

CHAPTER IV
ULTRAFINE ELECTROSPUN POLYAMIDE-6 FIBERS: EFFECT OF
EMITTING ELECTRODE POLARITY ON MORPHOLOGY AND
AVERAGE FIBER DIAMETER

ABSTRACT

Electrostatic spinning or electrospinning is a process by which a high electrical potential is applied to a polymers solution or melt across a finite distance between a nozzle and a collective target to produce ultrafine fibers with diameters in the sub-micrometer down to nanometer range. The polarity of the emitting electrode (i.e. the one that is in contact with the polymer solution or melt) can be either positive or negative. In the present contribution, the effect emitting electrode polarity on morphological appearance and average size of the electrospun polyamide-6 (PA-6) fibers were investigated. The effects of some influencing parameters (i.e. PA-6 concentration, molecular weight of PA-6, electrostatic field strength, solution temperature, solvent type, and addition of an inorganic salt) were also investigated. Scanning electron micrographs showed obvious morphological difference between fibers obtained from positive or negative polarities. The main differences were that the as-spun PA-6 fibers from the negative polarity were flat with average size being much larger than those from the positive polarity which appeared to be round.

KEY-WORDS: electrospinning process; ultrafine fibers; polyamide-6; electrode polarity

1. INTRODUCTION

Electrostatic spinning or electrospinning is a process by which ultrafine fibers with diameters in the sub-micrometer down to nanometer range can be produced. These ultrafine fibers exhibit several interesting characteristics, for examples, large surface area to mass or volume ratio, small pore size between depositing fibers of the electrospun web, and flexibility for surface functionalization. These unique properties render electrospun ultrafine fibers to be excellent candidates for various applications [1].

The basic principles of the electrospinning process are concerned with the application of a high electrostatic potential from an emitting electrode of a high-voltage power supply to the polymer solution or melt across a finite distance between a conductive nozzle and a grounded collective screen [2]. The Coulombic repulsion force between charges of the same polarity produced in the polymer solution or melt by the emitting electrode destabilizes the hemi-spherical droplet of the polymer solution or melt located at the tip of the nozzle to finally form a droplet of a conical shape (i.e. the Taylor cone). With further increase in the electrostatic field strength beyond a critical value, the Coulombic repulsion force finally exceeds that of the surface tension which finally results in the ejection of an electrically charged stream of the polymer solution or melt (i.e. the charged jet). The electrically charged jet travels in a straight trajectory for only a short distance before undergoing a bending instability, which results in the formation of looping trajectory [3]. During its flight to the collector, the charged jet thins down and, at the same time, dries out or solidifies to leave ultrafine fibers on the collective screen.

The polarity of the emitting electrode (i.e. the one that is in contact with the polymer solution or melt) can be either positive or negative. Lenggoro and co-workers [4] prepared zinc sulfide nanoparticles by electrospaying pyrolysis using either positive or negative polarity and found that, with application of the negative polarity, higher flow rates were required to form a stable jet. They attributed the phenomenon to the formation of corona discharges which were more favored when the negative polarity was used. They, however, found no correlation between the polarity used and size distribution of the obtained particles. Schmid and co-workers [5] studied the change in surface tension of water when the pendant drop was

charged with either positive or negative polarity. They found that both polarities decreased the surface tension, but a larger decrease was observed with the application of negative than with positive polarity. Matsui and co-workers [6] measured the discharge current of electrostatic discharges which occurred between a charge insulator and a grounded electrode, paying a particular interest on the charge polarity dependence. They found that the discharge current from the negatively charged surface of insulator was much larger than that from the positively charged one, at the same surface charge density.

In the electrospinning process, there have not been prior studies focussing particularly on the effect of the polarity of the emitting electrode on morphological appearance of electrospun fibers obtained. A number of studies, however, paid attention on the effects of various parameters, such as solution (e.g. solution concentration, viscosity, surface tension, and conductivity) and process (e.g. applied potential, collection distance, and feed rate), on the resulting electrospun fibers. Baumgarten [7] was one of the early researchers who paid strong interest in studying the effects of some of these parameters on the obtained fiber diameter and jet length. He found that an increase in solution viscosity was responsible for the increase in the diameters of the as-spun acrylic fibers obtained, while an increase in the flow rate of the acrylic solution did not affect the diameters of the fibers. Deitzel and co-workers [8] studied the effect of applied potential and solution concentration on structure and morphology of the as-spun poly(ethylene oxide) (PEO) fibers. Buchko and co-workers [9] found the dependence of process parameters (i.e. solution concentration, applied potential, collection distance, and collection time) on morphology of electrospun webs obtained. Demir and co-workers [10] observed that the diameters of as-spun polyurethaneurea increased as the third power of solution concentration. They also found that the morphology of these as-spun fibers correlated strongly with the solution viscosity. Zong and his co-workers [11] also found strong influence of the solution concentration and salt addition on diameters of as-spun poly(D,L-lactic acid) (PDLLA) and poly(L-lactic acid) (PLLA). Addition of NaCl into PEO solutions [12] and pyridinium formate into PLA solutions [13] helped increase solution conductivity values and, in turn, helped decrease the possibilities for bead formation. Choice of the solvent system used also found to have a strong influence

on the morphology and diameters of the as-spun cellulose acetate [14], poly(ϵ -caprolactone) (PCL) [15], and poly(vinyl chloride) (PVC) [16] fibers, respectively. Since, as previously mentioned, there have not been prior studies focussing on the effect of the emitting electrode polarity on morphology and size of electrospun fibers obtained, it is of our particular interest in investigating the effect of emitting electrode polarity (either positive or negative) on morphology and size of the as-spun polyamide-6 (PA-6) fibers. In addition, the effects of other influencing parameters (i.e. PA-6 concentration, molecular weight of PA-6, electrostatic field strength, solution temperature, addition of an inorganic salt, and solvent system) were also investigated.

2. EXPERIMENTAL DETAILS

2.1. Preparation of characterization of polyamide-6 solutions

Three fiber spinning grades of polyamide-6 (PA-6) (i.e. AFC-2002, AFC-2001, and AFC-3003) were supplied by Asia Fiber Public Co., Ltd. (Thailand). The weight-average molecular weights for these resins were reported to be 17,000, 20,000, and 32,000 Da, respectively. From this point forward, these resins will be called PA-6-17, PA-6-20, and PA-6-32, respectively. Solutions for electrospinning were prepared by dissolving each resin of a specified amount in formic acid (85% v/v, Carlo Erba). Slight stirring was used to expedite dissolution. Solutions of varying concentrations (i.e. 10 to 46% w/v for PA-6-17 and PA-6-20 and 10 to 34% w/v for PA-6-32) were used to elucidate the effects of solution concentration and average molecular weight of PA-6 on morphological appearance of the obtained fibers. NaCl salt in various amounts (i.e. 1 to 5% w/v) was added in 32% w/v PA-6-20 solution in formic acid to study the effect of inorganic salt addition on morphological appearance of the as-spun fibers. To investigate the effect of solvent system on the obtained fibers, *m*-cresol (Carlo Erba) was mixed with 85% v/v formic acid in various compositional ratios (i.e. 10/90, 20/80, 30/70, 40/60, and 50/50 v/v) and these mixed solvents were used to dissolve PA-6-20 at a fixed concentration of 32% w/v. Some properties of each solution, i.e. viscosity, surface tension, and conductivity, were measured at $30 \pm 1^\circ\text{C}$ prior to spinning, using a Brookfield DV-III

programmable viscometer, a Krüss K10T Tensiometer, and a Orion 160 conductivity meter, respectively.

2.2. Electrospinning process

To electrospin PA-6 fibers, each solution was contained in a 50-ml glass syringe. A 1 cm-long flat-tipped stainless steel gauge 26 needle was used as the nozzle. To minimize solution drippings at the needle tip, both the syringe and the nozzle were tilted approximately 10° from a horizontal baseline. The feed rate of PA-6 solutions was controlled by pressurized nitrogen gas through a flow meter. A piece of thick aluminum sheet was used as the collective screen. A Gamma High Voltage Research D-ES30PN/M692 power supply was used to charge the spinning PA-6 solutions by connecting the emitting electrode of either positive or negative polarity to the nozzle and the grounding electrode to the collective screen. The distance between the tip of the nozzle and the collective screen defines a collection distance. In this particular work, a fixed electrostatic DC potential of 21 kV with either positive or negative emitting electrode polarity was applied over a fixed collection distance of 10 cm. The collection time was fixed at 30 seconds. To elucidate the effect of the electrostatic field strength on morphological appearance of the as-spun fibers, the electrostatic field strength was varied (i.e. 15, 18, 21, 24, and 27 kV/10 cm) for both electrode polarities. To study the effect of solution temperature on morphological appearance of the as-spun fibers, solutions of an elevated temperature (i.e. 40, 50, or 60°C) could be prepared by using a home-made double-chambered syringe, in which the outer chamber was circulated with warm water of a specified temperature.

2.3. Characterization of electrospun PA-6 fibers

The morphological appearance of the as-spun PA-6 fibers was investigated visually from optical scanning photographs of the as-spun webs collected on Al sheets using a HP ScanJet 4300c optical scanner (OS) and from scanning electron micrographs of a small section of the same webs using a JEOL JSM-4200 scanning electron microscope (SEM). The specimens for SEM observation were prepared by

cutting an Al sheet covered with the as-spun webs and the cut section was carefully affixed on a SEM stub. Each specimen was gold-coated using a JEOL JFC-1100E sputtering device before being observed under SEM. For each spinning condition, at least 80 readings for the fiber diameters were recorded. Statistical analysis of the data obtained was carried out by constructing a histogram, from which an arithmetic mean and a standard deviation were obtained and reported.

3. RESULTS AND DISCUSSION

3.1. Effect of polyamide-6 concentration

In order to investigate the effect of PA-6 concentration and emitting electrode polarity on the morphological appearance of the as-spun fibers, solutions of PA-6-20 in 85% v/v formic acid were prepared in various concentrations, ranging from 10 to 46% w/v. The viscosity of these solutions was found to increase from 40 to 4058 cp., whereas the surface tension was found to slightly increase from 42 to 44.7 mN.m⁻¹, while the conductivity was in the range of 3.42 to 4.37 mS.cm⁻¹. The electrospinning of these solutions was carried out at a fixed applied electrostatic field strength of 21 kV/10 cm and the emitting electrode polarity was either positive or negative.

Figure 1 shows selected SEM images of as-spun PA-6-20 fibers from solutions of various concentrations (i.e. 14, 16, 18, and 26% w/v) by either positive or negative polarity of the emitting electrode. For a given concentration, dissimilarity between the as-spun products from either positive or negative polarity of the emitting electrode was obvious. For solutions of low concentrations or low viscosities (i.e. from 10 to ca. 14% w/v), a large number of sub-micron droplets were present from use of both polarities (see Figure 1a and 1b), but negative polarity produced droplets of much smaller sizes. At low concentrations or low viscosities, the viscoelastic force (i.e. a result of low molecular entanglements) in a given jet segment was not large enough to counter the higher Coulombic force, resulting in the break-up of the charged jet into small droplets. This phenomenon has been familiarized in the industries as the electro spraying process and has commonly been used in many applications such as paint spraying, ink-jet printing, and powder coating, among others [17].

For solutions of higher concentrations or higher viscosities, the charged jet did not break up into small droplets, a direct result of the increased molecular entanglements (i.e. hence an increase in the viscoelastic force) that were sufficient to prevent the break-up of the charged jet and to allow the Coulombic stress to further elongate the charged jet during its flight to the grounded target which ultimately thinned down the diameter of the charged jet. However, if the concentration was not high enough (e.g. 16% w/v), a mixture of sub-micron droplets and slight trace of ultrafine fibers was obtained (see Figure 1c and 1d). Again, negative polarity produced much smaller droplets with much greater amount of ultrafine fibers. Further increase in the concentration of the solution to 18% w/v, as-spun products from positive polarity still were still a mixture of sub-micron droplets and slight trace of ultrafine fibers (see Figure 1e), while as-spun products from negative polarity produced mainly the ultrafine fibers with slight trace of sub-micron beads (see Figure 1f). At 26% w/v, negative polarity produced practically smooth fibers (see Figure 1h), while a mixture between beaded fibers and smooth fibers was obtained with positive polarity (see Figure 1g). The critical concentrations for the formation of bead-free fibers were 28% w/v for negative polarity and 40% w/v for positive polarity.

Regardless of the emitting electrode polarity used, further increase in the solution concentration beyond the critical values mentioned resulted in an increase in the fiber diameters, a direct result of the much greater increase in the viscoelastic force with respect to the increase in the Coulombic repulsion force. Interestingly, electrospinning of solutions of very high concentrations (i.e. from 38 to 46% w/v) with negative polarity showed a much decrease in the number of fibers per unit area and a large number of fibers formed loops as they deposited on the collective screen (see Figure 2a to c). These loops may be reminiscent of the secondary bending instability which appeared in electrospinning of solutions of high viscosities [18]. Formation of flat fibers was also observed in as-spun fibers from 30% w/v polystyrene solution in dimethylformamide (DMF) and was attributed to the uneven evaporation of the solvent between the skin and the bulk of the charged jet, which caused the charged jet to collapse, leaving flat fibers on the target [19]. Flat fibers

have recently been reported in electrospun poly(vinyl alcohol) (PVA) fibers from solutions of high concentrations and high molecular weights [20].

Figure 3 illustrates effect of positive and negative emitting electrode polarities on as-spun non-woven PA-6-20 webs. Evidently, deposition of the as-spun fibers when the emitting electrode was positive confined within a tight circular area (see Figure 3a and b), while deposition of the as-spun fibers from negative polarity confined to a ring pattern (see Figure 3c and d). Interestingly, the deposition area of the fibers from negative polarity was much larger than that of the fibers from positive polarity. More importantly, the diameter of the deposition area, regardless of the emitting electrode polarity, was found to decrease with increasing concentration of the solutions. With increasing solution concentration or increasing solution viscosity, the ejected charged jet had greater resistance towards the thinning of its diameter. This caused the charged jet to travel in a straight trajectory for a longer distance before undergoing a bending instability [3] and this is postulated to be the main reason for the observed smaller diameter of the non-woven webs collected from the solutions of higher concentrations.

To illustrate the effect of solution concentration and the emitting electrode polarity on the sizes of the as-spun PA-6-20 fibers, as-spun fibers with small amount of beads present or no beads at all were measured for their diameters and the solution concentration that resulted in such fibers ranged between 30 and 46% w/v. It should be noted that, when negative polarity was used, flat fibers were formed when the solution concentration exceeded 38% w/v, thus, at these concentrations, the measurement of those fibers went by their width. Figure 4 shows plots of the average diameter of the as-spun PA-6-20 fibers as a function of solution concentration for both positive and negative polarities. Apparently, at low concentrations of 30 and 32% w/v, the average diameters between fibers obtained from both positive and negative polarities appeared to be quite similar, while, at higher concentrations, the discrepancy between the average diameters was more obvious. Regardless of the polarity used, the average fiber diameter was found to increase monotonically with increasing solution concentration, with such a relationship could be approximated by an exponential growth equation (see corresponding equations in Figure 4).

The dissimilarity between as-spun fibers from positive and negative polarities might result from the difference in the nature of charge species which are present when either positive or negative polarity is applied. The difference in the nature of charges related directly to the dissolution of PA-6 in formic acid, in which the ammonium chain ends of PA-6 was protonated to form ammonium cations. Thus, the clear solution of PA-6 in formic acid comprised mainly of PA-6 cations and formate anions. Due to the large difference in the sizes of these two charge species, when the positive polarity was applied at the emitting electrode, the much larger PA-6 cations would result in a much less surface charge density when comparing with that from the much smaller formate anions when the negative polarity was applied. When the negative polarity was applied, the higher surface charge density of formate anions could result in higher conductivity of the solutions and higher conductivity resulted in higher electrostatic force which could, in turn, result in an increase in the mass throughput and the increase in the mass throughput was responsible for the increase in the sizes of the as-spun fibers. A direct evidence to such a postulation was the fact that as-spun fibers from negative polarity deposited on a collective screen in a loosened ring pattern, which implied the much greater repulsion force between adjacent fibers prior to deposition on the collective screen (see Figure 3).

3.2. Effect of PA-6 average molecular weight

To illustrate the effect of weight average molecular weight of PA-6 and emitting electrode polarity on morphological appearance and size of the as-spun fiber, solutions of PA-6-17, PA-6-20, and PA-6-32 in 85% v/v formic acid were prepared in various concentrations, ranging from 10 to 46% w/v for PA-6-17 and PA-6-20 and from 10 to 34% w/v for PA-6-32. The viscosity of these solutions was found to increase with increasing PA-6 concentration, with the viscosity values for PA-6-32 being much greater than those for PA-6-17 and PA-6-20, which were found to be quite comparable. Both surface tension and conductivity values were not found to be much affected with variation in the concentration of these PA-6 solutions.

Figure 5 shows selected SEM images illustrating effect of average molecular weight of PA-6 and emitting electrode polarity on morphological appearance of the as-spun fibers from 34% w/v PA-6 solutions. Obviously, positive polarity produced

tight electrospun webs in comparison with those produced by negative polarity. For positive polarity, smooth fibers with slight trace of beaded fibers were observed for PA-6-17 (see Figure 5a), while only smooth fibers were obtained for PA-6-20 and PA-6-32 (see Figure 5b and c). For negative polarity, only smooth fibers were observed for all of the PA-6 resins (see Figure 5d to f). According to Figure 5, the sizes of the as-spun fibers were found to increase with increasing average molecular weight and, for a given resin, the sizes of the as-spun fibers from negative polarity were larger than those from positive polarity. Quantitatively, the average sizes of the as-spun fibers from positive polarity shown in Figure 5 were 83.1 nm for PA-6-17, 94.9 nm for PA-6-20, and 286.7 nm, while those from negative polarity were 140.8 nm for PA-6-17, 145.4 nm for PA-6-20, and 371.3 nm. The increase in the sizes of the as-spun fibers with increasing average molecular weight should be due to the increase in the viscoelastic force, while the observed greater sizes of fibers from negative polarity than those from positive polarity should be due to the nature of the charge species previously mentioned.

As previously shown in Figure 4 for PA-6-20, plots of the average fiber diameter versus solution concentration for PA-6-17 and PA-6-32 resins, regardless of the polarity used, also showed a similar trend, but, instead of plotting the average fiber diameter versus solution concentration, Figure 6 shows plots of the average fiber diameter versus solution viscosity for all of the PA-6 resins investigated. Interestingly, for both polarities, the average fiber diameters for all of the PA-6 resins studied fell on a common curve in which they were all found to increase monotonically with increasing solution viscosity. Apparently, for positive polarity, the relationship between the observed average fiber diameter and the solution viscosity could be best described by an exponential growth equation of the form:

$$\text{Average fiber diameter (nm)} = 88.7 + 0.804\exp[0.00137 \times \text{Viscosity (cp)}] \quad (1)$$

and, for negative polarity, the relationship could be best described by a power-law equation of the form:

$$\text{Average fiber diameter (nm)} = -73.8 + 0.545[\text{Viscosity (cp)}]^{0.839}. \quad (2)$$

3.3. Effect of electrostatic field strength

To investigate the effect of applied electrostatic field strength and emitting electrode polarity on morphological appearance of the obtained electrospun PA-6 fibers, 32% w/v solution of PA-6-17 in 85% v/v formic acid was prepared and electrospun under an application of either positive or negative emitting electrode polarity. The applied electrostatic field strength was 15, 18, 21, 24, or 27 kv/10 cm, respectively. Figure 7 shows selected as-spun non-woven PA-6-17 webs on the collective targets for a fixed collection time of 30 seconds. Obviously, the fiber density in the non-woven webs from positive polarity was much higher than that in the webs from negative polarity. Furthermore, the fiber density in the non-woven webs, regardless of the polarity, was found to increase with increasing applied electrostatic field strength. Increasing electrostatic field strength caused the electrostatic force acting on a jet segment to increase. The increased electrostatic force not only caused the jet segment to move faster to the collective screen, but might also help decrease the possibility for the bending instability to occur, which resulted in the decrease in the deposition area of the as-spun webs with increasing applied electrostatic field strength.

Figure 8 shows a selected series of SEM images to illustrate the effect of applied electrostatic field strength and emitting electrode polarity on morphological appearance and size of the obtained electrospun fibers from 32% w/v PA-6-17 solution in 85% v/v formic acid under an applied electrostatic potential of 15, 21, or 27 kV/10 cm under both positive and negative polarities. Obviously, smooth and beaded fibers were obtained in the as-spun fibers from positive polarity of 15 and 21 kV/10 cm (see Figure 8a to c), with the number of beads being found to decrease with increasing applied electrostatic field strength, while only smooth fibers were obtained in the fibers from negative polarity (see Figure 8d to f), with the average diameter of these fibers being found to increase from ca. 54.6 nm at 15 kV/10 cm to ca. 92.3 nm at 27 kV/10 cm. The increase in the average fiber diameter with increasing electrostatic field strength was also reported by others [7,21], which could be a result of the increase in the mass throughput in response to the increase in the electrostatic force [8,22]. Nonetheless, conflicting results have also been reported [9,23].

3.4. Effect of solution temperature

To exhibit the effect of solution temperature on morphological appearance of the as-spun PA-6 fibers, 26% w/v PA-6-32 solution in 85% v/v formic acid was first stocked in a home-made double-chambered syringe. Once the temperature of the solution was equilibrated to a spinning temperature of 30, 40, 50, or 60°C, which was done by warm water circulating within the outer chamber of the syringe, the solution was electrospun under an applied electrostatic field strength of 21 kV/10 cm with either positive or negative emitting electrode polarity.

In a similar manner, the density of the as-spun fibers from positive polarity was found to be much less than that from negative polarity. Under positive polarity, only smooth fibers were obtained from the solutions of all elevated temperatures and these fibers were all found to be very similar in their morphological appearance. With regards to the sizes of the fibers, the average fiber diameter was found to decrease slightly from ca. 98.3 nm at the solution temperature of 30°C to ca. 89.7 nm at 60°C. Since the concentration of the solution was fixed, variation in the average fiber diameters should be a result of the decrease in the viscosity of the solutions with increasing solution temperature. The decreased solution viscosity caused the viscoelastic force to also decrease, resulting in the Coulombic repulsion force being able to thin down the charged jet more effectively. Under negative polarity, coiled fibers with low fiber density were observed in as-spun fibers obtained from solutions of low temperatures (i.e. 30 and 40°C) (see Figure 9a), while straight fibers with higher fiber density were observed in as-spun fibers obtained from solutions of higher temperatures (see Figure 9b). Demir and co-workers [10] observed that solutions of polyurethaneurea of which temperature were higher than room temperature produced fibers with more uniform diameters and also observed that the deposition rate of the fibers increased with increasing temperature of the solutions, which is in accord with what has been observed in this work. Moreover, as-spun fibers from negative polarity were much larger in size than those from positive polarity. Quantitatively, the average fiber diameter was found to decrease from ca. 179.4 nm at the solution temperature of 30°C to ca. 92.2 nm at 60°C.

3.5. Effect of inorganic salt addition

To investigate the effect of inorganic salt addition on morphological appearance and size of the as-spun fibers, NaCl in the amount of 1 to 5% w/v was added to 32% w/v PA-6-20 solution in 85% v/v formic acid. The as-prepared solutions were electrospun under an applied electrostatic field strength of 21 kV/10 cm with either positive or negative emitting electrode polarity. Addition of NaCl salt did not affect much the viscosity and the surface tension values of the solutions, while the conductivity value of the solutions was found to increase with addition and with increasing salt content (cf. 6.2 mS/cm at 1% w/v NaCl to 12.2 mS/cm at 5% w/v NaCl). The increase in the solution conductivity resulted in an increase in the charge density of the polymer solutions, which, under electrostatic field, translated an increase in both the electrostatic and the Coulombic repulsion forces.

Under positive polarity, the morphology of the as-spun PA-6-20 fibers was not affected much with addition of NaCl salt. Only diameters of the as-spun fibers were affected. Quantitatively, the average fiber diameter was found to increase from ca. 98.6 nm at 1% w/v NaCl to ca. 154.2 nm at 5% w/v NaCl. The increase in the average fiber diameters should be a direct result of an increase in the electrostatic force, hence an increase in the mass throughput, with increasing salt content. The increase in the mass throughput, in turn, caused the fiber diameters to be larger [10], despite an increase in the Coulombic repulsion force which should result in thinner fibers. Under negative polarity, interesting results were observed with addition of NaCl in which the as-spun fibers appeared to be flat (see Figure 10), which were similar to those obtained at high solution concentrations or viscosities (see Figure 2). Quantitatively, the average width of the as-spun fibers was found to increase from ca. 148.5 nm at 1% w/v NaCl to ca. 428.5 nm at 5% w/v. The increase in the electrostatic force (from both the contributions from formate anions and Cl⁻ ions) was also responsible for the large fibers observed, while the collapse of the rapidly evaporated charged jet was responsible for the flat morphology observed.

3.6. Effect of solvent system

To investigate the effect of solvent system on morphological appearance of the as-spun PA-6 fibers, 32% w/v solutions of PA-6-20 in a mixed solvent between

85% v/v formic acid and *m*-cresol in various volumetric compositional ratio between formic acid and *m*-cresol of 90:10, 80:20, 70:30, 60:40, or 50:50 were prepared. These mixed solvent systems were shown to dissolve 32% w/v PA-6-20 to form homogeneous solutions very well. With the addition and increasing content of *m*-cresol, the viscosity of the resulting solutions was found to increase (i.e. from ca. 1160 cp for pure formic acid to ca. 4550 cp for 50:50 v/v mixed solvent), the surface tension to decrease slightly (i.e. from ca. 44.1 mN/m for pure formic acid to ca. 39.3 mN/m for 50:50 v/v mixed solvent), and the conductivity to decrease substantially (i.e. from ca. 4.0 mS/cm for pure formic acid to ca. 0.4 mS/cm for 50:50 v/v mixed solvent). The decrease in the conductivity of the solutions with increasing amount of *m*-cresol could be a result of the much lower dielectric constant of *m*-cresol (i.e. 11.5 at 23.9°C [24]) in comparison with that of formic acid (i.e. 58.5 at 15.6°C [24]).

Figure 11 shows selected SEM images of as-spun fibers from solutions of 32% w/v PA-6-20 in a mixed solvent of 85% v/v formic acid and *m*-cresol in the 80:20, 60:40, and 0:100 v/v (i.e. for pure *m*-cresol) compositional ratios under either positive or negative polarity. Regardless of the polarity used, while only smooth were observed in the as-spun fibers from the 32% w/v PA-6-20 solution in formic acid (see previously), the 32% w/v PA-6-20 solution in *m*-cresol produced nothing but blobs of the solution on the collective screen (see Figure 11c and f). The most likely explanation for phenomenon might be due to the much higher boiling point of *m*-cresol (i.e. 202°C [25]) in comparison with that of formic acid (i.e. 101°C [26]). With such a high boiling point, the ejected charged jet did not have enough time to "dry" prior to depositing on the target. The "rather wet" depositing jet then fused with adjacent ones to form blobs of the solution observed.

In the mixed solvents of formic acid and *m*-cresol, the as-spun PA-6-20 fibers from solutions in the 90:10, 80:20, and 70:30 v/v compositional ratios under positive polarity (see, for examples, Figure 11a) were smooth, while fused fibers were observed from solutions of higher *m*-cresol content (see, for examples, Figure 11b). The fused fibers observed in solutions of higher *m*-cresol content should be, again, due to the increased boiling point of the solutions. With regards to fiber sizes, the average fiber diameter was found to increase with increasing *m*-cresol content in the solutions (i.e. ca. 93.5 nm for the solution in formic acid to ca. 200.5 nm for the

solution in mixed solvent of 50:50 v/v). The increase in the average fiber diameter with increasing *m*-cresol content could be due to both the increase in the solution viscosity (hence the increase in the viscoelastic force) and the decrease in the solution conductivity (hence the decrease in the Coulombic repulsion force) with increasing *m*-cresol content. Under negative polarity, the obtained as-spun webs had much less fiber density than that observed in the as-spun webs from the application of the positive polarity (cf. Figure 11a and f, and b and e), which could be attributable to the much greater surface charge density in the as-spun fibers obtained. Furthermore, the fiber sizes of the as-spun fibers from negative polarity were much larger than those from positive polarity.

4. CONCLUSIONS

In the present contribution, the effects of either positive or negative polarity of the emitting electrode and other influencing parameters (i.e. polyamide-6 (PA-6) concentration, molecular weight of PA-6, electrostatic field strength, solution temperature, addition of an inorganic salt, and solvent system) on morphological appearance and size of the as-spun PA-6 were thoroughly investigated using optical scanning (OS) and scanning electron microscopy (SEM) techniques. Regardless of the emitting electrode polarity, the as-spun PA-6 fibers appeared to be droplets at low concentration or viscosity range, a combination between droplets and smooth fibers at slightly higher concentration or viscosity range, a combination of beaded fibers and smooth fibers at even higher concentration or viscosity range, and only smooth fibers at the highest concentration or viscosity range, with the size of the beads on beaded fibers being a decrease function, while the as-spun fibers being an increase function, of the concentration and the viscosity. The onset for the formation of smooth fibers from negative polarity occurred at a lower concentration or viscosity, with the as-spun fibers from negative polarity being larger for at a given concentration of the solutions. Interestingly, under negative polarity, solutions of high concentrations or high viscosity values produced flat fibers.

Regardless of the emitting electrode polarity, average diameter (or average width) of the as-spun PA-6 fibers of different average molecular weights exhibited a common relationship with the solution viscosity, with such the relationship for as-

spun fibers from positive polarity being best described by an exponential growth equation, while that for as-spun fibers from negative polarity being a power-law equation. An increase in the applied electrostatic field strength resulted in as-spun webs of decreasing diameter, but resulted in an increase in the diameters of the as-spun fibers. Interestingly, the fiber density of the as-spun fiber webs from negative polarity was much lower than that of as-spun fibers from positive polarity. An increase in the temperature of the spinning solutions caused a decrease in the diameters of obtained fibers with higher deposition rates. Addition and increasing content of NaCl caused the conductivity of the spinning solutions to increase, which, in turn, resulted in larger as-spun fibers. Under negative polarity, as-spun fibers from the salt-containing solution were flat and the average width increased with increasing salt content. Lastly, regardless of the polarity applied, PA-6 solutions in a mixed solvent of formic acid and *m*-cresol produced as-spun fibers of larger diameters with increasing *m*-cresol content, most likely a result of the observed increase in the solution viscosity and the observed increase in the solution conductivity with increasing *m*-cresol content.

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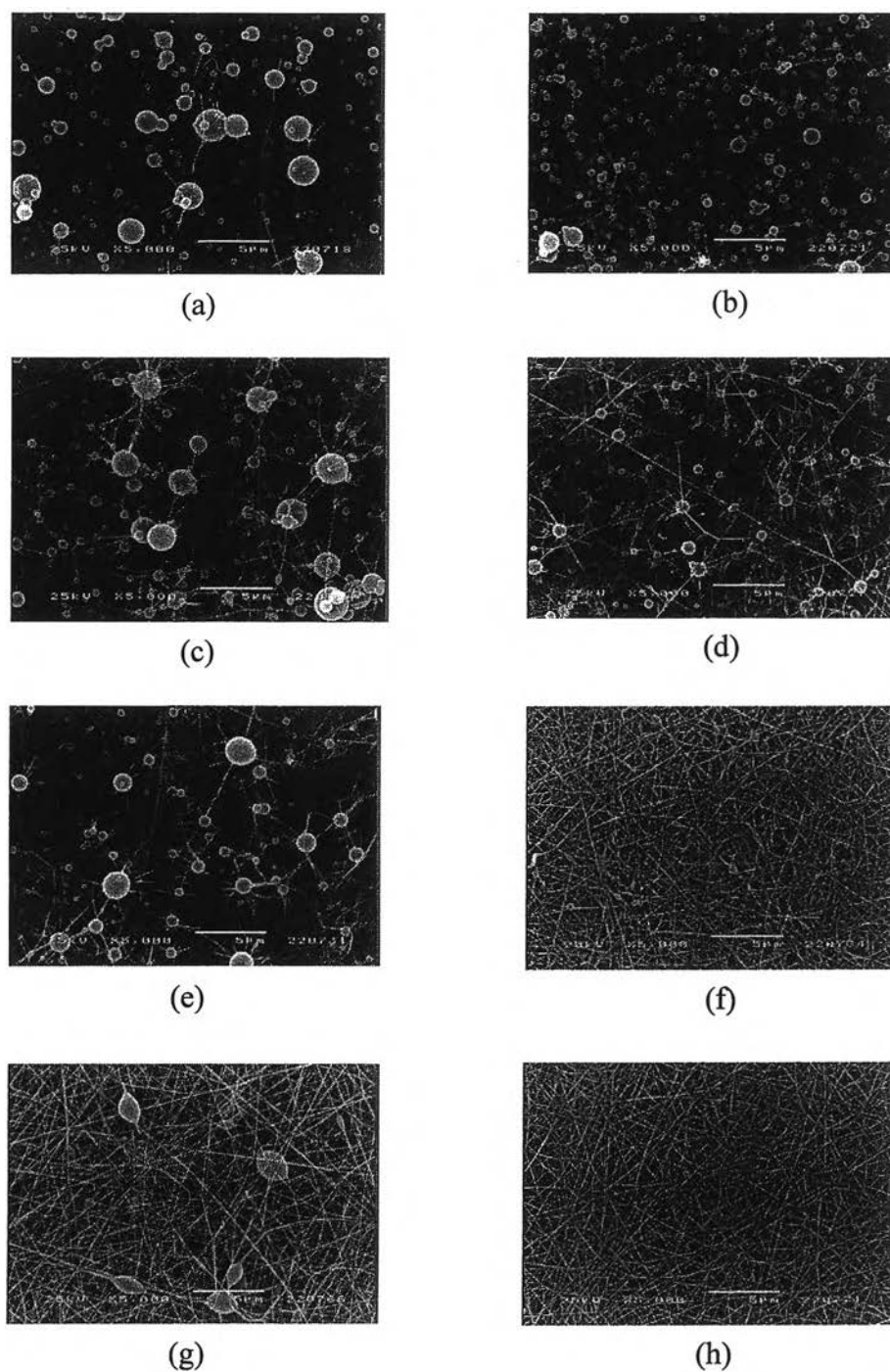


Figure 1. SEM images (magnification = 5000x and the scale bar = 5 μm) of electrospun products from solutions of PA-6-20 in 85 v/v formic acid at the concentrations: a) 14; c) 16; e) 18; and g) 26% w/v under positive polarity and at the concentrations: b) 14; d) 16; f) 18; and h) 26% w/v under negative polarity. The electrostatic field strength used was 21 kV/10 cm.

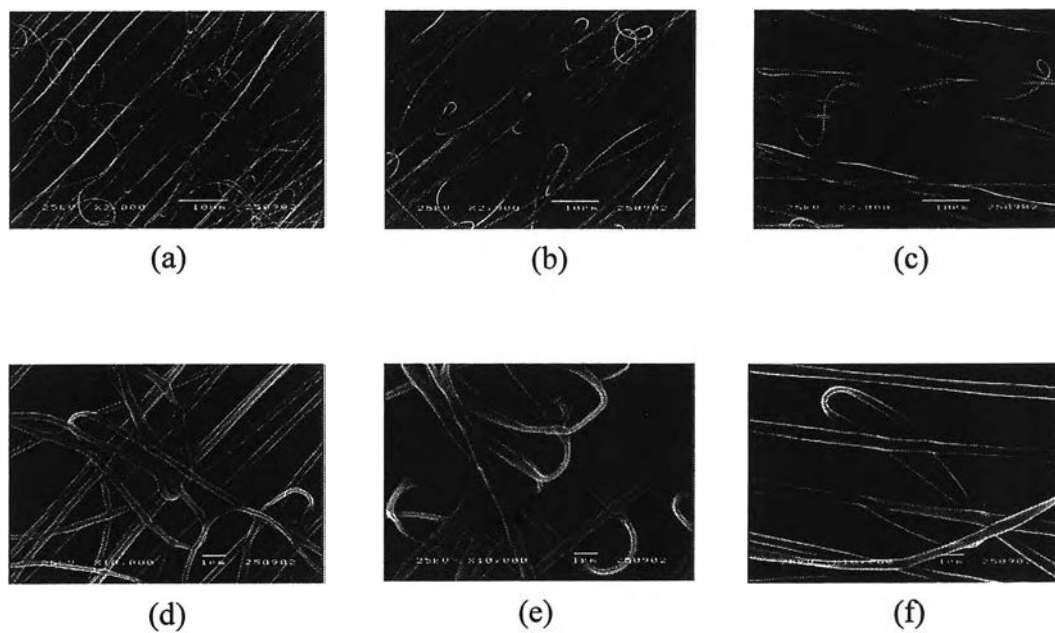


Figure 2. SEM images of electrospun fibers from solutions of PA-6-20 in 85% v/v formic acid under negative polarity at the concentrations: a) 38; b) 40; and c) 42% w/v (magnification = 2000x and the scale bar = 10 μm) and at the concentrations: d) 38; e) 40; and f) 42% w/v (magnification = 10000x and the scale bar = 1 μm). The electrostatic field strength used was 21 kV/10 cm.

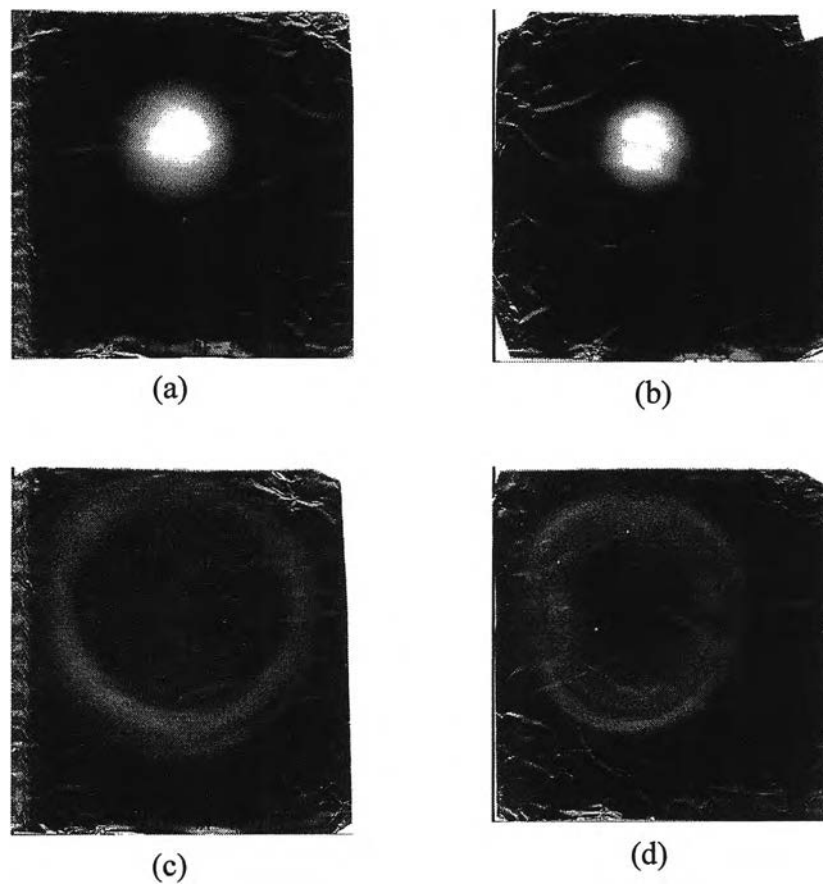


Figure 3. OS images of as-spun webs from solutions of PA-6-20 in 85% v/v formic acid at the concentrations: a) 40; and b) 42% w/v under positive polarity and at the concentrations: c) 40; and d) 42% w/v under negative polarity. The electrostatic field strength used was 21 kV/10 cm and the collection time was 30 seconds.

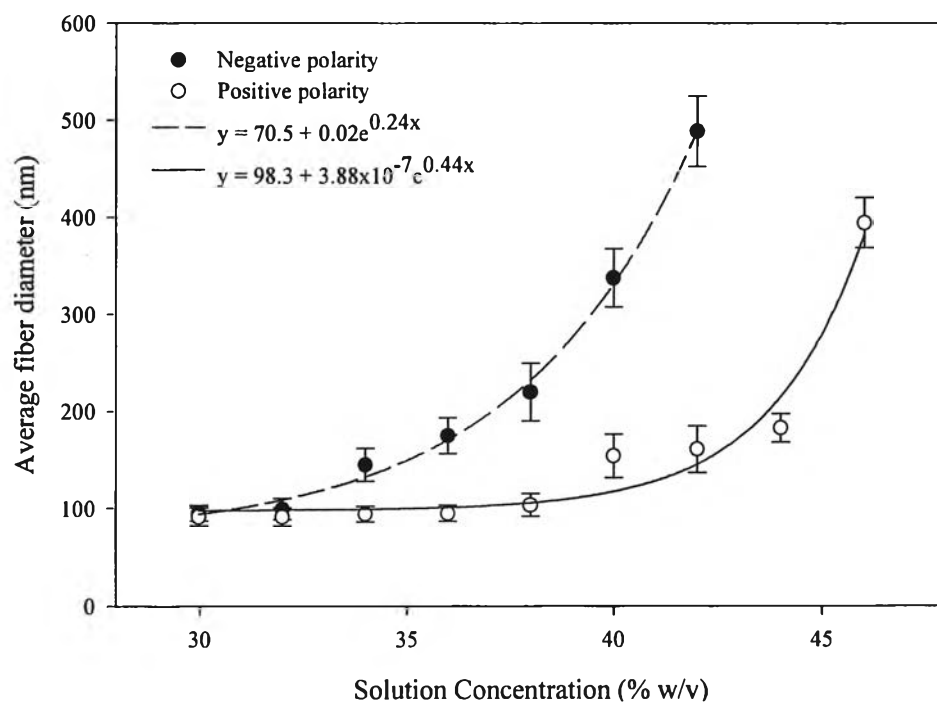


Figure 4. Average diameter of as-spun PA-6-20 fibers plotted as a function of PA-6-20 concentrations under either positive or negative polarity.

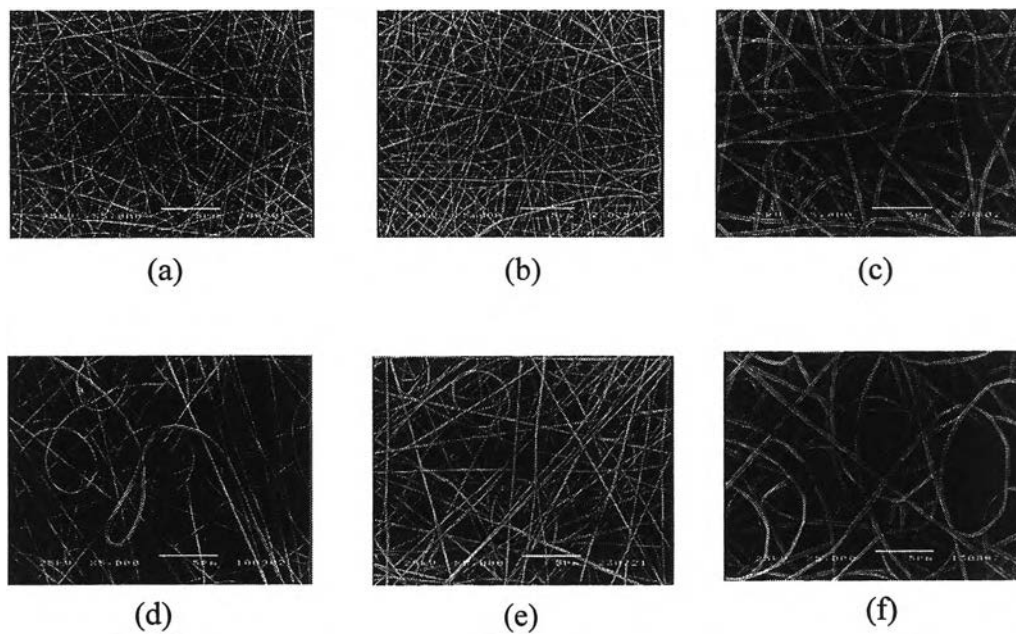
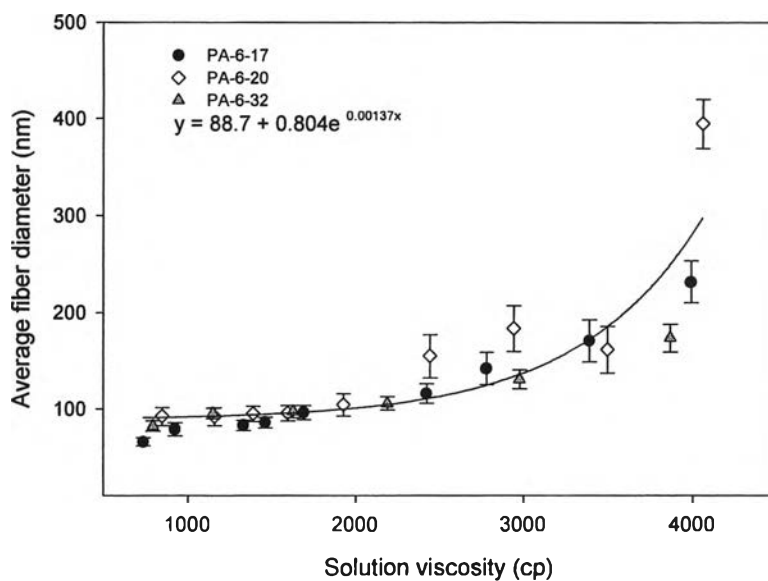
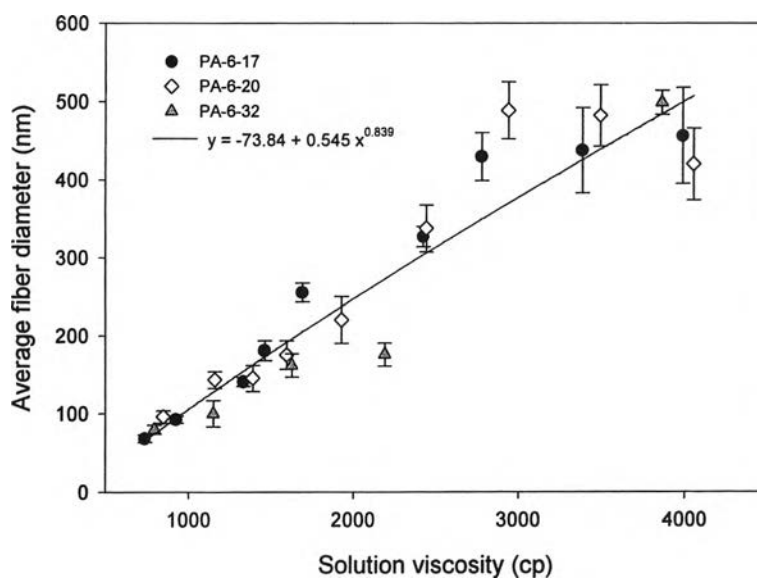


Figure 5. SEM images (magnification = 5000x and the scale bar = 5 μm) of electrospun fibers from solutions of: a) PA-6-17; b) PA-6-20; and c) PA-6-32 under positive polarity and of: d) PA-6-17; e) PA-6-20; and f) PA-6-32 under negative polarity at a fixed concentration of 34% w/v. The electrostatic field strength used was 21 kV/10 cm.



(a)



(b)

Figure 6. Average diameter of as-spun PA-6-17, PA-6-20, and PA-6-32 fibers from: a) positive; and b) negative polarity plotted as a function of the solution viscosity.

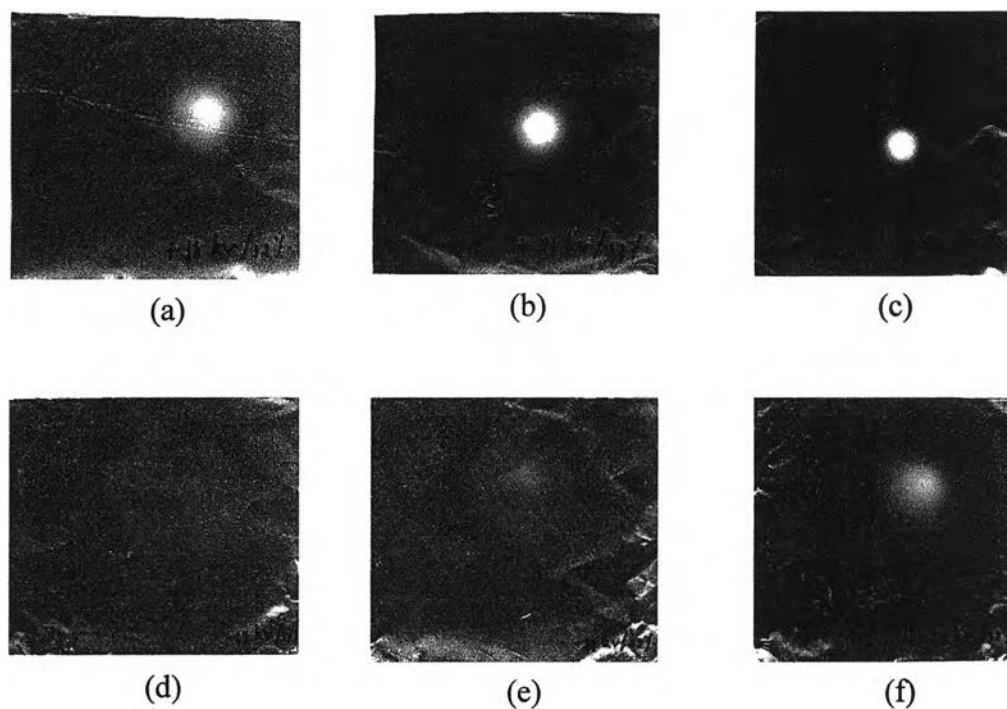


Figure 7. OS images of as-spun webs from 32% w/v PA-6-17 solution in 85% v/v formic acid under positive polarity and the applied electrostatic field strengths: a) 18; b) 21; and c) 24 kV/10cm and under negative polarity and the applied electrostatic field strengths: d) 18; e) 21; and f) 24 kV/10cm. The collection time was 30 seconds.



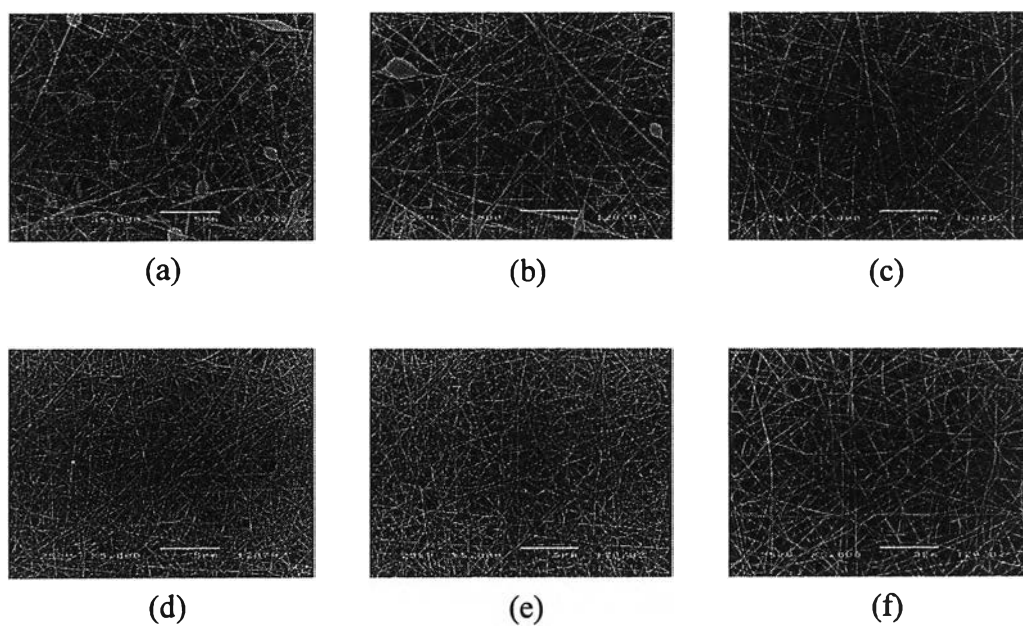
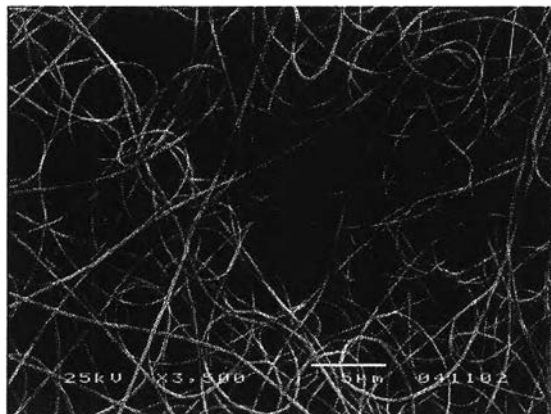


Figure 8. SEM images (magnification = 5000x and the scale bar = 5 μm) of electrospun fibers from 32% w/v PA-6-17 solution in 85% v/v formic acid under positive polarity and the electrostatic field strengths: a) 15; b) 21; and c) 27 kV/10cm and under negative polarity and the applied electrostatic field strengths: d) 15; e) 21; and f) 27 kV/10cm .



(a)



(b)

Figure 9. SEM images (magnification = 3500x and the scale bar = 5 μm) of electrospun fibers from 26% w/v PA-6-32 solution in 85% v/v formic acid under negative polarity at the solution temperatures: a) 30; and b) 60°C. The electrostatic field strength used was 21 kV/10 cm.

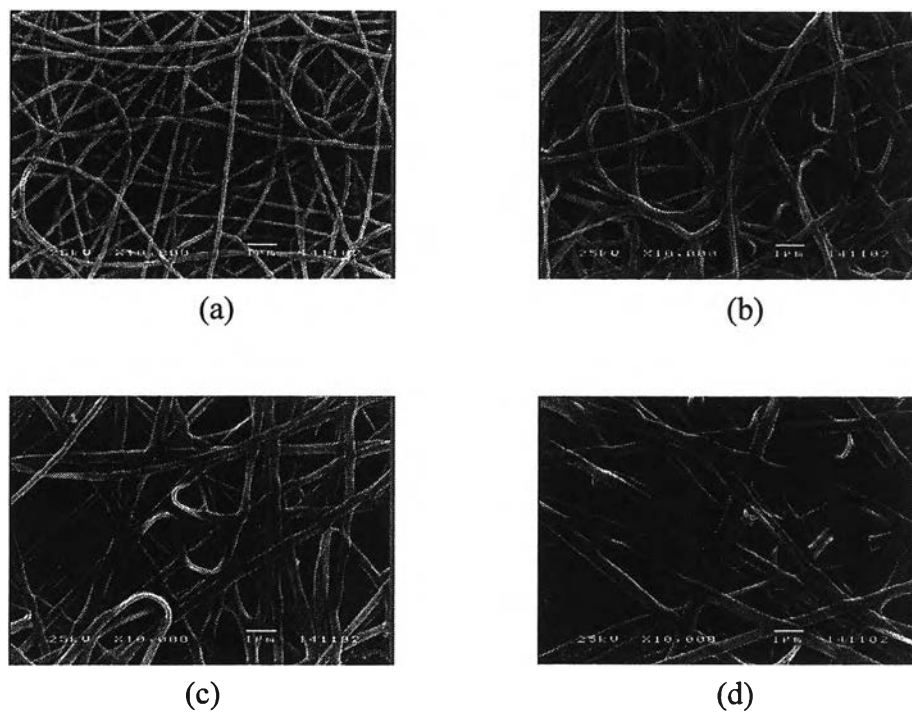


Figure 10. SEM images (magnification = 10000x and the scale bar = 1 μm) of electrospun fibers from 32% w/v PA-6-20 solutions in 85% v/v formic acid containing NaCl in the amount: a) 1; b) 2; c) 3; and d) 4% w/v under negative polarity. The electrostatic field strength used was 21 kV/10 cm.

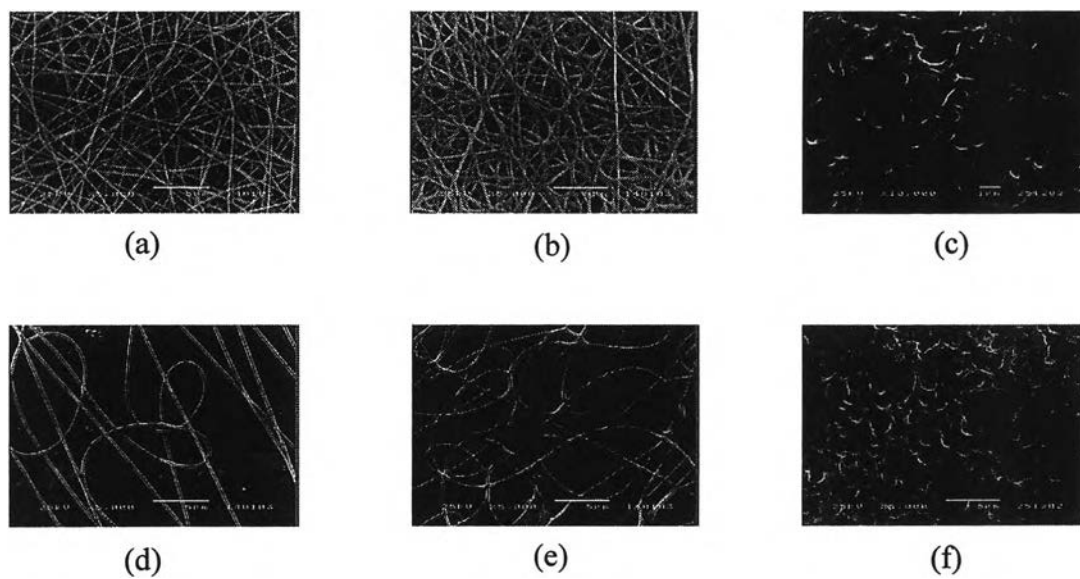


Figure 11. SEM images (magnification = 5000x and the scale bar = 5 μm) of electrospun products from 32% w/v PA-6-20 solutions in a mixed solvent of 85% v/v formic acid and *m*-cresol in the volumetric compositional ratios: a) 80:20; b) 60:40; and c) 0:100 (i.e. pure *m*-cresol) under positive polarity and in a mixed solvent in the volumetric compositional ratios: d) 80:20; e) 60:40; and f) 0:100 under negative polarity.