



*Original Article*

## Electrospun poly(bisphenol A-co-4-nitrophthalic anhydride-co-1,3-phenylenediamine) fibers: Preparation and potential for use in filtration applications

Patcharaporn Thitiwongsawet<sup>1\*</sup>, Prapaporn Sae-Lee<sup>1</sup>, Preeya Kwanduen<sup>1</sup>, Watchanida Chinpa<sup>1</sup>, and Pitt Supaphol<sup>2</sup>

<sup>1</sup> Department of Materials Science and Technology, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla, 90112 Thailand.

<sup>2</sup> The Petroleum and Petrochemical College and The Center for Petroleum, Petrochemicals and Advanced Materials, Chulalongkorn University, Pathum Wan, Bangkok, 10330 Thailand.

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### Abstract

Poly(bisphenol A-co-4-nitrophthalic anhydride-co-1,3-phenylenediamine) (PEI) fibers were successfully prepared by electrospinning from PEI solutions in dichloromethane (DCM), 1,2-dichloroethane (DCE), *N*-methylpyrrolidone (NMP) and certain mixtures between NMP and *N,N*-dimethylformamide (DMF). Electrospinnability of PEI solutions in NMP was greater than that in DCM and DCE. The addition of DMF with NMP for the preparation of PEI solutions helped improve electrospinnability of the PEI solutions. The effect of solution concentration on morphological appearance and/or size of the obtained products was investigated. At low concentrations of the PEI solutions, discrete beads and/or beaded fibers was formed. Smooth fibers were obtained at the highest concentration investigated, i.e., 20% (w/v). The size of the obtained fibers was found to be an increasing function with the solution concentration or, to be exact, the solution viscosity. The water fluxes through the electrospun fiber mats prepared from 20% (w/v) PEI solutions in 75/25 and 50/50 NMP/DMF mixtures were investigated in comparison with the films prepared by phase immersion-precipitation technique. The fiber mats exhibited much greater fluxes of water than the films, which implied their potential for uses as filtration membranes.

**Keywords:** electrospinning, polyetherimide, filtration, fiber

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### 1. Introduction

In the past decades, electrospinning has become a powerful and highly sought-after technique for fabricating ultrafine fibers with diameters in the range of tens of micrometers down to tens of nanometers. The principle of this technique is the application of electrical forces as the means for fiber formation (Doshi *et al.*, 1995; Reneker *et al.*, 2008). When an electric field of a critical magnitude is applied to a

polymer liquid (i.e., solution or melt), a pendant droplet of the polymer liquid at the open end of a capillary tip is deformed into a conical shape. Upon increasing the magnitude of the imposed electric field beyond a critical value, a stream of the charged polymer liquid (i.e., charged jet) is ejected towards a collection device and driven by the electrical forces. Both, the Coulombic repulsion and electrostatic forces are responsible for the thinning of the charged jet during its flight to the collector. This usually results in the deposition of ultrafine polymeric fibers on a collector as a non-woven fibrous membrane.

Due to the high surface area-to-volume or mass ratio and high porosity of the electrospun fibrous membranes,

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\* Corresponding author.

Email address: [tpatchar@engr.tu.ac.th](mailto:tpatchar@engr.tu.ac.th)

these materials are ideal for various applications. Some of the proposed uses are as carriers for delivery of drugs (Zeng *et al.*, 2003), wound dressings (Min *et al.*, 2004), scaffolding matrices for cell/tissue culture (Li *et al.*, 2005), active components in electronic and optical devices (Norris *et al.*, 2000), and filters (Yoon *et al.*, 2006). In filtration applications, the porous polymeric membranes were conventionally fabricated by means of the phase immersion method (Asatekin *et al.*, 2007; Zhu *et al.*, 2007; Rahimpour *et al.*, 2008). Some limitations associated with this type of membranes are, for example, low flux rate and high fouling (Wrasidlo *et al.*, 1984). Non-woven fibrous membranes as prepared by electrospinning have been found to overcome some of these disadvantages and have been tested for applications in filtration (Yoon *et al.*, 2006; Gopal *et al.*, 2007; Sang *et al.*, 2008). The advantageous characteristic of electrospun fibers for these purposes is their interconnected pore structure with high porosity which is likely to improve the flux rate.

Various types of polymers have been fabricated into filtration membranes. Some of these are poly(amide imide) (Rahimpour *et al.*, 2008), poly(ethylene glycol) (Hilal *et al.*, 2007), cross-linked poly(ethylene oxide) (Ju *et al.*, 2008), poly(ether sulfone) (Kaeselev *et al.*, 2001; Rahimpour *et al.*, 2008; Ma *et al.*, 2009), polysulfone (Kaeselev *et al.*, 2001), and poly(ether imide) (Xu *et al.*, 2003; Albrecht *et al.*, 2006). Poly(ether imide) was chosen here as the candidate for further fabrication into electrospun fibrous membranes because of its good thermal, mechanical, and chemical stabilities (Barbosa-Coutinho *et al.*, 2003) that are highly applicable for applications in filtration. The successful fabrication of electrospun fibers of the blends of poly(ether imide)/poly(3-hydroxybutyrate-co-3-hydroxyvalerate) was reported (Han *et al.*, 2004) but not for the neat poly(ether imide). Polymers in the form of electrospun fibrous membranes that have been investigated for their filtration performance are, for example, polysulfone (Ma *et al.*, 2006; Gopal *et al.*, 2007), poly(vinyl alcohol) (Sang *et al.*, 2008), cross-linked poly(vinyl alcohol) (Wang *et al.*, 2006), and polyacrylonitrile (Yoon *et al.*, 2006). Chitin-coated electrospun polyacrylonitrile (Yoon *et al.*, 2006) and cross-linked electrospun poly(vinyl alcohol) (Wang *et al.*, 2006; Tang *et al.*, 2009) fibrous membranes have been shown to provide higher flux rates than that of the commercial membranes. Electrospun polysulfone fibrous membranes were capable of filtering up to 99% of 7, 8 and 10  $\mu\text{m}$ -particles with a high flux performance and without a permanent fouling (Gopal *et al.*, 2007). Modified electrospun polysulfone fibrous membranes showed higher fluxes than the corresponding membranes prepared by the phase immersion method (Ma *et al.*, 2006).

In the present contribution, electrospinning of poly(bisphenol A-co-4-nitrophthalic anhydride-co-1,3-phenylenediamine), a polymer in the poly(ether imide) family, or PEI was carried out to study the effects of solvent type and solution concentration on morphological appearance and size of the obtained fibers. Filtration performance of the electrospun fiber mats was preliminarily investigated in terms of the water

flux rate in comparison with the corresponding films prepared from the phase immersion-precipitation technique.

## 2. Experimental Part

### 2.1 Materials

Poly(bisphenol A-co-4-nitrophthalic anhydride-co-1,3-phenylenediamine) or poly(ether imide) (PEI) was purchased from Sigma-Aldrich (USA). The chemical structure of PEI is shown in Figure 1. Dichloromethane (DCM; Lab-Scan (Asia), Thailand), 1,2-dichloroethane (DCE; Sigma-Aldrich, USA), *N*-methylpyrrolidone (NMP; Sigma-Aldrich, USA), and *N,N*-dimethylformamide (DMF; Lab-Scan (Asia), Thailand) were used as solvents for PEI.

### 2.2 Preparation and characterization of spinning solutions and electrospun fiber mats

To investigate the effects of solvent type and solution concentration on morphological appearance and average diameters of the obtained fibers, PEI solutions were prepared by dissolving weighed amounts of PEI pellets in DCM, DCE, NMP, 75/25 (v/v) NMP, and DMF or 50/50 (v/v) NMP and DMF to achieve the concentrations of 10, 15, and 20% (w/v). Prior to electrospinning, each of the spinning solutions was characterized for the shear viscosity using a Brookfield DV-II programmable viscometer at room temperature (i.e.,  $25 \pm 1^\circ\text{C}$ ).

In electrospinning, each of the as-prepared spinning solutions was contained in a 5 mL syringe, the opening end of which was connected to a 20-gauge stainless steel needle (OD=0.91 mm) that was used as the nozzle. A rotating drum (width and OD of the drum is 25 and 7.6 cm, respectively, rotational speed is 50 rpm) was used as a collector. The outer surface of the rotating drum was set at 10 cm from the tip of the needle. A Gamma High-Voltage Research ES30P-5W power supply was used to generate a high DC potential. The applied potential used was 15 kV and the polarity of the emitting electrode was positive. The collection time was fixed at about 5 min. The electrospun fiber mats used in the filtration test were prepared from 20% (w/v) PEI solutions in 75/25 and 50/50 (v/v) NMP/DMF, and the collection time was fixed at three hours. The thickness of the fiber mats was 130  $\mu\text{m}$  on average.

The electrospun fiber mats were dried *in vacuo* at  $40^\circ\text{C}$  overnight to remove as much solvent as possible. The morphological appearance of the individual fiber segments

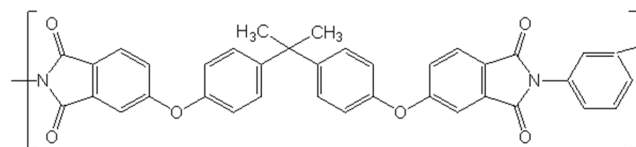


Figure 1. Chemical structure of poly(bisphenol A-co-4-nitrophthalic anhydride-co-1,3-phenylenediamine) (PEI).

was examined by a JEOL JSM-5200 scanning electron microscope (SEM). Each sample was coated with a thin layer of gold using an SPI Supplies sputtering device prior to the SEM observation. Diameters of the individual fiber segments were measured directly from SEM images. At least 100 readings of the fiber diameters for each spinning condition were statistically analyzed using SemAfore 4.0 software. Certain physical characteristics (i.e., average number of fiber segments per unit area, average pore size and surface porosity) of the fiber mats were determined. The average number of fiber segments per unit area of the obtained fiber mats was measured from SEM images. The average pore size of the fiber mats was taken as an average of both the vertical and the horizontal dimensions of the pores which were examined from the SEM images. The surface porosity of the fiber mats was measured on SEM images using Scion Image software, which was taken as the percentage ratio between the areas of the space (the area without fiber segments) divided by the total area.

### 2.3 Preparation and characterization of cast films prepared by phase immersion-precipitation technique

Cast films fabricated from the phase immersion-precipitation technique were used to compare the performance related to filtration applications with the electrospun fiber mats. The 20% (w/v) PEI solutions in 75/25 and 50/50 (v/v) NMP/DMF were cast into glass molds, each of which consisted of two pieces of glass plates. The gap between the glass plates was about 130  $\mu\text{m}$ . The molds were later immersed in de-ionized (DI) water at room temperature (i.e.,  $25\pm 1^\circ\text{C}$ ) to allow the phase inversion to occur. After 15 min of immersion, the films were demolded and were immersed in DI water at  $70^\circ\text{C}$  for two hours to remove as much solvents as possible. The films were then stored in DI water at room temperature for at least another two days to allow further removal of residual solvents. The thickness of the films was about 130  $\mu\text{m}$ .

### 2.4 Evaluation of water flux

A dead-end filtration system was used to characterize the filtration performance of the electrospun fiber mats and the cast films. The dead-end filtration set-up is shown in Figure 2. The effective membrane area was circular in shape with diameter of 4.8 cm. A membrane was placed in the membrane cell, which was filled with 200  $\text{cm}^3$  of DI water. The water flux was calculated at each constant pressure of 0.5, 1.0, 1.5, and 2.0 bars by weighing the cumulative amount of DI water that had been permeated through the membrane for 1 min for the total observation period of 15 min. The flux measurements were repeated three times to confirm the performance of each sample. The permeation flux was calculated according to the following equation:

$$J = \frac{Q}{A\Delta t}, \quad (1)$$

where  $J$  is the permeation flux ( $\text{L}\times\text{m}^{-2}\times\text{h}^{-1}$ ),  $Q$  is the cumulative volume of permeated DI-water,  $A$  is the effective area of the tested membrane ( $\text{m}^2$ ), and  $t$  is the sampling time (h). Practically, the water flux is taken as the slope of a plot between  $Q$  and  $t$ .

## 3. Results and Discussion

### 3.1 Effect of solvent type

To investigate the effect of solvent type on morphological appearance of the electrospun PEI fibers, DCM, DCE, and NMP were chosen as the solvents because they were able to dissolve PEI over a reasonably wide range of concentrations investigated in this work. It should be noted that tetrahydrofuran (THF) and DMF had also been tested, but no complete dissolution was observed when the concentrations of the solutions were greater than about 10% (w/v) (even the solutions had been continuously stirred for five days). THF and DMF were therefore proven to be inferior solvents for PEI to DCM, DCE and NMP.

To investigate the effect of solvent type, the solutions of 10, 15, and 20% (w/v) PEI in DCM, DCE, or NMP were electrospun at a fixed electric field of 15 kV/10 cm for 5 min. Figure 3 shows a series of SEM images of the products obtained from each type of solutions at the magnification of 500x. Equivalent images, but at a greater magnification of 3,500x, are shown in Figure 4. Considering at 15 and 20% (w/v) of the PEI solutions, the numbers of the smooth or beaded fiber segments within a viewing area obtained from the solutions in NMP (see Figure 3h and i) were obviously greater than those obtained from the solutions in DCM (see Figure 3b and c) and DCE (see Figure 3e and f). In other words, the electrospinnability of the solutions was greater when NMP was used as the solvent, in comparison with DCM and DCE. The possible explanation of this should be

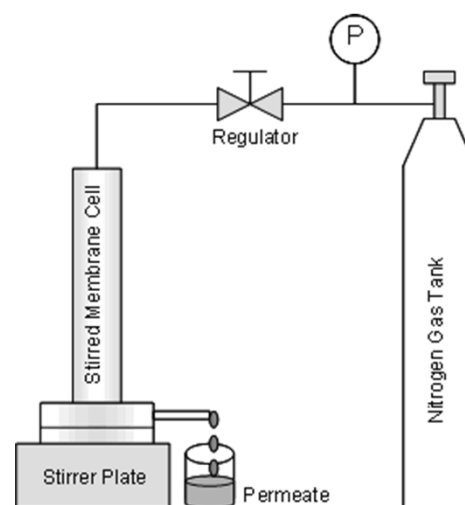


Figure 2. Schematic diagram of the flux measurement setup.

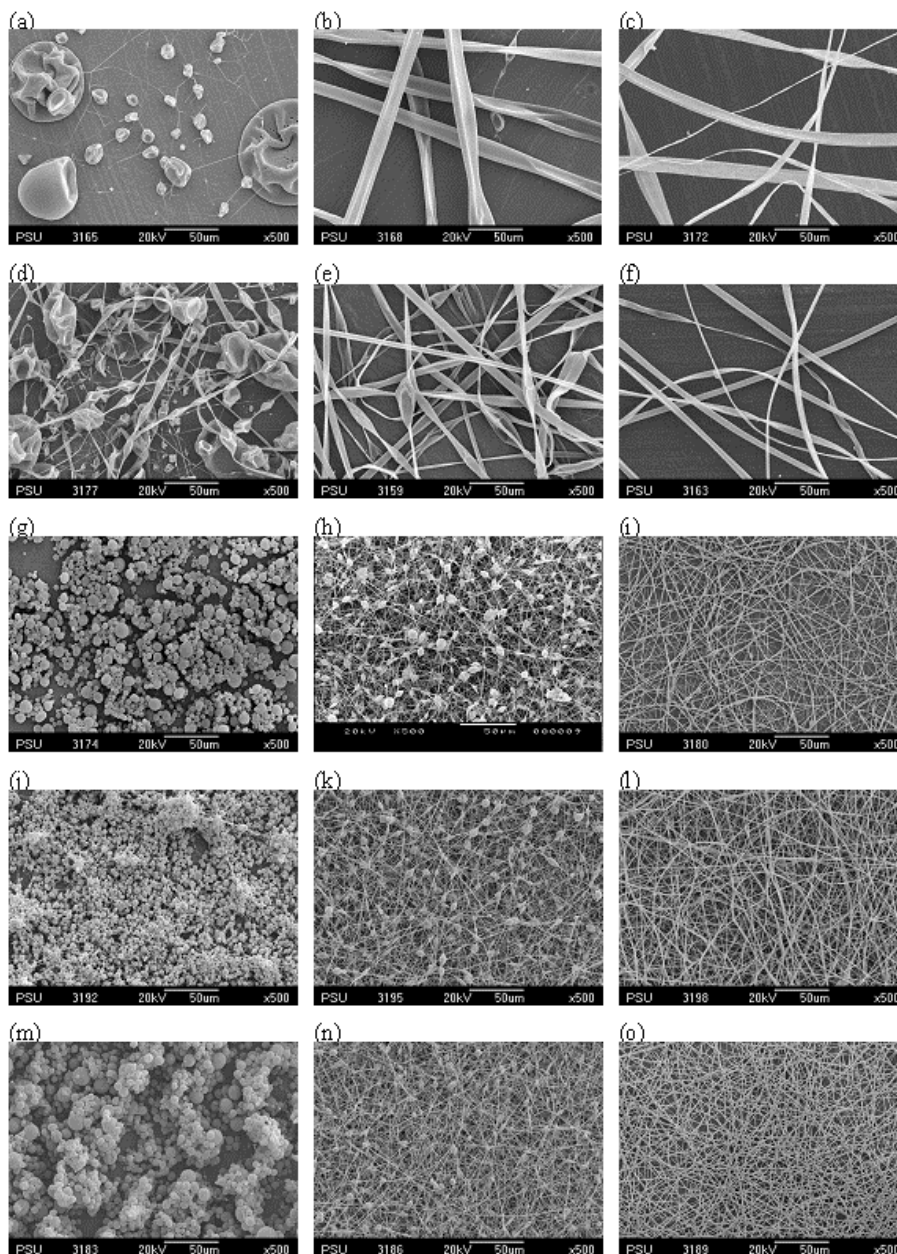


Figure 3. Selected SEM images (magnification 500x, scale bar is 50  $\mu\text{m}$ ) of electrospun fibers obtained from solutions of PEI in DCM at concentrations of (a) 10, (b) 15 and (c) 20% (w/v), in DCE at concentrations of (d) 10, (e) 15, and (f) 20% (w/v), in NMP at concentrations of (g) 10, (h) 15, and (i) 20% (w/v), in 75/25 (v/v) NMP/DMF at concentrations of (j) 10, (k) 15, and (l) 20% (w/v), and in 50/50 (v/v) NMP/DMF at concentrations of (m) 10, (n) 15, and (o) 20% (w/v).

concerned with the dielectric constants of the solvents. Since the dielectric constant of NMP (i.e., 32.6 at 20°C) is greater than those of DCM (i.e., 9.1 at 20°C) and DCE (i.e., 10.4 at 20°C) (Dean, 1999), the PEI solutions in NMP should exhibit greater electrical conductivity than those in DCM and DCE. The greater electrical conductivity of the PEI solutions in NMP comparing to those in DCM and DCE leads to greater Coulombic repulsion (responsible for the stretching of the charged jet) and electrostatic (responsible for the transport of the charged jet to the collector) forces (Wannatong *et al.*,

2004), which are responsible for the greater mass throughput rate, hence greater electrospinnability.

To further improve the electrospinnability of the PEI solutions, DMF was used as the modifying co-solvent with NMP. DMF, due to its relatively high dielectric constant (i.e., 38.3 at 20°C) (Dean, 1999), was used to increase the electrospinnability of a polymer solution (Lee *et al.*, 2003). The PEI solutions in the mixed solvent systems of NMP and DMF at 75/25 and 50/50 (v/v) were electrospun at a fixed electric field of 15 kV/10 cm for 5 min. It was found that beaded fibers

were obtained from the 15% (w/v) PEI solutions in NMP, 75/25 NMP/DMF, and 50/50 NMP/DMF (see Figure 3h, k, and n), but the number of beads was found to decrease with an increase in the DMF content (higher magnification images can be seen in Figure 4h, k, and n). In other words, electrospinnability of the PEI solutions was improved with the increasing of DMF content in the solutions. A similar result was observed for the electrospun products from the 20% (w/v) PEI solutions in NMP, 75/25 NMP/DMF and 50/50 NMP/DMF (see Figures 3 and 4i, l, and o).

The improvement in the electrospinnability of the PEI solutions due to the addition of DMF as the modifying co-solvent could be assessed quantitatively by observing the average numbers of fiber segments per unit area (see Table 1), which were measured directly from SEM images (see Figure 3i, l, and o). Only the fibers obtained from the 20% (w/v) PEI solutions were used in the analysis. According to Table 1, the value for the electrospun fibers from the solution in 75/25 NMP/DMF (ca.  $9.9 \times 10^6$  #/cm<sup>2</sup>) was comparable to that for the fibers from the solution in 50/50 NMP/DMF (ca.  $10.4 \times 10^6$  #/cm<sup>2</sup>). These values were much greater than that for the fibers from the solution in NMP (ca.  $7.1 \times 10^6$  #/cm<sup>2</sup>). The increase in the numbers of fiber segments per unit area corresponded to the increased electrospinnability of the solutions. As mentioned, the greater dielectric constant of DMF in comparison with that of NMP should be responsible for this. The greater dielectric constant of DMF would cause the PEI solutions in NMP/DMF to exhibit greater electrical conductivities than the solutions in NMP alone. The greater electrical conductivity would lead to greater Coulombic repulsion (responsible for the stretching of the charged jet) and electrostatic (responsible for the transport of the charged jet to the collector) forces (Wannatong *et al.*, 2004) subjected to the jet segments. This finally leads to increased mass throughput rate, hence greater electrospinnability.

The average pore size of the obtained electrospun fibers was investigated (see Table 1). The average pore size of the electrospun fibers from the solutions in 75/25 NMP/DMF and 50/50 NMP/DMF were approximately similar (i.e. 2  $\mu$ m) which was smaller than that from the solution in NMP (i.e. 2.8  $\mu$ m). The higher electrospinnability of the solutions in 75/25 NMP/DMF and 50/50 NMP/DMF than that in NMP, which was previously mentioned could be the reason that the fibers overlapped more on the surface and therefore leading to the smaller pore size. According to Table 1, the surface

porosity of the obtained electrospun fibers was also investigated. The surface porosities of the electrospun fibers from the solutions in 75/25 NMP/DMF and 50/50 NMP/DMF were about 45% which were lower than that from the solution in NMP (i.e. 52%). These results can be explained in term of the electrospinnability as well. Due to the higher electrospinnability, the lower surface porosities were observed for the electrospun fibers from the solutions in 75/25 NMP/DMF and 50/50 NMP/DMF. Yoon *et al.* (2006) reported the results that the surface porosity of the electrospun polyacrylonitrile membrane analyzed from image analysis program was found to be very close to its bulk porosity and stated the relationship between the flux and the surface porosity.

### 3.2 Effect of solution concentration

The effect of solution concentration on the morphological appearance and size of the electrospun PEI fibers was also investigated and it can be evaluated from the results summarized in Figures 3 and 4. For the electrospun products from the 10% (w/v) PEI solution in DCM, discrete beads were the predominant features of the obtained products (see Figure 3a), with trace amounts of beaded fibers with fine fibrous texture between adjacent beads being observed in a greater-magnification image (see Figure 4a). Increasing the solution concentration to 15 and 20% (w/v) resulted in the complete disappearance of the discrete beads, with flat ribbon-like fibers being the predominant features of the obtained products (see Figures 3, 4b, and c). The size of these fibers was relatively large (i.e.,  $\geq 10$  mm on average) (see Table 2). In case of the PEI solutions in DCE, a combination of discrete beads and beaded fibers was obtained at 10% (w/v) (see Figures 3 and 4d). Increasing the solution concentration to 15 and 20% (w/v) resulted in a dramatic decrease in the number of beads (see Figures 3, 4e, and f). Similar to the case of the fibers obtained from the solutions in DCM, flat ribbon-like fibers were the common features, with their size ranging between 6 and 7 mm on average (see Table 2).

For the products that were obtained from the PEI solutions in NMP, discrete and spherical beads were predominant features of the products obtained at 10% (w/v) (see Figures 3 and 4g). However, trace amount of very fine fibers was also observed. Increasing the solution concentration to 15% (w/v), only beaded fibers were the common features and the shape of the beads became more elongated (see Figures 3

Table 1. Number of fiber segments per unit area, pore size and surface porosity values of electrospun fiber mats obtained from 20% (w/v) PEI solutions in NMP, 75/25 (v/v) NMP/DMF and 50/50 (v/v) NMP/DMF.

Solvent	# Fiber/cm <sup>2</sup>	Pore Size ( $\mu$ m)	Surface Porosity(%)
NMP	$(7.1 \pm 1.5) \times 10^6$	$2.8 \pm 1.0$	52
75/25 (v/v) NMP/DMF(ES 75/25)	$(9.9 \pm 1.3) \times 10^6$	$2.0 \pm 1.3$	45
50/50 (v/v) NMP/DMF(ES 50/50)	$(10.4 \pm 1.8) \times 10^6$	$2.0 \pm 0.9$	45

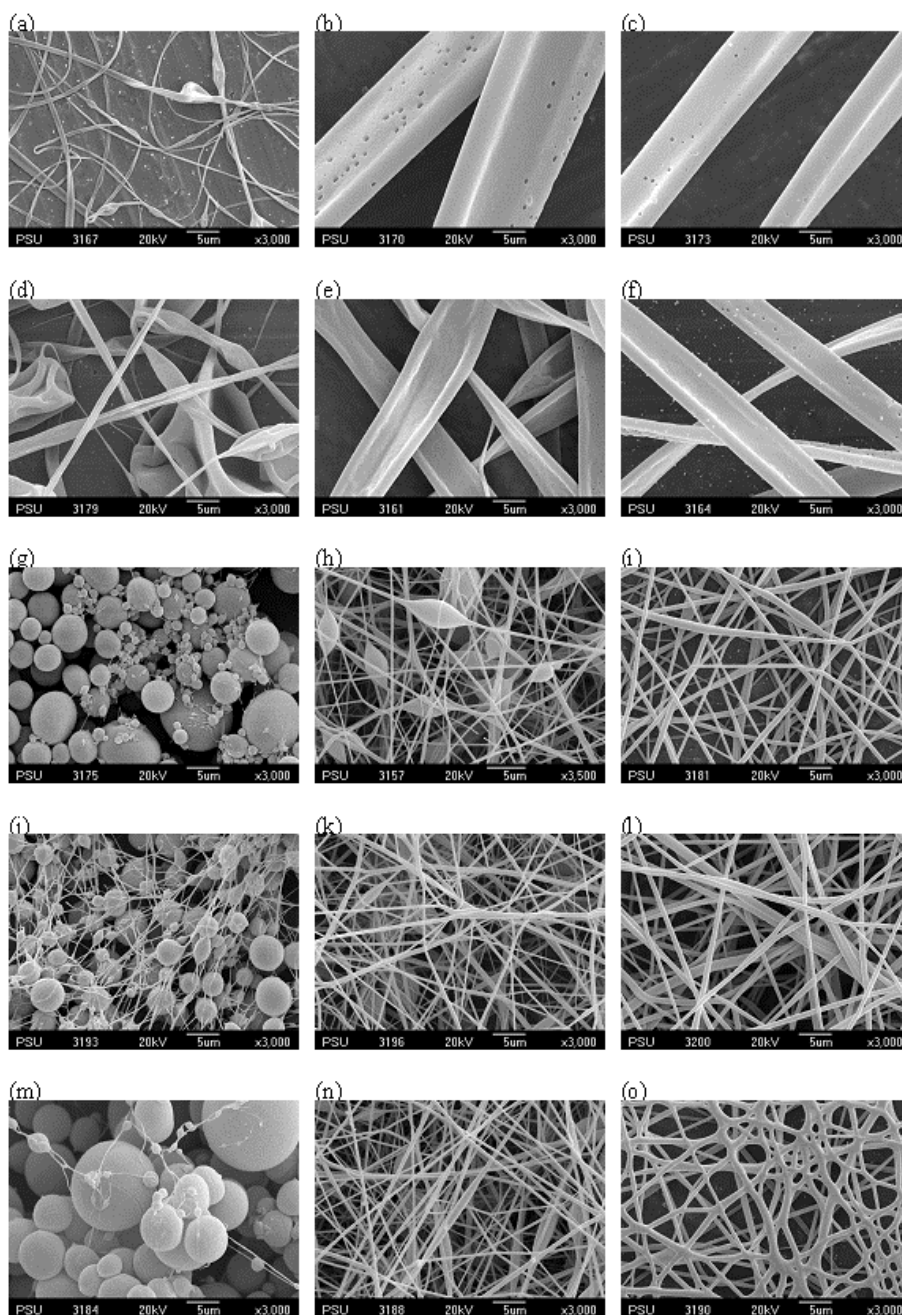


Figure 4. Selected SEM images (magnification 3500x, scale bar is 5  $\mu\text{m}$ ) of electrospun fibers obtained from solutions of PEI in DCM at concentrations of (a) 10, (b) 15, and (c) 20% (w/v), in DCE at concentrations of (d) 10, (e) 15, and (f) 20% (w/v), in NMP at concentrations of (g) 10, (h) 15, and (i) 20% (w/v), in 75/25 (v/v) NMP/DMF at concentrations of (j) 10, (k) 15, and (l) 20% (w/v), and in 50/50 (v/v) NMP/DMF at concentrations of (m) 10, (n) 15, and (o) 20% (w/v).

and 4h). The size of the fiber segments between beads was about 0.5 mm on average (see Table 2). At 20% (w/v), only smooth fibers were the common features (see Figures 3 and 4i) and the size of these fibers increased slightly to 0.8 mm on average (see Table 2). It is obvious that the size of the fibers from the PEI solutions in NMP was considerably smaller than that of the fibers from the solutions in both DCM and DCE, likely a result of the much greater dielectric

constant value of NMP in comparison with those of DCM and DCE. The addition of DMF as the modifying co-solvent did not affect much the morphology of the obtained products (see Figures 3 and 4j-o). According to Table 2, the size of the fiber segments between beads for the beaded fibers obtained from the PEI solutions in both mixed solvent systems was practically the same as that of the fibers obtained from the PEI solution in NMP alone (i.e., about 0.5 mm on average). At

Table 2. Viscosities of PEI solutions in different solvent systems at concentrations of 10, 15, and 20% (w/v) and diameters of the obtained electrospun fibers.

Solvent	Viscosity (cP)			Fiber Diameters ( $\mu\text{m}$ )		
	10% (w/v)	15% (w/v)	20% (w/v)	10% (w/v)	15% (w/v)	20% (w/v)
DCM	62 $\pm$ 1	164 $\pm$ 2	312 $\pm$ 1	0.41 $\pm$ 0.13	13.97 $\pm$ 1.97	10.17 $\pm$ 2.34
DCE	73 $\pm$ 2	143 $\pm$ 2	322 $\pm$ 2	2.63 $\pm$ 1.87	6.45 $\pm$ 1.69	5.73 $\pm$ 1.38
NMP	120 $\pm$ 1	389 $\pm$ 2	585 $\pm$ 2	0.22 $\pm$ 0.04	0.48 $\pm$ 0.10	0.77 $\pm$ 0.10
75/25 NMP/DMF	95 $\pm$ 2	276 $\pm$ 2	420 $\pm$ 2	0.25 $\pm$ 0.06	0.49 $\pm$ 0.09	0.77 $\pm$ 0.10
50/50 NMP/DMF	81 $\pm$ 2	337 $\pm$ 2	668 $\pm$ 2	0.23 $\pm$ 0.05	0.48 $\pm$ 0.10	0.79 $\pm$ 0.10

20% (w/v), on the other hand, the size of the fibers from the solutions in the mixed solvent systems was found to increase from that of the fibers from the solution in NMP to about 0.9 and 1.0 mm on average, when the DMF content in the mixed solvent systems increased from 25 to 50 vol.%.

Irrespective of the solvent systems investigated, electrospinning of PEI solutions at the lowest concentration investigated (i.e., 10% (w/v)) resulted in the formation of discrete beads or beaded fibers as the major features. According to Table 2, it is obvious that the viscosity of the solutions increased with an increase in the solution concentration. As expected, this is due to the increase in the entanglements of PEI molecules, hence the increase in the viscoelastic contribution, with an increase in the solution concentration. At low solution viscosities, the contribution from the viscoelastic forces was not large enough to overcome the contribution from the electrical, stretching forces (Wannatong *et al.*, 2004). This would finally lead up to the break-up of the jet into smaller ones which were later rounded up, due to the action of the surface tension, to form beads (Mit-uppatham *et al.*, 2004). As the solution concentration increased, the viscoelastic contribution would ultimately become greater than the electrical counterpart, thus preventing the total break-up of the jet into smaller ones (Mit-uppatham *et al.*, 2004). This eventually caused the morphology of the products to change from discrete beads to beaded fibers and, ultimately, to smooth fibers. Simultaneously, as the magnitude of the viscoelastic contribution became greater with increasing solution concentration (or, to be exact, solution viscosity), the jet would be less subservient to being stretched by the electrical forces, hence an observed increase in the size of the fibers. The relationship between the average fiber diameters and the viscosities of polyamide-6 solutions was correlated well with exponential growth equation (Mit-uppatham *et al.*, 2004).

Figure 5 shows plots of the diameters of the fibers that had been obtained from 20% (w/v) PEI solutions in NMP, 75/25 NMP/DMF, and 50/50 NMP/DMF as a function of solution viscosity. Clearly, for a given data set, the diameters of the fibers correlated well with the viscosity of the solutions and the relationship between the average fiber diameters and the solution viscosities could be approximated with exponential growth equations, as indicated in the figure.

### 3.3 Water flux

The filtration performance of the electrospun PEI fiber mats was investigated and the result was compared with the corresponding films prepared by the phase immersion-precipitation technique. Both, the fiber mats and the films were prepared from 20% (w/v) PEI solutions in 75/25 and 50/50 NMP/DMF. The thickness of all specimens was carefully controlled at 130  $\mu\text{m}$  on average. The permeation flux ( $J$ ) of each specimen was determined at each constant pressure of 0.5, 1.0, 1.5, and 2.0 bars. The results in Figure 6 show that the permeation fluxes measured from the electrospun fiber mats prepared from the PEI solutions in 75/25 and 50/50 NMP/DMF (denoted in the figure as ES 75/25 and ES 50/50, respectively) were comparable. The values were much greater than those of the corresponding films, which also showed comparable values between them. The greater water fluxes of the fiber mats in comparison with those of the cast films were due obviously to the greater porosity of the fiber mat membranes. Based on the SEM images of the fiber mats, the surface porosity of the membranes was about 45%. Yoon *et al.* (2006) reported a high porosity value (about 70%) for the

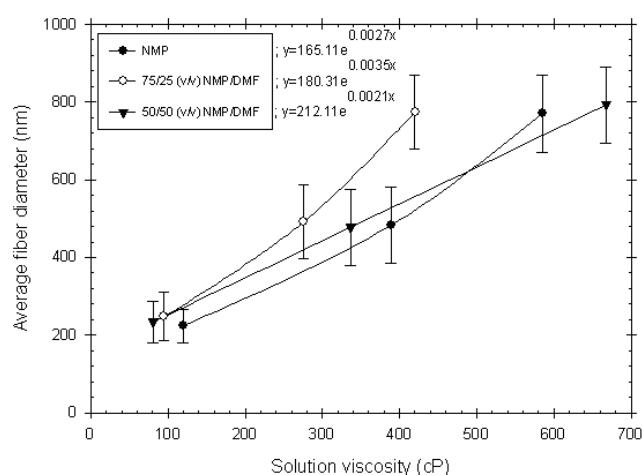


Figure 5. Average diameters of electrospun fibers obtained from 20% (w/v) PEI solutions in NMP, 75/25 (v/v) NMP/DMF and 50/50 (v/v) NMP/DMF as a function of the solution viscosity.

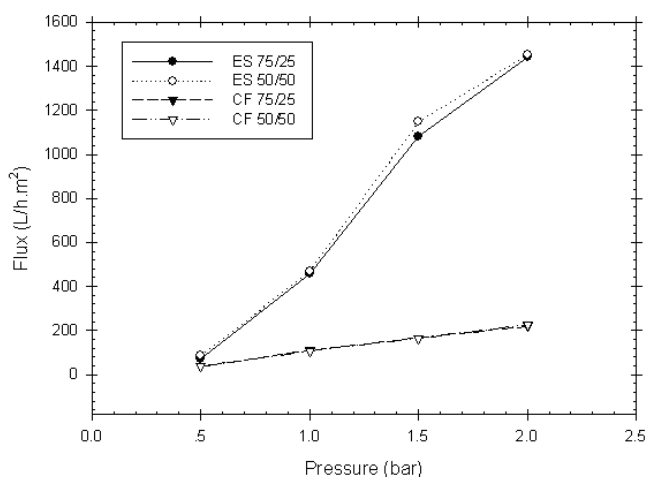


Figure 6. Water fluxes of the electrospun fiber mats (ES) obtained from 20% (w/v) PEI solutions in 75/25 and 50/50 (v/v) NMP/DMF and the corresponding cast films (CF) as prepared from the phase immersion-precipitation technique as a function of pressure.

electrospun polyacrylonitrile fiber mats, which was found to provide higher flux rates than the commercial membranes with the porosity of about 30%. The electrospun poly(ethylene terephthalate) nanofibrous membrane with the porosity of about 80% shown the higher flux and the better performance in apple juice clarification process than a traditional clarification technique (using clarification agents) and ultrafiltration (using a commercial membrane) (Veleirinho *et al.*, 2009). The electrospun polyacrylonitrile nanofibrous membrane with the porosity of about 90% and pores size of less than 2  $\mu\text{m}$ , was found to provide high water permeability and high ability to remove more than 90% of particles in the range of 1–20  $\mu\text{m}$  from water (Bazargan *et al.*, 2011).

Even though the results obtained herein suggested the applicability of the electrospun PEI fiber mats in water filtration applications, other aspects associated with such applications, e.g., rejection efficiency should be investigated further.

#### 4. Conclusions

In the present contribution, electrospinning was used to fabricate PEI fibrous membranes for potential for uses in filtration applications. Electrospun fiber mats of PEI were prepared from the solutions in dichloromethane (DCM), 1,2-dichloroethane (DCE), *N*-methylpyrrolidone (NMP) and certain mixtures between NMP and *N,N*-dimethylformamide (DMF). It was found that the electrospinnability of PEI solutions in NMP was greater than that of the solutions in DCM and DCE. Electrospinnability of the PEI solutions could be improved further with the use of DMF as the modifying cosolvent. The effect of solution concentration on the morphological appearance and size of the obtained products was investigated. At the lowest solution concentration investi-

gated, i.e., 10% (w/v), discrete beads and/or beaded fibers were the common features. Increasing the solution concentration to 15% (w/v) resulted in the marked reduction in the number of beads, while beaded fibers were the common features. At the highest solution concentration investigated (i.e., 20% (w/v)), only smooth fibers were the common features. An increase in the solution concentration, and by this also in the solution viscosity, resulted in a monotonous increase in the fiber diameters. For the fibers that were obtained from the PEI solutions in NMP and its mixtures with DMF, the average diameters of the fibers were in the range of about 0.1 to 1 mm. Lastly, the applicability of the electrospun fiber mats obtained from 20% (w/v) PEI solutions in 75/25 and 50/50 (v/v) NMP/DMF as water filtration membranes was tested against the corresponding cast films that had been prepared from the same solutions by the phase immersion-precipitation technique. Clearly, the fiber mats exhibited much greater water fluxes than the films, especially at pressures greater than 0.5 bars.

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