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The Morphology of Electrospun Polystyrene Fibers

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Abstract–Electrospinning is a process of electrostatic fiber formation which uses electrical forces to produce polymer nanofibers from polymer solution. The electrospinning system consists of a syringe feeder system, a collector system, and a high power supplier. The important parameters in the morphology of electrospun polystyrene fibers are concentration, applied voltage, and solvent properties. Higher concentrations of the polymer solution form thicker fibers and fewer beads. When the concentration is 7 wt%, electrospun fibers have an average diameter of 340 nm, but as the concentration of PS increases to 17 wt%, the fiber diameter gradually thickens to 3,610 nm. The fiber morphology under different solvent mixture ratios and solvent mixtures has also been studied.

Key words: Electrospinning, Nanofibers, Polystyrene, Concentration, Spinning Distance

INTRODUCTION

Since the beginning of the nineteenth century, polymers have replaced metals in various applications for their lightweight and flexibility. Commercially, most synthetic manufactured fibers are created by extrusion, which consists of forcing a thick, viscous liquid through the tiny holes of a device called a spinneret to form continuous filament of semi-solid polymer.

Electrospinning is a process of electrostatic fiber formation which uses electrical forces to produce polymer fibers from polymer solution, with nanometer-scale diameters. Electrospinning is not a new technology for polymer fiber production. It was first introduced in 1930, but it did not gain significant industrial importance due to the low output of the process, inconsistent and low molecular orientation, poor mechanical properties and high diameter distribution of the electrospun fibers. But polymeric fiber can have nanosized diameter [Shawon, 2002; Jo et al., 2002].

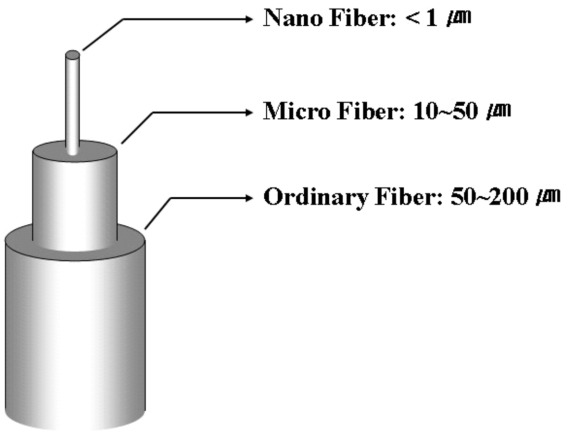


Fig. 1. Classification by the fiber diameters [Jo et al., 2002].

Fig. 1 shows the classification by the fiber diameter. Nanofibers have a large specific surface area and a small pore size in comparison with commercial textiles. So polymer nanofibers are being used, or finding uses, in filtration, protective clothing, biomedical applications including wound dressings and drug delivery systems, as structural elements in artificial organs, and in reinforced composites. Recently, there has been a renewed interest in these commercially variable processes, making literature involving the quantitative technical and scientific information of the process and product characterization extremely limited. Polymer fibers encouraged the invention of technology for manufacturing nanofibers such as electrospinning [Reneker et al., 2000; Kim et al., 2003].

This paper investigates the fiber morphology of the polystyrene fibers made by electrospinning process. The important parameters in the morphology of electrospun polystyrene fibers such as concentration, applied voltage, and solvent properties are investigated experimentally. Also the fiber morphology under different solvent mixture ratios and solvent mixtures has been observed.

EXPERIMENTAL

Fig. 2 shows a schematic diagram of the electrospinning process. It consists of the syringe feeder system, the collector system, and the high power supplier. High electric field strength is generated between a polymer fluid contained in a glass syringe and a metallic collector. The hemispherical shape of pendant droplets at the end of the syringe tip is changed into a conical shape with increasing voltage, which is known as the Taylor cone. When the voltage reaches a critical value, the electric force overcomes the surface tension of the deformed drop of the suspended polymer solution formed on the tip of the syringe, and a jet is produced. A jet travels through the air; the solvent evaporates leaving behind polymer fibers to be collected on an electrically grounded target. This means that the electrospinning jet can be thought of as a string of charge elements connected by a viscoelastic medium, with one end fixed at the point

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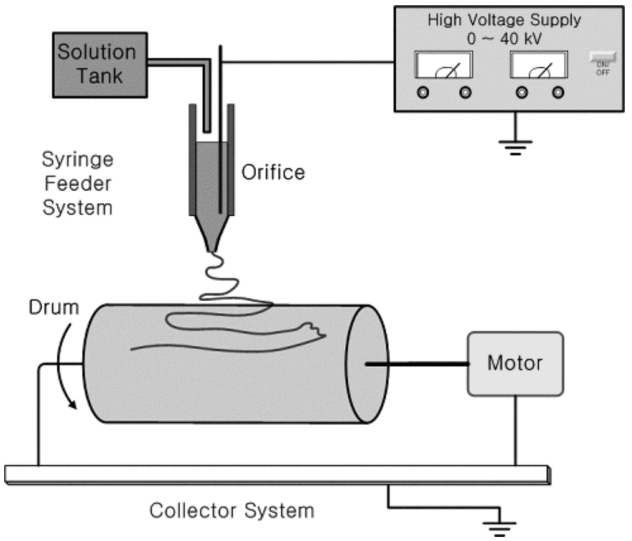


Fig. 2. Schematic diagram of the electrospinning.

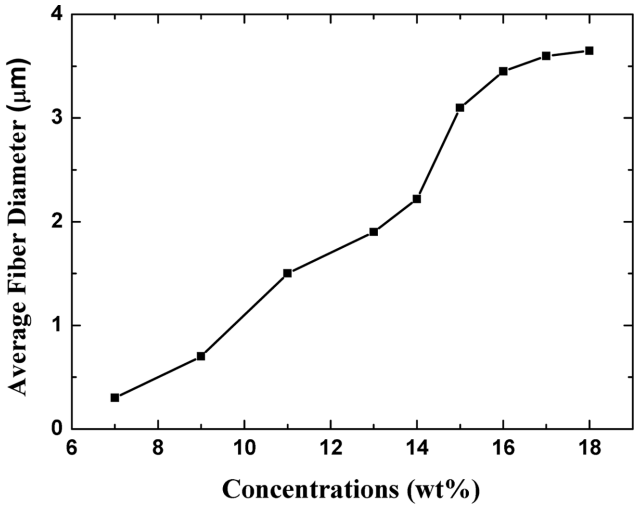


Fig. 4. The change of average fiber diameter as a function of concentration (solvent mixing ratio of THF by DMF=60 : 40, applied voltage=15 kV, spinning distance=10 cm).

of origin and the other end free. The free end of the electrospinning jet follows a chaotic path as it travels toward the grounded collector [Deitzl et al., 2001; Jung et al., 1999]. This chaotic motion is the result of a complicated interaction of variables that involves viscosity, conductivity, surface tension, electrostatic force, air friction, gravity and ambient parameters [Lee et al., 1995; Reneker et al., 1996; Fong et al., 1999].

Polystyrene (PS) solution is prepared from PS pellet (Aldrich, molecular weight 170,000 g/mol). PS is dissolved by Tetrahydrofuran (THF) and Dimethylformamide (DMF) in the ultrasonicator. The concentration of the PS solution tested ranges from 7 to 17 wt%. Spinning occurs from the droplet of solution protruding from the 0.7 mm internal diameter of the tip. A positive electric potential is applied to the polymer blend solution, by attaching the lead to the variable high voltage power supply (Chung-pa Co., EMT) directly to the copper wire, to the solution inside a syringe. The voltage ranges from 0 to 40 kV. A drum collector covered with aluminum foil is placed 5-25 cm vertically from the tip of the syringe as a grounded collector. The morphology and diameter of the electrospun fibers aggregates are determined with a scanning electron microscope (HITACHI, 4200) and image analyzer (IMT, IMT-2000).

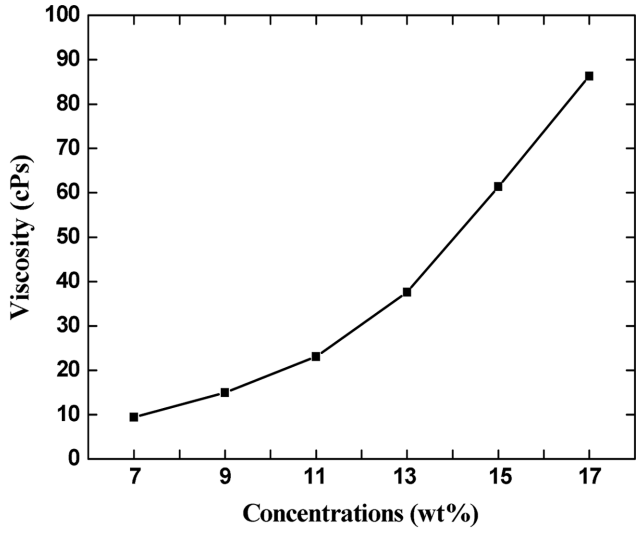


Fig. 3. The change of viscosity as a function of PS concentration (polystyrene, THF : DMF=60 : 40).

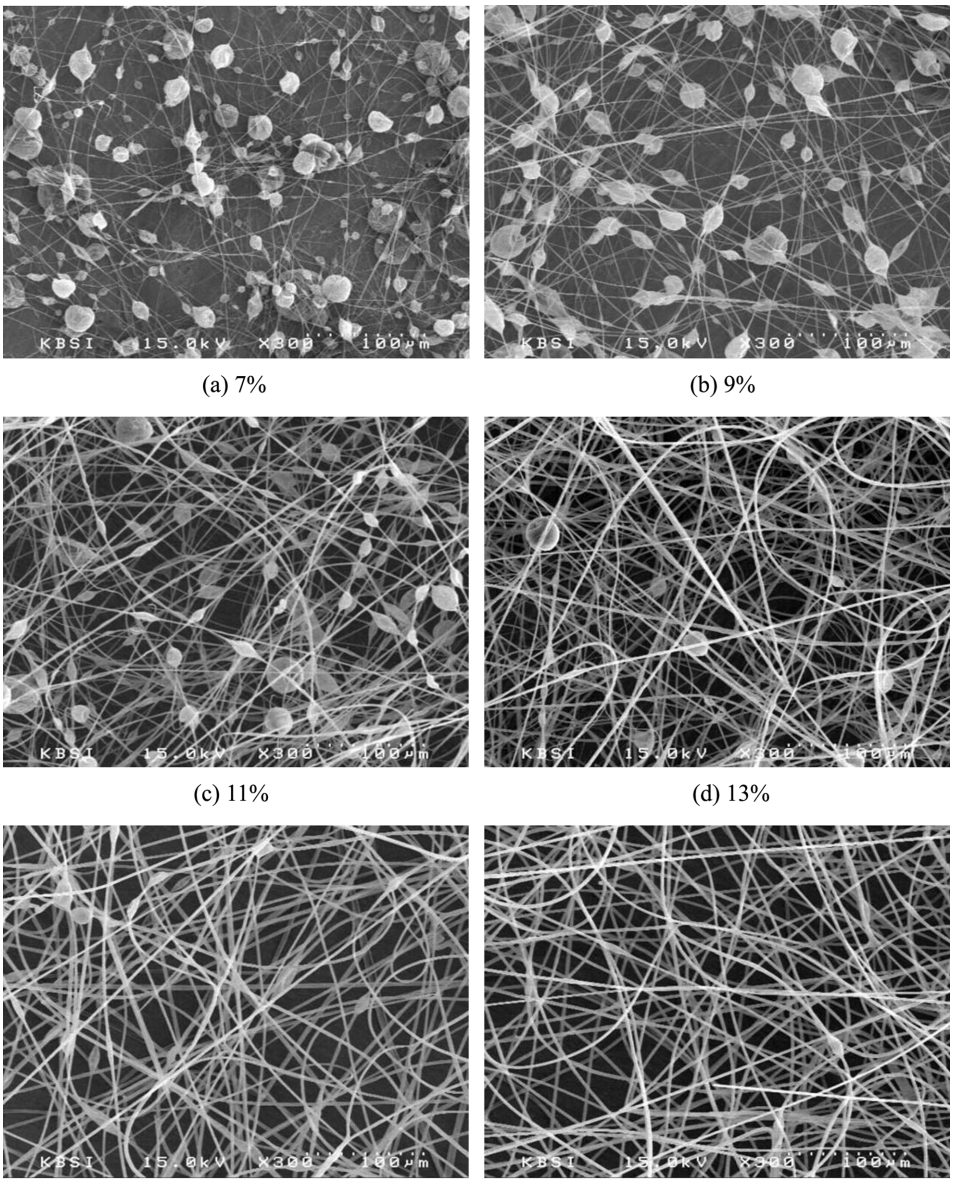
RESULTS AND DISCUSSIONS

1. Effect of PS Concentration on Fibers Morphology

Fig. 3 shows the relationship between PS concentration and viscosity in PS solution. The viscosity of PS solution increases with increasing PS concentration. The polymer concentration shows an important factor on the viscosity representing the characterization of the intermolecular interactions in polymer solution.

Fig. 4 shows the change of fiber diameters as a function of PS concentration at the applied voltage of 15 kV. When the concentration is 7 wt%, electrospun fibers have an average diameter of 340 nm, but as the concentration of PS increases to 17 wt%, the fiber diameter gradually thickens to 3,610 nm. The higher concentration of the polymer solution tries to form thicker fibers by preventing the stretching of fibers. The fibers are not produced by electrospinning below a PS concentration of 6 wt%, because a stable drop at the end of spinneret is maintained. So the concentration of the PS solution tested ranges from 7 to 17 wt% with the fixed voltage of 15 kV and the spinning distance of 10 cm.

Fig. 5 shows the results of SEM images as a function of PS concentration. Polymer concentration also has an effect on bead formation and bead density. Fibers produced from lower concentrated solution exhibit more beads, while other parameters remain constant. A mixture of large beads and fibers is generated by electrospinning PS solution at concentrations below 13 wt%. The reason is that at lower concentrations, electrospun fibers are harder to dry before they reach the collection drum. When solidification process is underway on the surface of the collection drum, surface tension makes beads spherical shaped. At low concentration, surface tension becomes dominant influence over viscosity and forms more



(a) 7% (b) 9%

(c) 11% (d) 13%

(e) 15% (f) 17%

Fig. 5. Scanning electron micrographs for the change of morphology as a function of concentration (solvent mixing ratio of THF by DMF= 60 : 40, applied voltage=15 kV, spinning distance=10 cm).

beads. But as the viscosity increases in the solution, surface tension becomes dominated by viscosity and results in fewer beads, while the other variables are maintained constant.

2. Effect of Applied Voltage and Spinning Distance on Fibers Morphology

Fig. 6 shows the change of fiber diameters as a function of applied voltage and spinning distance at the PS concentration of 16%. The spinning voltage performed a role on the fiber structure and morphology. When the voltage increases from 10 to 25 kV with the spinning distance of 15 cm, the diameter of PS fibers decreases from 3,300 to 2,400 nm. The polymer jet is discharged with a greater electrostatic repulsion that causes it to undergo higher levels of drawing stress and the jet velocity increases. The increasing electrostatic force reinforces the stretch ability of a droplet. During the travel of the fibers towards the target, the higher voltage has the opportunity to stretch the fibers more and results in thin fibers. And as the voltage increases, it is found that the shape of beads gradually changes from spherical to spindle like. However, when the spinning distance is getting closed the morphology changes from cylindrical fibers to flat fibers. At a spinning distance of 5 cm, the width is used instead of the diameter, because the aspect ratio of fiber increases with increasing applied voltage.

For a spinning distance of 5 cm, electrospun fiber width gradually thickened with increasing applied voltage. When the applied voltage is 10 kV, electrospun fibers have an average width of 3,910 nm, but as the applied voltage increases to 25 kV, the fiber diameter significantly widens to 9,520 nm. The reasons are evaporation rate and inertial impaction. The electrostatic force is associated with voltage. With increasing electric potential, in the short distance, the solution reaches the collection drum before the solvent fully evap-

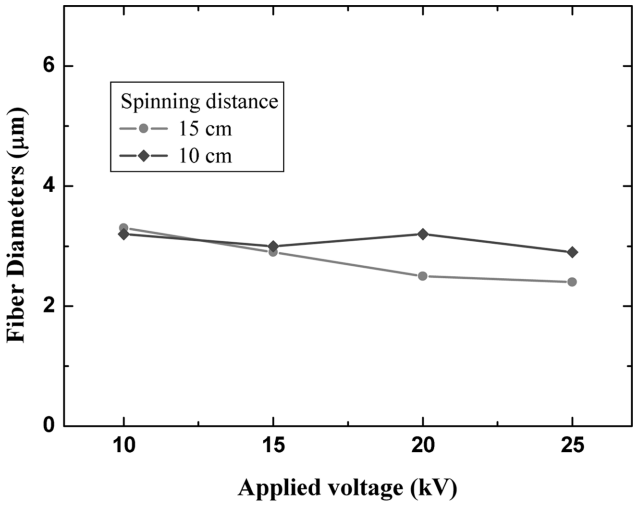


Fig. 6. The change of average fiber diameter as a function of applied voltage and spinning distance (solvent mixing ratio of THF by DMF=60 : 40, PS concentration=16 wt%).

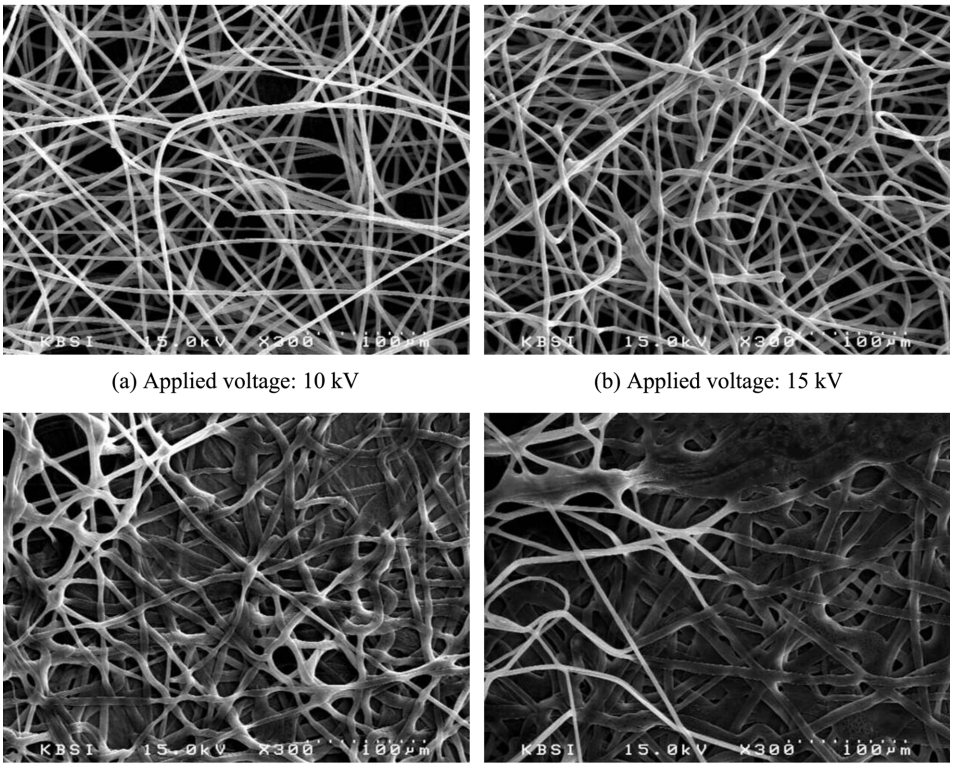
orates. At higher electric potential, the solution jet is faster. The faster jet has more big inertial force. In other words, when the wet electrospun fibers collide against the collector drum, cylindrical fibers change to flat fibers by impact. The results of SEM images at the spinning distance of 5 cm and 15 cm are shown in Fig. 7 and Fig. 8, respectively.

3. Effect of Solvent Mixing Ratio on Fibers Morphology

Fig. 9 and Fig. 10 show the change of fiber diameters as a function of solvent mixing ratios at the PS concentration of 16% and spinning distance of 15 cm. The fiber diameter steadily increases with increasing DMF and reaches a maximum at a THF: DMF ratio of 60 : 40. It then seems to level off with the subsequent increase of DMF. The solvent mixing ratios cause significant changes of the fiber size distribution, shape and overall morphology. The reason is that the solvent of DMF is more viscous solution than the one of THF. So the viscosity of PS solution slightly increases at higher DMF content with the range of 73-82 centipoise (cPs). Another reason is that the fiber diameter decreases due to the evaporation of the solvent. The evaporation rate of DMF is slower than THF. In the present electrospinning experiment with PS solution at higher ratios of THF to DMF solvent mixtures, more solvent evaporation is observed due to the higher vapor pressure of THF at the tip of the capillary. The higher ratio of THF in the polymer solution makes the fibers charging more within the unit mass. As a matter of fact, it makes the fiber thinner because of the stretch by the higher charge density on the surface. The diameters of fiber are almost similar after the mixing ratios of 60% THF and 40% DMF, since a non-solidified region is occupied more. Based on this phenomenon, the capacity of fiber stretch is stronger than the solidification of fiber itself.

CONCLUSIONS

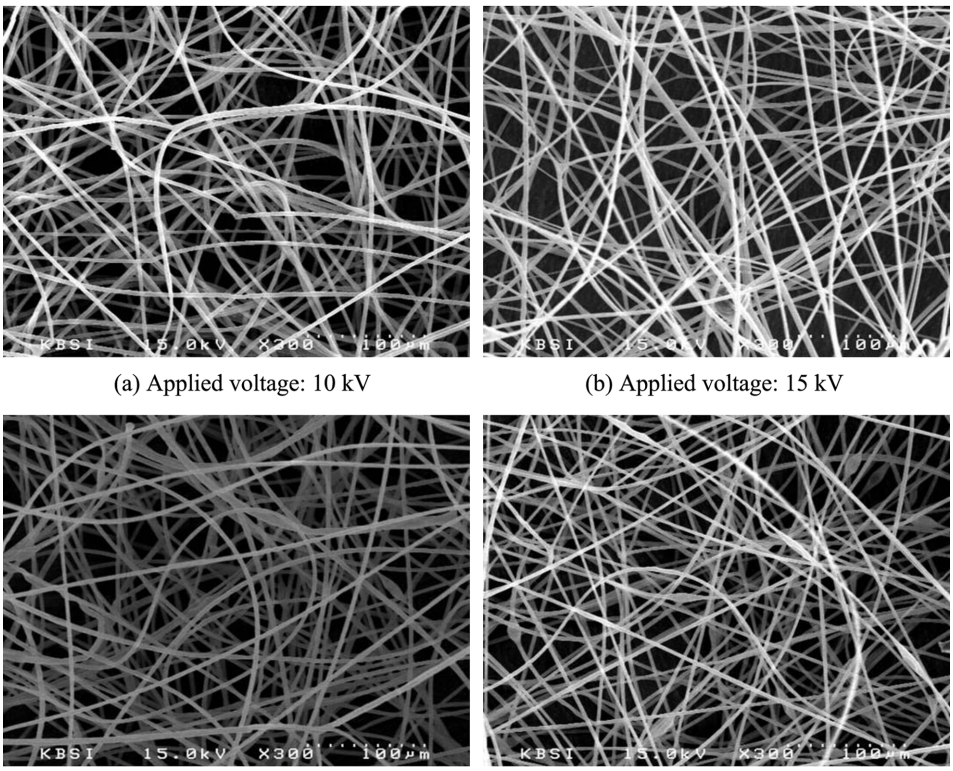
The morphology of electrospun polystyrene fiber is investigated by studying the influence of polymer concentrations, electric field, distance and solvent mixture ratios of THF and DMF. The solution



(a) Applied voltage: 10 kV (b) Applied voltage: 15 kV

(c) Applied voltage: 20 kV (d) Applied voltage: 25 kV

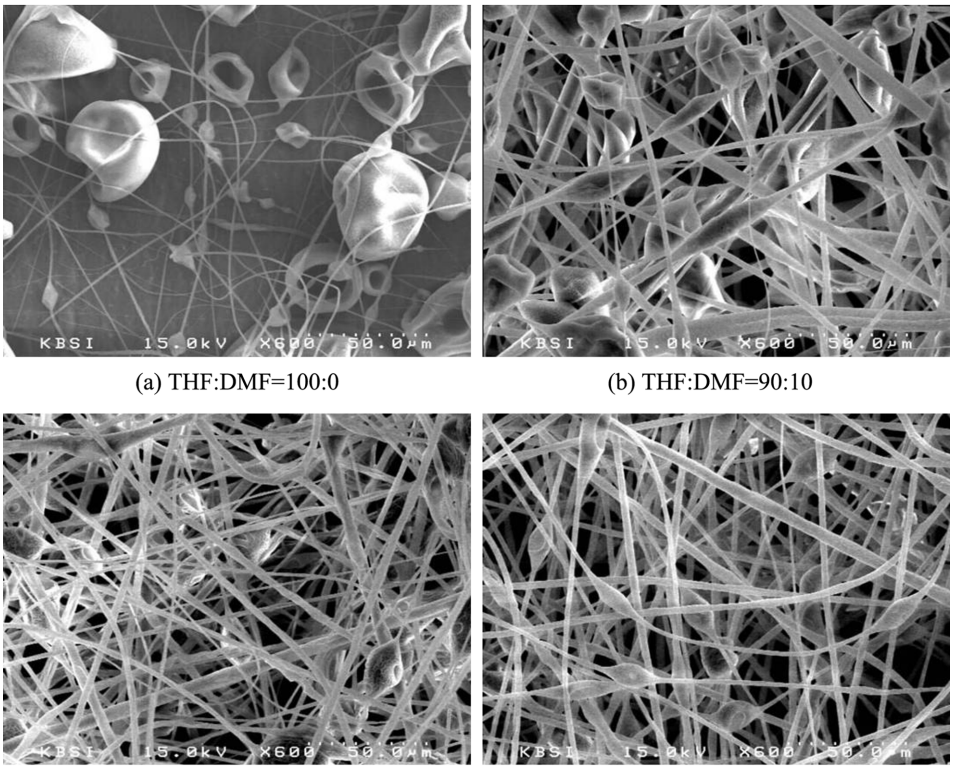
Fig. 7. Scanning electron micrographs for the change of morphology as a function of applied voltage at the spinning distance of 5 cm (solvent mixing ratio of THF by DMF=60 : 40, PS concentration=16 wt%).



(a) Applied voltage: 10 kV (b) Applied voltage: 15 kV

(c) Applied voltage: 20 kV (d) Applied voltage: 25 kV

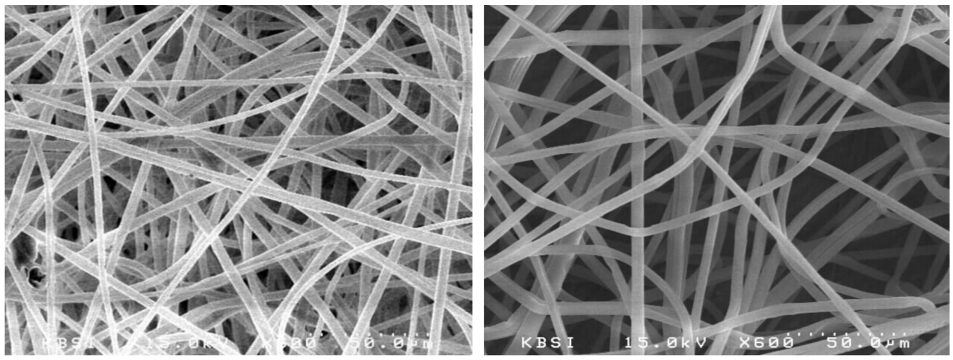
Fig. 8. Scanning electron micrographs for the change of morphology as a function of applied voltage at the spinning distance of 15 cm (solvent mixing ratio of THF by DMF=60 : 40, PS concentration=16 wt%).



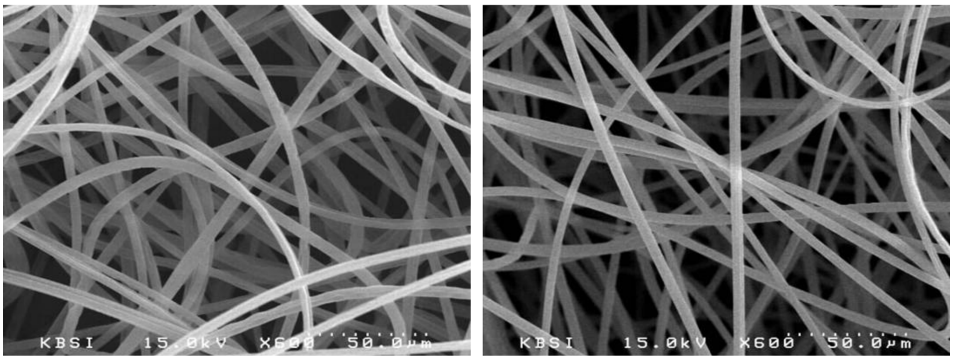
(a) THF:DMF=100:0 (b) THF:DMF=90:10

(c) THF:DMF=80:20 (d) THF:DMF=70:30

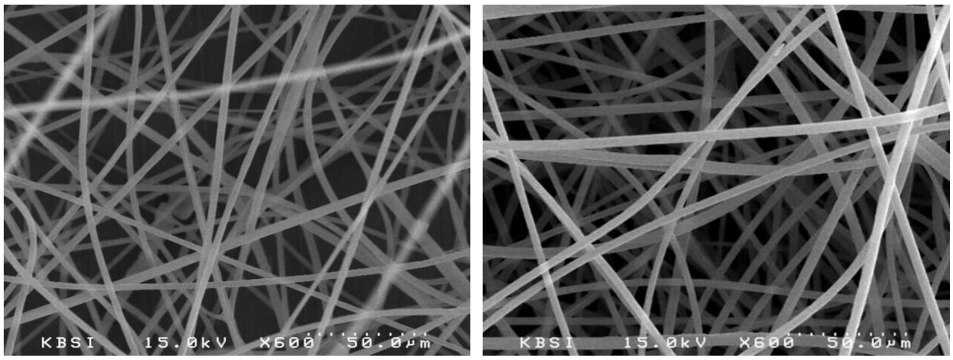
Fig. 9. Scanning electron micrographs for the change of morphology as a function of solvent mixing ratios (PS concentration=16 wt%, spinning distance=15 cm).



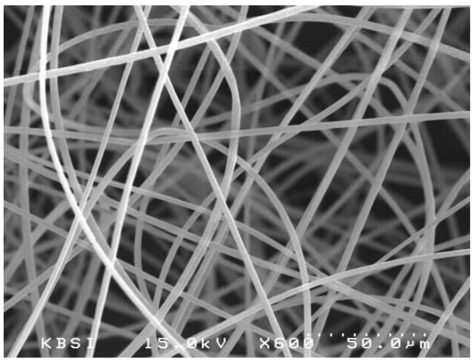
(e) THF:DMF=60:40 (f) THF:DMF=50:50



(g) THF:DMF=40:60 (h) THF:DMF=30:70



(i) THF:DMF=20:80 (j) THF:DMF=10:90



(k) THF:DMF=0:100

Fig. 9. Continued.

viscosity or the concentration of the polymer solution has shown a great influence on the fiber diameter as well as on bead. When the PS concentration is 7 wt%, electrospun fibers have an average diameter of 340 nm, but as the concentration of PS increases to 17 wt%, the fiber diameter gradually thickens to 3,610 nm. The higher concentration of the polymer solution makes thicker fibers with fewer

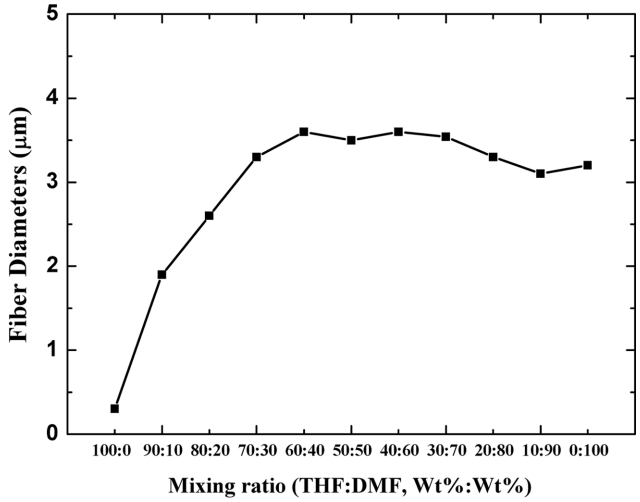


Fig. 10. The change of fiber diameters as a function of solvent mixing ratios (PS concentration=16 wt%, spinning distance= 15 cm).

beads and the evaporation of the solvents effects a splaying or splitting of the fibers during the electrospinning.

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