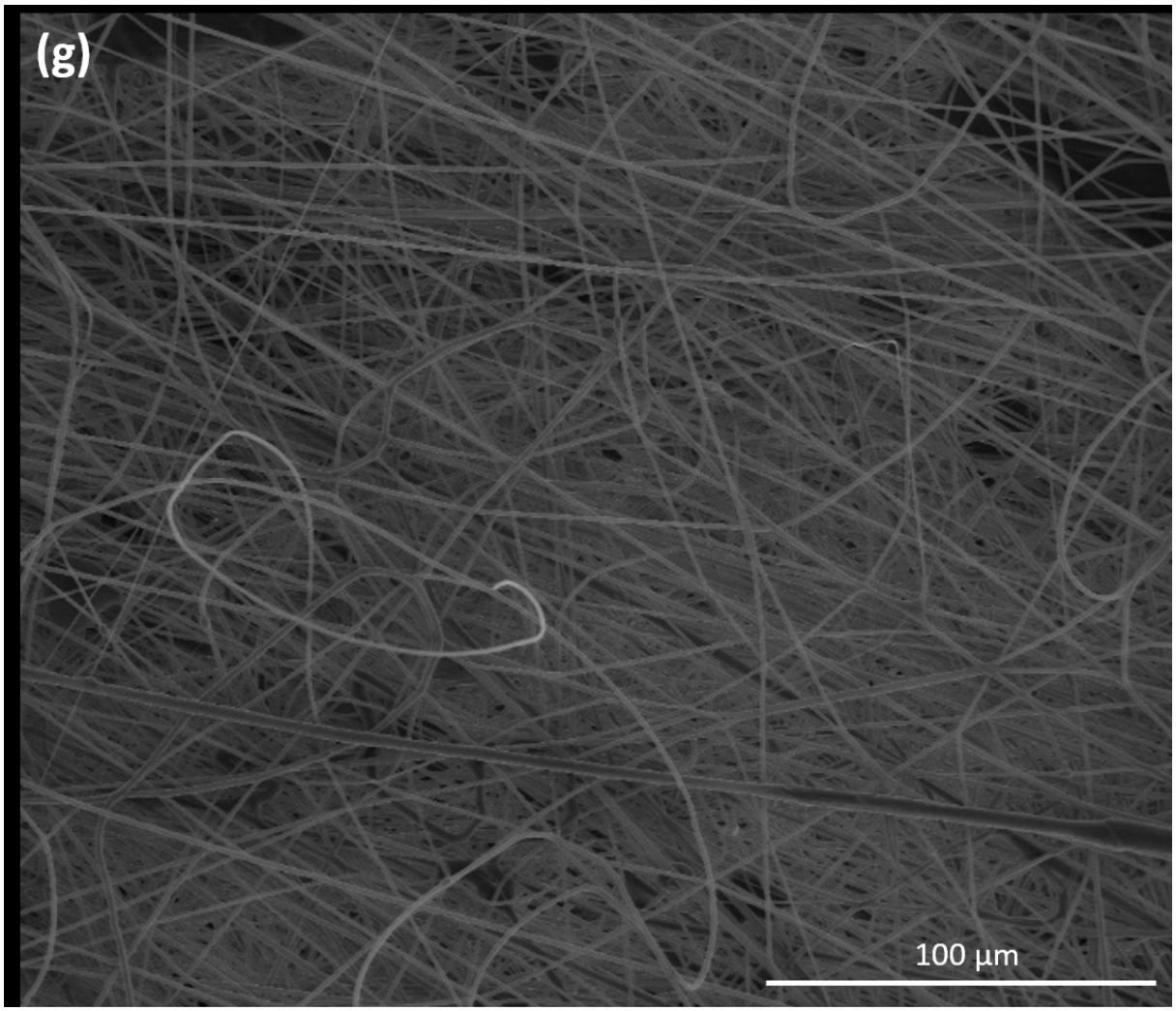

Fig. 2g. P/T-0.2 at 1000x magnification

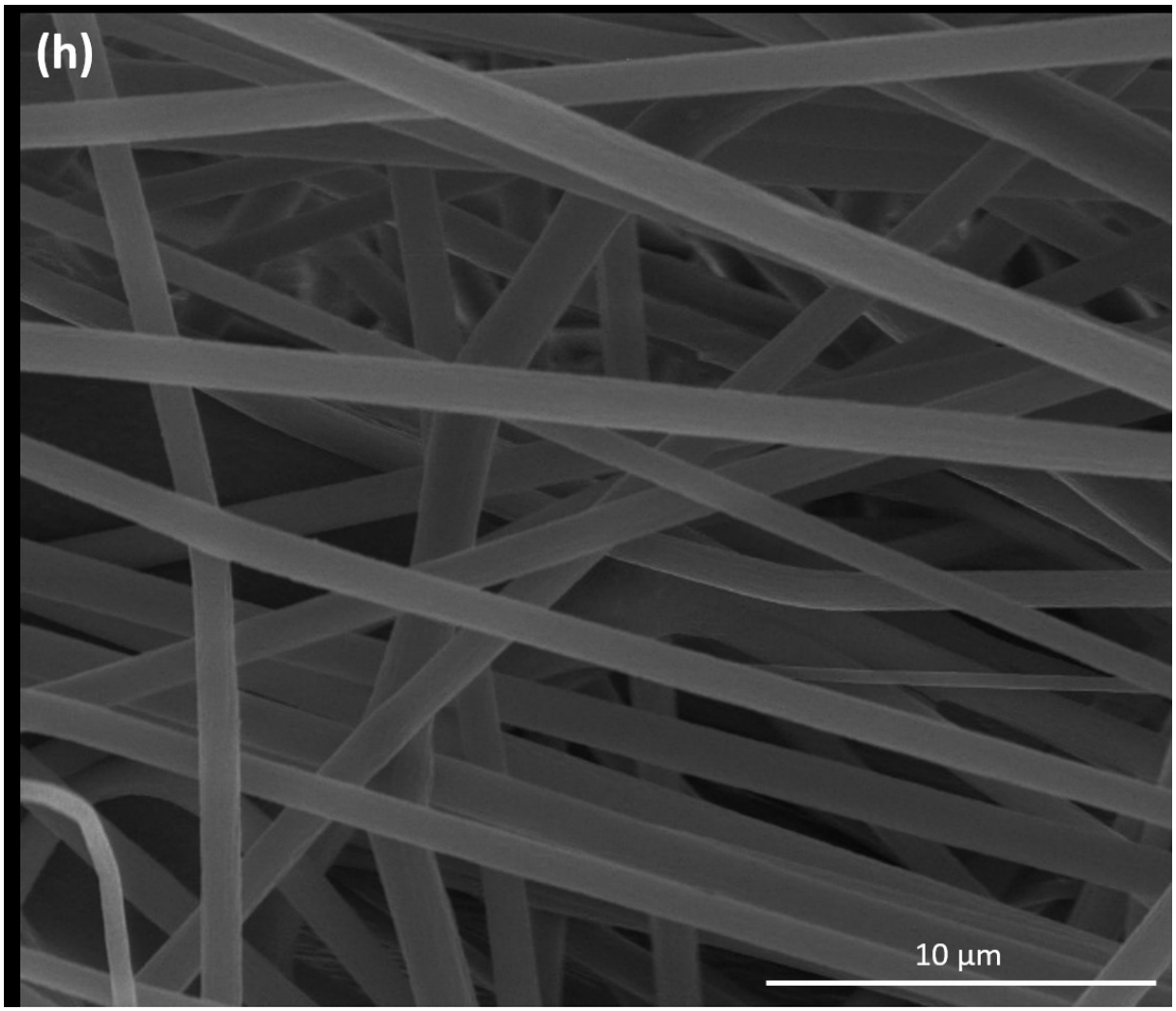

Fig. 2h. P/T-0.2 at 10000x magnification

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Tables

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Fig. 4. FTIR spectra of electrospun membranes

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Fig. 3. Fiber thicknesses of the electrospun membranes

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Fig. 2b. P/T-0 at 10000x magnification

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Fig. 2c. P/T-0.05 at 1000x magnification

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Fig. 2d. P/T-0.05 at 10000x magnification

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Fig. 2e. P/T-0.1 at 1000x magnification

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Fig. 2f. P/T-0.1 at 10000x magnification

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Fig. 2g. P/T-0.2 at 1000x magnification

Figure 13 - Download source file (797.51 kB)
Fig. 2h. P/T-0.2 at 10000x magnification