Effects of Solution Concentration, Emitting Electrode Polarity, Solvent Type, and Salt Addition on Electrospun Polyamide-6 Fibers: A Preliminary Report

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Summary: Electrospinning is a process by which ultrafine fibers which have diameters in the range of tens of nanometers to less than ten of micrometers can be produced. This process utilizes expulsion of charges as a means to very thin fiber formation. In this short report, the effects of some of the influencing solution and process parameters (i.e. solution concentration, emitting electrode polarity, solvent type, and salt addition) on morphological appearance of electrospun polyamide-6 fibers were investigated based on visual observation of a series of scanning electron micrographs. It was found that all of the parameters studied played important roles in determining morphology and sizes of the fibers obtained.

Keywords: electrostatic spinning; polyamide-6; ultrafine fibers

Introduction

Electrostatic spinning or electrospinning is a newly-arrived fiber spinning process for producing ultra-fine fibers with average diameters in the range of tens of nanometers to sub-micrometers. Naturally, the ultra-fine fibers from this process are obtained as a non-woven fabric, which exhibits several interesting characteristics, such as small pore sizes between adjacent fibers, high porosity, and high specific surface area. These characteristics can be of tremendous uses in some applications.[1]

The basic principles of the electrospinning process are concerned with the application of a high electrical potential to a polymer solution or melt across a finite distance between a nozzle and a collective target. 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. When an electrostatic field is applied, charges are built up on surface of a droplet of the polymer solution or melt at the tip of the nozzle. The charges destabilize the hemispherical shape of the droplet into a cone shape at a critical value of the applied electrostatic field. With further

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increase in the applied electrostatic field, the electrostatic force overcomes the surface tension, causing a charged stream of polymer solution or melt (i.e. a charged jet) to be ejected from the tip of the cone. The charged jet travels in a straight line for a few centimeters as its diameter thins down appreciably, before undergoing a bending instability during which the diameter of the jet continues to decrease tremendously. Finally, fibers are collected on a grounded collector plate.[2]

In the electrospinning from a polymer solution, various solution properties are affecting the morphology of the obtained fibers. Some of these are solution concentration, viscosity, surface tension, and conductivity. Deitzel and co-workers[3] found that, in order to obtain poly(ethylene oxide) (PEO) fibers of good appearance, the viscosity of the PEO solution should be in the range of 1 to 20 poise and the surface tension in the range of 35 to 55 dyne/cm. At viscosity values greater than 20 poise, electrospinning became prohibitive due to the extremely high cohesiveness of the solutions which restricts the flow; whereas, at viscosity values lower than 1 poise, droplets were abundant due to the extremely low cohesiveness of the solutions which causes the jet to break up.[3] Baumgarten[4] found that uniform acrylic fibers were obtained when the viscosity of the stock solutions was in the range of 1.7 to 215 poise. He also found that addition of small amount of inorganic salts into the solutions helped promote the fiber formation with no beads present, a result of the increased charge density in a jet segment. The fiber diameters were also found to decrease with addition of the salts.[5,6]

In the present contribution, the effects of some of the influencing solution and process parameters (i.e. solution concentration, emitting electrode polarity, solvent type, and salt addition) on morphological appearance of electrospun polyamide-6 fibers are preliminarily reported.

Experimental Details

Polyamide-6 resin ($\overline{M}_w$ = 20,000 Da) was courteously supplied by Asia Fiber Public Co., Ltd. (Thailand). In order to elucidate the effect of solution viscosity on morphology of the obtained fibers, solutions of polyamide-6 in 85% v/v formic acid (Carlo Erba) were prepared in various concentrations, ranging from 10 to 46 percent by weight (wt.%). The effect of solvent type was investigated by mixing *m*-cresol with formic acid in various ratios, while sodium chloride (NaCl) was added in solutions of polyamide-6 in formic acid in order to observe the effect of salt addition. Each stock solution prepared was characterized for

viscosity, surface tension, and conductivity using a Brookfield DV-III programmable rheometer, a KrÜss K10T tensiometer, and a Orion 160 conductivity meter, respectively.

Each as-prepared polyamide-6 solution was stocked in a 50-ml glass syringe before electrospinning. A stainless steel needle of gauge no. 26 was used as the nozzle. Feed rate of the solution was controlled by fixing the flow rate of nitrogen gas, connected to the feed side of the glass syringe. A piece of aluminum sheet was used as the grounded collective screen. A Gamma High Voltage Research D-ES30PN/M692 DC power supply (Florida, USA) was connected to the nozzle and the grounded collective screen. The polarity of the emitting electrode (e.g. the one connecting to the nozzle) could either be positive or negative. In this particular report, the nozzle-to-collector distance of 10 cm and the applied DC potential (either positive or negative polarity) of 21 kV were fixed.

The morphological appearance of the obtained polyamide-6 fibers was observed by a JEOL JSM-5200 scanning electron microscope.

Results and Discussion

It has been shown to some extent that solution properties (i.e. viscosity, surface tension, and conductivity) play an important role in the morphological appearance of the obtained electrospun polymeric fibers. In order to elucidate such a statement to the case of electrospun polyamide-6 fibers, polyamide-6 solutions in 85% v/v formic acid with the concentration being in the range of 10 to 46 wt.% were characterized for their viscosity, surface tension, and conductivity values. It was found that the viscosity value of the solutions was found to tremendously increase from 40 to 4058 cp with increasing polyamide-6 concentration from 10 to 46 wt.%, while the surface tension and conductivity values were found to increase very slightly.

Qualitatively, the results showed that when the viscosity value of the polyamide-6 solutions was lower than 135 cp (corresponding to the concentration of the solution of 16 wt.%), only droplets were present. The formation of the droplets for solutions having viscosity values lower than 135 cp can be described based on the analysis of forces acting on a small segment of a charged jet. In this case, six types of forces can be considered: they are 1) body or gravitational force, 2) electrostatic force which carries the charged jet from the nozzle to the collective target, 3) Coulombic force which tries to push apart adjacent charged carriers within the jet segment and is responsible for the stretching of the charged jet during its flight to the target, 4) viscoelastic force which tries to prevent the charged jet from stretching, 5)

surface tension which prevents the surface of the charged jet from stretching, and 6) drag force from the friction between the charged jet and the surrounding air.[7]

To explain the occurrence of the droplets for solutions having viscosity value lower than 135 cp can be described by considering the interplay between three most important forces being responsible for the formation of elongated jet, i.e. Coulombic force, viscoelastic force, and surface tension. At low viscosity values, the viscoelastic force was comparatively smaller than the Coulombic force. This resulted in the over-stretching of a charged jet, hence the break-up of the charged jet into many small spherical droplets as a result of the surface tension. On the contrary, for solutions of higher viscosity, the viscoelastic force became larger in comparison with the Coulombic force (due mainly to the increased number of chain entanglements). The increase in the viscoelastic force was sufficient to prevent a charged jet from breaking up into small droplets and to allow the electrostatic stress to further elongate the jet which finally thins down the diameter of the jet tremendously.

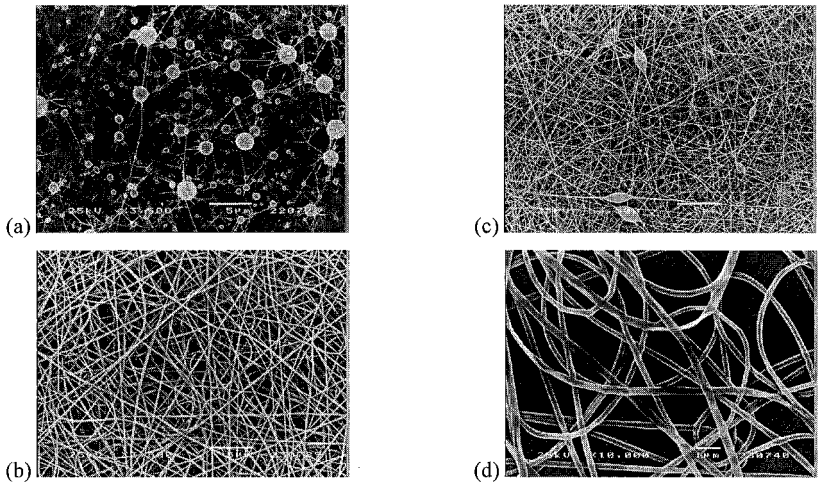
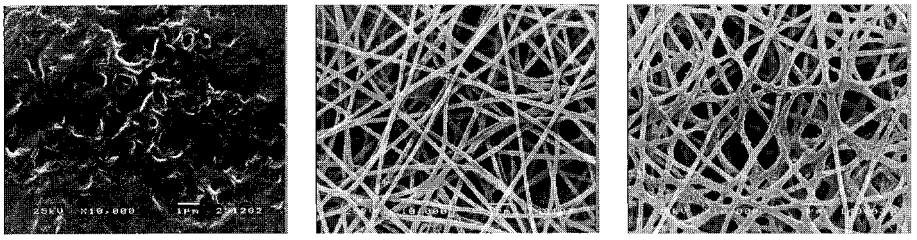


Figure 1. Electrospun products from solutions of polyamide-6 in formic acid as a function of solution concentration (solution viscosity) with the positive polarity of the emitting electrode for (a) 16 wt.% (135 cp), (b) 28 wt.% (689 cp), and (c) 40 wt.% (2445 cp) and with the negative polarity of the emitting electrode for (d) 38 wt.% (1928 cp).

Figure 1 shows selected scanning electron micrographs of products obtained from the electrospinning of polyamide-6 solutions in formic acid for four different concentrations (and hence four different viscosity values) using either positive or negative polarity of the emitting electrode. Evidently, droplets were more prevalent when the viscosity of the polyamide-6 solution was 135 cp (see Figure 1a). With an increase in the viscosity of the solution to 689

cp, fibers with spindle-like droplets were present along with pure fibers (see Figure 1b). With further increase in the viscosity of the solution to 2445 cp, only uniform fibers were obtained (see Figure 1c). Qualitatively, diameters of the obtained fibers were found to increase with increasing viscosity of the solutions.

What has been presented in Figure 1a to 1c was obtained from spinning polyamide-6 solutions with the polarity of the emitting electrode being positive. Interestingly, when the polarity of the emitting electrode was negative, flat-shaped fibers were instead observed, particularly when the viscosity of the solutions exceeded 1928 cp (see Figure 1d). In addition to the formation of flat fibers, it is observed that the negative polarity of the emitting electrode resulted in fibers with much larger diameters than the positive one. The reasons for the larger diameters of the obtained fibers when the negative polarity was used might be an increase in the mass flow rate (a result of the higher charge density) and for the formation of flat fibers might be the collapsing of the dried skin layer of a jet after the solvent inside the jet had evaporated.[8]



(a) (b) (c)

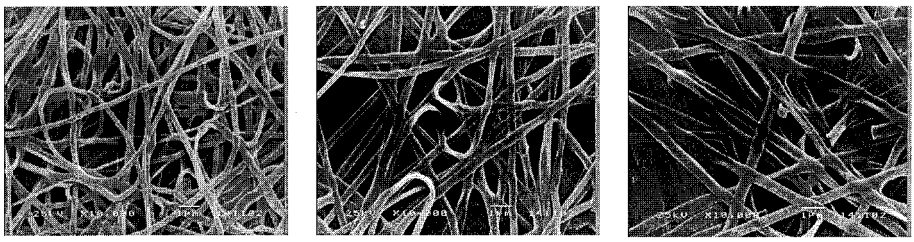
Figure 2. Electrospun products from solutions of 32 wt.% of polyamide-6 in a) *m*-cresol and mixed solvents of formic acid and *m*-cresol having the compositional ratio between formic acid and *m*-cresol of b) 80:20 and c) 60:40 v/v with positive polarity of the emitting electrode.

The effect of solvent type on morphological appearance of the obtained polyamide-6 fiber was investigated by dissolving polyamide-6 in *m*-cresol or mixed solvents of formic acid and *m*-cresol having the compositional ratio between formic acid and *m*-cresol of 90:10, 80:20, 70:30, 60:40, and 50:50 v/v prior to electrospinning. The viscosity of the mixed solvents was found to increase, while the conductivity was found to decrease, with increasing amount of added *m*-cresol. Figure 2 illustrated selected results of fibers obtained from solutions of polyamide-6 in *m*-cresol and the mixed solvents of 80:20 and 60:40 compositional ratios.

According to Figure 2a, electrospun fibers were not observed when pure *m*-cresol was used as the solvent. The most likely explanation may be due to the higher viscosity and lower

conductivity of the resulting solution and to the higher boiling point of *m*-cresol (i.e. 203°C) in comparison with that of formic acid (i.e. 118°C). Lee and co-workers[9] found that both dielectric constant and conductivity of the spinning solution were key factors signifying the electrospinning process.

Fibers of smooth surface were observed with the solutions having *m*-cresol content between 10 to 30 percent by volume (i.e. vol.%) (see, for example, Figure 2b), while fused fibers were observed with the solutions having *m*-cresol content greater than 40 vol.% (see, for example, Figure 2c). The higher boiling point of *m*-cresol should be responsible for the formation of fused fibers observed from solutions of polyamide-6 in mixed solvents having high *m*-cresol content. Additionally, diameters of the fibers were found to increase with increasing amount of *m*-cresol in the solutions, likely a result of the increased viscosity and the decreased conductivity values.



(a) (b) (c)

Figure 3. Electrospun products from solutions of 32 wt.% of polyamide-6 in formic acid using negative polarity of the emitting electrode with a) 2, b) 3, and c) 4 percent by weight of NaCl salt addition.

The effect of solution conductivity on morphological appearance of the obtained polyamide-6 fibers was also investigated. The solution conductivity was varied by varying the content of NaCl salt in the system. The concentration of NaCl was varied in the range of 1 to 5 wt.%. Note that the low concentrations of NaCl salt added were to ensure complete solubility of the salt in the solutions. The conductivity of the resulting solutions was found to increase with increasing amount of NaCl salt added. Figure 3 shows morphological appearance of the obtained polyamide-6 fibers as a result of salt addition at different amounts using negative polarity of the emitting electrode. Clearly, the fibers obtained were flat and, with increasing salt content, the size of the fibers was found to increase. It is hypothesized that both the application of the negative polarity and the addition of NaCl salt helped increase the mass

flow rate, hence an increase in the size of the fibers obtained with the flat shape being formed by the much slower evaporation rates as a result of the larger size of the fibers.

Conclusions

In this short report, the electrospinning technique was used to produce ultra-fine polyamide-6 fibers. The effects of some of the influencing solution and process parameters (i.e. solution concentration, emitting electrode polarity, solvent type, and salt addition) on morphological appearance of the obtained fibers were visually observed from a series of scanning electron micrographs. It was found that solutions with high enough viscosity values were necessary to result in electrospun polyamide-6 fibers having uniform diameters. Mixing *m*-cresol with formic acid to be used as the mixed solvent for dissolving polyamide-6 affected the morphological appearance a great deal. It was found that diameters of the fibers obtained increased with increasing amount of *m*-cresol and, at *m*-cresol content of greater than 40 percent by weight, fused fibers were formed, attributable to the higher boiling of *m*-cresol. It was found that flat fibers were obtained with use of the negative polarity of the emitting electrode. Lastly, increased conductivity of the solutions by increasing amount of NaCl salt addition resulted in fibers of larger sizes.

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[1] J. Doshi, D. H. Reneker, *J. Electrostatics* **1995**, *35*, 151.
[2] D. H. Reneker, A. L. Yarin, H. Fong, S. Koombhongse, *J. Appl. Phys.* **2000**, *87*, 4531.
[3] J. M. Deitzel, J. Kleinmeyer, D. Harris, N. C. Beck Tan, *Polymer* **2001**, *42*, 261.
[4] P. K. Baumgarten, *J. Colloid Interface Sci.* **1971**, *36*, 71.
[5] H. Fong, I. Chun, D. H. Reneker, *Polymer* **1999**, *40*, 4585.
[6] X. Zong, K. Kim, D. Fang, S. Ran, B. S. Hsiao, B. Chu, *Polymer* **2002**, *43*, 4403.
[7] L. Wannatong, A. Sirivat, P. Supaphol, *Polym. Int.*, accepted for publication.
[8] S. Koombhongse, W. Liu, D. H. Reneker, *J. Polym. Sci. B: Polym. Phys.* **2001**, *39*, 2598.
[9] K. H. Lee, H. Y. Kim, M. S. Khil, Y. M. Ra, D. R. Lee, *Polymer* **2003**, *44*, 1287.