CHAPTER V
ELECTROSPUN POLYAMIDE-6 NANOFIBERS:
EFFECT OF SOLVENT SYSTEMS

ABSTRACT

In this work, polyamide-6 (PA-6) solutions were prepared in various single solvent and mixed solvent systems. The concentration of PA-6 in the solutions was fixed at 32% (w/v). Some of the solution properties, i.e. shear viscosity, surface tension, and conductivity, were measured. For single solvent systems, only the solution of PA-6 in 85 wt.% formic acid gave a uniform electrospun fibers, with the average diameters being about 83.5 nm, while the solutions of PA-6 in *m*-cresol and 20 and 40 wt.% sulfuric acid did not form uniform fibers. For mixed solvent systems, the solvent mixtures were prepared by mixing 85 wt.% formic acid with *m*-cresol, 20 and 40 wt.% sulfuric acid, acetic acid, ethanol, dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO) in the compositional ratios of 10 to 40% (v/v). In general, the average diameters of the as-spun fibers were found to increase with increasing content of the second solvent. In mixed solvents of high compositional ratios of *m*-cresol and sulfuric acids (i.e. greater than 20%), fibers with rough surface were obtained.

KEYWORDS: electrostatic spinning; electrospinning; nanofibers; polyamide-6; solvent

INTRODUCTION

Electrostatic spinning or electrospinning is a process from which ultra-fine fibers with the diameters in the range of nanometers to sub-micrometers can be produced. The non-woven fabric obtained from the deposition of these ultra-fine fibers exhibit several interesting characteristics, for examples, high surface area to mass ratio and small inter-fibrous pore size with high porosity which can be of use in a number of applications (Doshi and Reneker, 1995).

The basic principles of this spinning technique concern with application of an intense electrostatic field to a polymer solution or melt across a finite distance. When an electrostatic field is applied, charges start to accumulate around the surface of a droplet of the polymer solution or melt located at the tip of the nozzle. The Coulombic repulsion forces destabilize the hemispherical shape of the droplet, which gradually changes its shape to a cone-like one. When the Coulombic repulsive forces overcome the surface tension, a charged stream of polymer solution or melt (i.e. the charged jet) is ejected. The electrically charged jet travels for a few centimeters before undergoing a bending instability which is thought to be responsible for the thinning of the fibers during their flight to a grounded collector (Reneker, et al., 2000).

In the electrospinning process of a polymer solution, solvent is one of the main contributors for solution properties, such as viscosity, surface tension, and conductivity (Deitzel, et al., 2001). These properties can be tailored through physical mixing with another component, e.g. conductivity of the solution can be enhanced through addition of inorganic salts. Lee and co-workers (2003) electrospun poly(ε-caprolactone) (PCL) from the PCL solutions in the mixture of methylene chloride and dimethylformamide (DMF). They found that the spinnability and the diameter of the obtained fibers dramatically decreased with increasing DMF content, due possibly to the increased conductivity dielectricity of the resulting solutions. Lee and co-workers (2002) found that electrospun poly(vinyl chloride) (PVC) fibers from PVC solutions in tetrahydrofuran (THF) showed broad range of diameters from 500 nm to 6 μm, while those from PVC solutions in DMF showed diameters in the vicinity of 200 nm and those from PVC solutions in mixed THF and DMF showed

diameters of less than 1 μm. Liu and Hsieh (2002) produced ultrafine cellulose acetate (CA) from CA solutions in three solvents [i.e. acetone, acetic acid, and dimethylacetamide (DMAc)] and some mixtures of these solvents. They found that none of the CA solutions in single solvent could produce fibers continuously and only the CA solution in a mixture of acetone and DMAc (2:1 v/v) could produce smooth fibers with diameters ranging from 100 nm to 1 μm.

In this work, PA-6 solutions in three different solvents and some mixed solvent systems. The three solvents were formic acid, m-cresol, and sulfuric acid and the mixed solvent systems were binary blends of formic acid with another solvent or liquid [i.e. m-cresol, sulfuric acid, acetic acid, ethanol, DMF, and dimethyl sulfoxide (DMSO)]. The concentration of PA-6 in these solvent systems was fixed at 32% (w/v).

EXPERIMENTAL METHODS

Materials

The PA-6 resin (M_w = 20,000 Da) used was supplied by Asia Fiber Public Co., Ltd. (Thailand). The solvent used in this work were 85 wt.% formic acid (Carlo Erba), m-cresol (Carlo Erba), 96 wt.% sulfuric acid (Labscan), glacial acetic acid (Labscan), ethanol (Carlo Erba), N,N-dimethyl formamide (DMF) (Labscan), and dimethyl sulfoxide (DMSO) (J.T.Baker). These chemicals were used as-received.

Solution Properties

PA-6 solutions were prepared in three different solvents (i.e. formic acid, m-cresol, and sulfuric acid) and some mixed solvent systems of formic acid and another solvent or liquid (i.e. m-cresol, sulfuric acid, acetic acid, ethanol, DMF, and DMSO) in various compositional ratios. The concentration of PA-6 in these solvent systems was fixed at 32% (w/v). Some of the solution properties, i.e. shear viscosity, surface tension, and conductivity, were measured. These properties for each solution were determined by a Brookfield DV-III programmable rheometer, a KrÜss DSA 10 Mk2 drop shape analyzer, and a Orion 160 conductivity meter, respectively.

Electrospinning Process

To electrospin it into fibers, each solution was contained in a 50-ml glass syringe. A stainless steel needle of gauge no. 26 was used as the electrode. The feed rate of the PA-6 solution was controlled by pressurized nitrogen using a flow meter. An aluminum sheet was used as the collective screen. A Gamma High Voltage Research D-ES30PN/M692 power supply was used to generate high electrostatic potentials. The emitting electrode was connected to the needle and the ground electrode was connected to the aluminum sheet. The distance between the tip of the needle and the collective screen defined the collection distance. At appropriate conditions, fibers were collected onto the collective screen and were kept in a desiccator prior to further characterization. In this particular report, the applied electrostatic potential and the collection distance were fixed at 21 kV and 10 cm, respectively.

Characterization

The morphological appearance of the as-spun PA-6 fibers was investigated visually from optical scanning photographs using a Hewlett-Packard ScanJet 4300c optical scanner and from scanning electron micrographs using a JEOL JSM-5200 scanning electron microscope (SEM). Each sample was coated with gold prior to being observed under SEM by a JEOL JFC-1100E ion sputtering device. The diameters of the obtained fibers were measured from SEM micrographs. A large number of data points were compiled and used to construct a histogram profile, from which the arithmetic mean was calculated.

RESULTS AND DISCUSSION

Among the solvents used in this work, formic acid, *m*-cresol, and sulfuric acid are good solvents for PA-6 (Grulke, 1989). They were found to dissolve 32% (w/v) of PA-6 particularly well. 85 wt.% formic acid had the shortest time in dissolving PA-6 with a clear solution being observed after stirring the mixture for only 6 hours, while *m*-cresol and 96 wt.% sulfuric acid took a much longer time to dissolve PA-6 with clear solutions being observed after stirring the mixtures for about one day. Other liquids (i.e. acetic acid, ethanol, DMF, and DMSO) were not

able to dissolve 32% (w/v) of PA-6, but they were used to adjust some properties of the PA-6 solutions in 85 wt.% formic acid. Some properties of interest for the solvents and liquids used in this work (e.g. boiling point, dipole moment, dielectric constant, and surface tension) are summarized in Table 1.

To investigate the effect of solvents on the morphological appearance of the as-spun PA-6 fibers in this work, the solvent systems were divided into 2 parts, i.e. single solvent systems and mixed solvent systems.

Single Solvent Systems

32% (w/v) of PA-6 was separately dissolved in 85 wt.% formic acid, *m*-cresol, and 96 wt.% sulfuric acid. In spinning these solutions, the formation of continuous jets was well observed for the PA-6 solution in 85 wt.% formic acid, while only discrete jets were observed for the PA-6 solution in *m*-cresol and only droplets were observed in the case of PA-6 solution in 96 wt.% sulfuric acid. It was assumed that the very high viscosity of 96 wt.% sulfuric acid (see Table 1) was responsible for the formation of droplets rather than stable jets, so sulfuric acid was diluted to the concentrations of 20 and 40 wt.% which were found to dissolve PA-6 reasonably well. Even with the dilution, PA-6 solutions in both 20 and 40 wt.% sulfuric acid were not spinnable. The failure to generate stable jets may be a result of the high boiling point and the high viscosity of sulfuric acid which may be responsible for the jets to breakup into droplets, despite its high dielectric constant which should cause the solutions to become more spinnable.

SEM micrographs showed uniform electrospun fibers obtained from the PA-6 solution in formic acid with the average fiber diameter being 83.5 nm (see Figure 1a), while only fused fibers were observed from the PA-6 solution in *m*-cresol (see Figure 1b). This experimental observation could be described based on the low dielectric constant and the high boiling point of *m*-cresol.

Mixed Solvent Systems

Since PA-6 solution in 85 wt.% formic acid produced uniform fibers, formic acid was then used as the main solvent. In mixed solvents systems, various solvents and liquids (i.e. *m*-cresol, sulfuric acid, acetic acid, ethanol, DMF, and DMSO) were

mixed with formic acid in various compositional ratios (see Table 2). Viscosity, surface tension, and conductivity were then measured on these mixed solvents and are summarized in Table 2.

Formic acid + *m*-cresol

Since it was shown that the high boiling point of *m*-cresol was responsible for the fused as-spun fibers observed, *m*-cresol was then mixed with formic acid in the compositional ratios of 10 to 40% (v/v) in order to see whether the resulting solutions can be spinnable. The viscosity of the solutions was found increase, while both the surface tension and the conductivity were found to decrease, with increasing *m*-cresol content (see Table 2). Since changes in the surface tension and the conductivity were not so critical, the increase in the viscosity of these solutions with increasing *m*-cresol content should be responsible for the observed smaller area (hence denser fiber density per unit area) of the fiber fabric obtained (see Figure 2). The increased viscosity could result in the lower tendency for bending instability to occur (Koombhongse, 2001). SEM micrographs of as-spun PA-6 fibers from solutions of PA-6 in formic acid and *m*-cresol of various compositional ratios are shown in Figure 3. Obviously, discrete fibers having smooth surface were observed for the solutions having the *m*-cresol contents of 10 to 30%, while fused fibers were obtained for the solution having the *m*-cresol of 40%. The fused fibers obtained should be a direct result of the increased boiling point of the mixed solvents. Fused fibers were also observed from the electrospinning of PCL in a mixture of methylene chloride and toluene (Lee, et al., 2003). In our study, the average fiber diameter was found to increase with increasing *m*-cresol content (i.e. from 110.4 nm from the solution having *m*-cresol content of 10% to 170.3 nm from the solution having *m*-cresol content of 30%). The increased average fiber diameter should be a result of an increase in the viscosity as well as a decrease in the conductivity of the solutions with increasing *m*-cresol content.

Formic acid + 20 wt.% sulfuric acid or 40 wt.% sulfuric acid

Electrospinning of PA-6 solution in either 20 or 40 wt.% sulfuric acid was not possible. Mixtures of 85 wt.% formic acid and either 20 or 40 wt.% sulfuric acid

in the compositional ratios of 10 to 40 % (v/v) based on sulfuric acid were prepared. It was found that the conductivity of the solutions was found to increase, while the viscosity was found to decrease (despite the high viscosity value of the pure solvent), with increasing amount of sulfuric acid added (see Table 2). Since sulfuric acid is a strong acid, it can hydrolyze PA-6 molecules. Hydrolysis causes the molecular weights of PA-6 to decrease, hence a reduction in the solution viscosity.

SEM micrographs for PA-6 fibers obtained from PA-6 solutions in mixtures of 85 wt.% formic acid and either 20 or 40 wt.% sulfuric acid in the compositional ratio of 10 to 40% (v/v) based on sulfuric acid are shown in Figure 4. Fused fibers were formed from solutions having 20 and 30 % (v/v) of 20 wt.% sulfuric acid and large fibers were obtained from solutions having 40% (v/v) of 20 wt.% sulfuric acid. For solutions having 20 and 30% (v/v) of 40 wt.% sulfuric acid, large jets were directly ejected from the tip of needle to the aluminum foil collector, which may be a result of the high conductivity of these solutions. The high conductivity may cause the charge jets to travel to the grounded target before they can undergo bending instability.

Formic acid +acetic acid

Acetic acid was mixed with 85 wt.% formic acid in the compositional ratios of 10 to 40% (v/v). With increasing the amount of acetic acid, the average fiber diameter was found to increase from 93.6 nm from the solution having the acetic acid content of 10% (v/v) to 235.7 nm from the solution having the acetic content of 40% (v/v) (see Figure 5). The increase in the average fiber diameter may be a result of an increase in the solution viscosity or a decrease in the both of the solution surface tension and the solution conductivity with increasing amount of acetic acid or both.

Formic acid +ethanol

Due to the desirable low boiling point and low surface tension of ethanol for electrospinning, it was chosen as an adjusting liquid to be mixed with 85 wt.% formic acid. The mixture containing the amount of ethanol as high as 20% (v/v) could well dissolve 32% (w/v) of PA-6. It should be noted that the mixture containing the ethanol content of 20% (v/v) became inhomogeneous after setting for

one hour. Accordingly, the particular mixture was used to prepare PA-6 solution from which electrospun PA-6 was obtained for comparison, but its properties could not be measured. According to the SEM micrographs shown in Figure 6, the average fiber diameter was found to increase from 90.9 nm from the solution having the ethanol content of 10% (v/v) to 115 nm from the solution having the ethanol content of 20%(v/v).

Formic acid + DMF or DMSO

DMF and DMSO are solvents with rather high dielectric constant and high dipole moment, so they were chosen to be mixed with 85 wt.% formic acid to improve the electrical properties of the PA-6 solutions. These mixtures containing the amount of either DMF or DMSO only as high as 10% (v/v) could dissolve 32% (w/v) of PA-6 well. Similar to the case of ethanol, the mixture containing the DMF or DMSO content of 20% (v/v) became inhomogeneous after setting for one hour. Accordingly, the particular mixture was used to prepare PA-6 solution from which electrospun PA-6 was obtained for comparison, but its properties could not be measured. According to the SEM micrographs shown in Figure 7, the average fiber diameter was found to decrease with increasing amount of DMF or DMSO. In particular, the bead-on-string morphology was observed for the fibers obtained from the mixture containing the DMSO content of 20% (v/v) (see Figure 7d).

CONCLUSIONS

In this work, the electrospinning technique was used to produce ultra-fine PA-6 fibers. The effect of solvent systems on morphological appearance of the obtained fibers was investigated. PA-6 solutions were prepared in both single solvent systems and mixed solvent systems. The concentration of PA-6 in the solutions was fixed at 32% (w/v). For single solvent systems, only the solution of PA-6 in 85 wt.% formic acid gave uniform electrospun fibers, with the average diameters being about 83.5 nm, while the solutions of PA-6 in *m*-cresol and 20 and 40 wt.% sulfuric acid did not form ultra-fine fibers. For mixed solvent systems, the solvent mixtures were prepared by mixing 85 wt.% formic acid with *m*-cresol, 20 and 40 wt.% sulfuric acid, acetic acid, ethanol, DMF, and DMSO in the compositional ratios of 10 to 40% (v/v).

In general, the average fiber diameters of the as-spun fibers were found to increase with increasing content of the second solvent, with the exception of the mixtures containing DMF and DMSO that the average fiber diameters were, instead, found to decrease. In mixed solvents of high compositional ratios of *m*-cresol and sulfuric acids (i.e. greater than 20%), fibers of rough surface and fused fibers were observed.

ACKNOWLEDGMENTS

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**Table 1.** Properties of solvents and liquids used in this work.

Solvent	Density (g/cm^3)	Boiling point (°C)	Dipole moment (debye)	Dielectric constant	Surface tension (10^{-3} J/m^2)	Viscosity (10^{-3} Pa.s)
formic acid	1.2131	100.7	1.4	58.5	-	1.8
m-cresol	1.034	203	1.48	11.8	-	-
sulfuric acid	1.8305	274	2.7	101	-	25.54
acetic acid	1.0497	117.9	1.5	6.19	26.9	1.124
ethanol	0.7851	78.3	1.7	24.6	22	1.078
DMF	0.9445	153	3.8	37	36.3	0.796
DMSO	1.0958	189	3.9	46.7	43	1.996

Table 2. Solution properties of mixed solvent systems between formic acid and various solvents.

| Solvent systems (% v/v)	Viscosity (cP)	Surface tension (mN/m^2)	Conductivity (ms/cm)
Formic acid + *m*-cresol			
90 / 10	1709	42.4	2.93
80 / 20	2104	41.3	2.11
70 / 30	3127	40.6	1.39
60 / 40	4075	39.8	0.82
Formic acid + 20 wt.% sulfuric acid			
90 / 10	1291	43.8	7.31
80 / 20	830	44.5	14.94
70 / 30	792	44.5	24.0
60 / 40	513	44.7	41.31
Formic acid + 40 wt.% sulfuric acid			
90 / 10	1387	42.8	10.37
80 / 20	1091	43.4	20.32
70 / 30	930	43.8	34.80
60 / 40	685	44.2	59.10
Formic acid + acetic acid			
90 / 10	1450	42.8	3.48
80 / 20	1564	41.1	2.55
70 / 30	1765	39.8	1.82
60 / 40	2033	39.7	1.28
Formic acid + Ethanol			
90 / 10	1115	42.3	3.10
Formic acid + DMF			
90 / 10	1295	43.6	3.63
Formic acid + DMSO			
90 / 10	1750	43.6	3.09

(a)   (b)

Figure 1. The scanning electron micrographs of electrospun fibers of PA-6 in a single solvent: a) 85 wt.% formic acid; and b) *m*-cresol (10,000x).
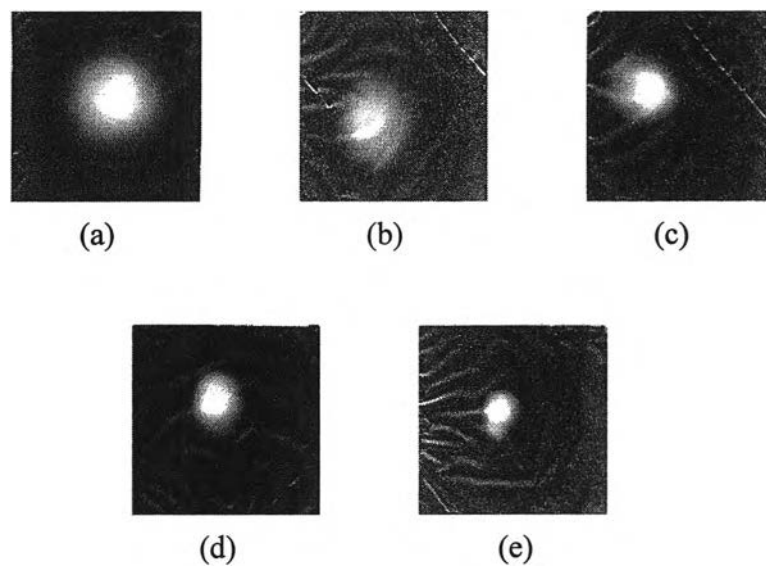
Figure 2. Optical scanning photographs for as-spun PA-6 fibers on Al foils from a single solvents: a) 85 wt.% formic acid; and mixed solvent of 85 wt.% formic acid with: b) 10; c) 20; d) 30; and e) 40% (v/v) *m*-cresol, respectively.
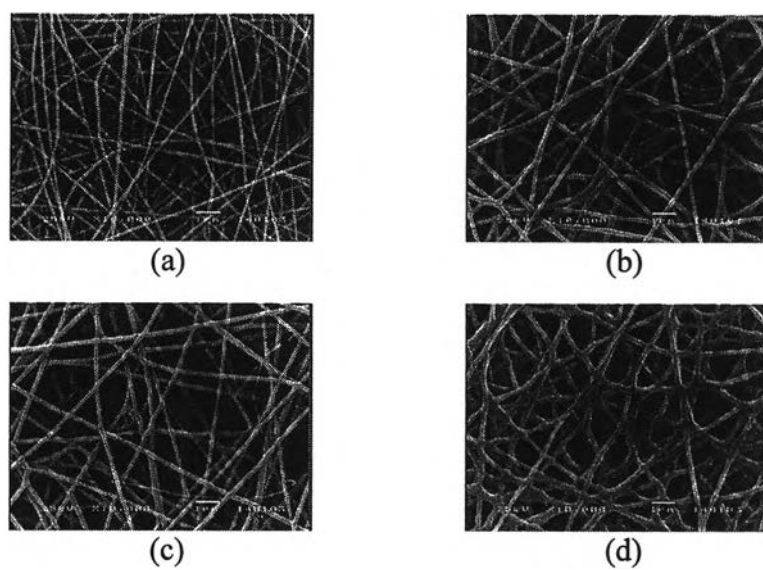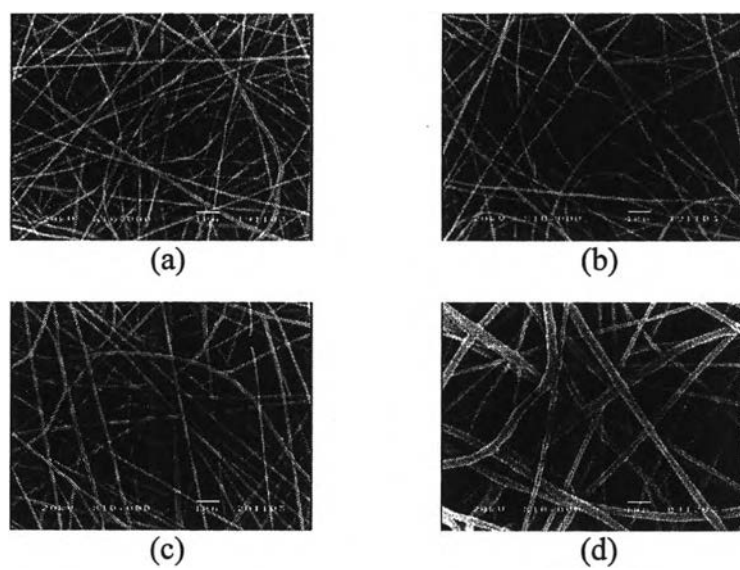
Figure 3. Scanning electron micrographs (10,000×) for as-spun PA-6 fibers from the mixed solvents of 85 wt.% formic acid with: a) 10; b) 20; c) 30; and d) 40% (v/v) *m*-cresol, respectively.
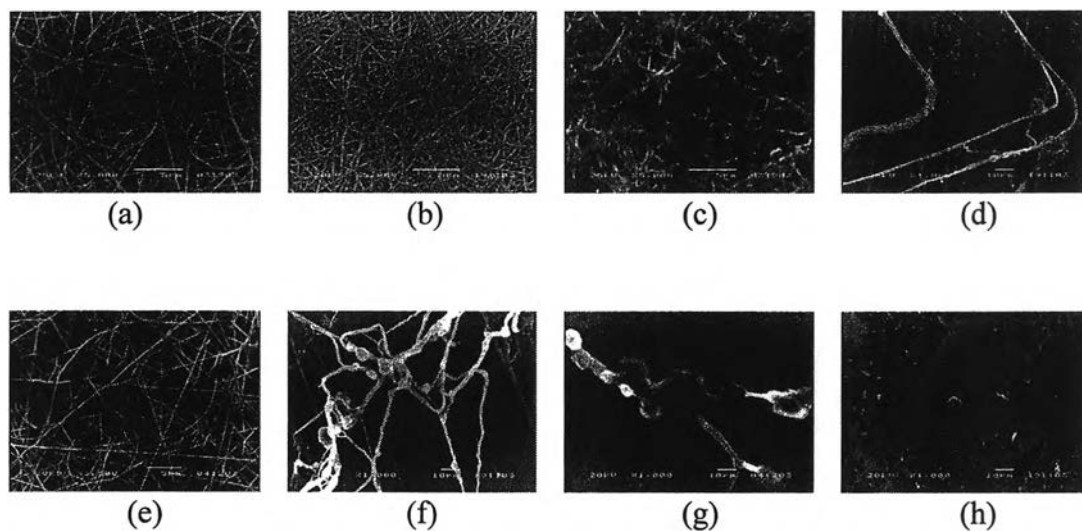
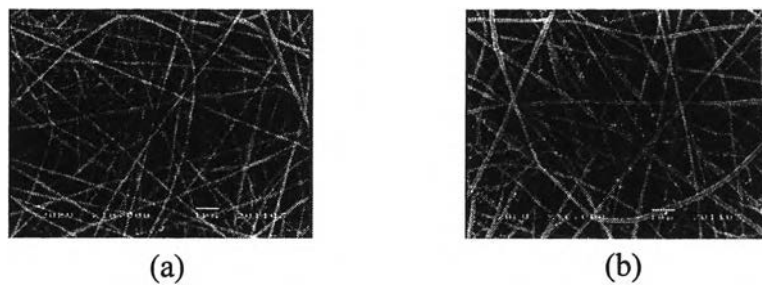**Figure 4.** Scanning electron micrographs for as-spun PA-6 fibers from the mixed solvents of 85 wt.% formic acid with: a) 10 (5000×); b) 20 (5000×); c) 30 (5000×); d) 40% (v/v) (1000×) 20 wt.% sulfuric acid and the mixed solvents of 85 wt.% formic acid with: e) 10 (3500×); b) 20 (1000×); c) 30 (1000×); and d) 40% (v/v) (1000×) 40 wt.% sulfuric acid, respectively.
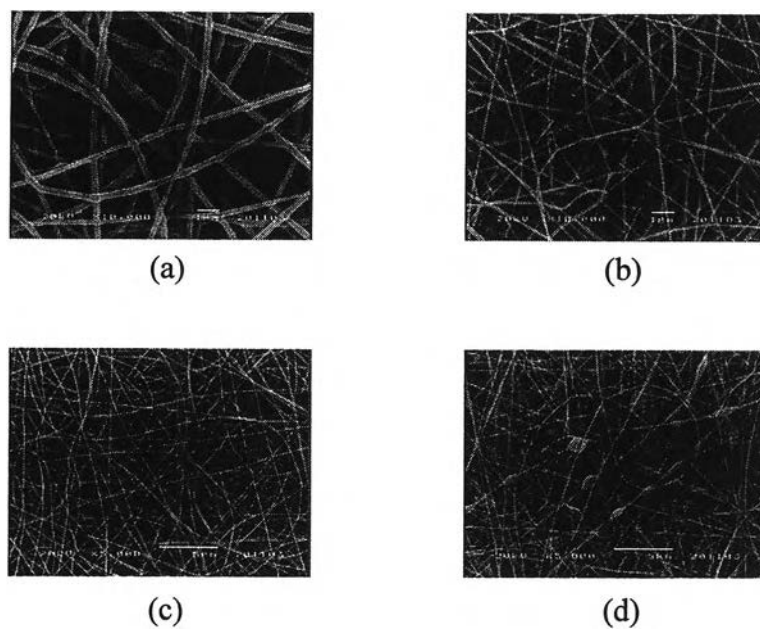
Figure 5. Scanning electron micrographs (10,000×) for as-spun PA-6 fibers from the mixed solvents of 85 wt.% formic acid with: a) 10; b) 20; c) 30; and d) 40 %(v/v) acetic acid, respectively.

(a)   (b)

Figure 6. Scanning electron micrographs (10,000×) for as-spun PA-6 fibers from the mixed solvents of 85 wt.% formic acid with: a) 10; and b) 20% (v/v) ethanol.

Figure 7. Scanning electron micrographs for as-spun PA-6 fibers from the mixed solvents of 85 wt.% formic acid with: a) 10; and b) 20% (v/v) of DMF (10000×), and the mixed solvents of 85 wt.% formic acid with: a) 10; and b) 20% (v/v) of DMSO (5000×).