Korean J. Chem. Eng., **22**(5), 783-788 (2005)

Investigation of Pore Formation for Polystyrene Electrospun Fiber: Effect of Relative Humidity

Gil-Tae Kim, Jun-Seok Lee*, Jin-Hyouk Shin*, Young-Chull Ahn,†, Yu-Jin Hwang, Hee-Soo Shin, Jae-Keun Lee and Chang-Mo Sung*****

Department of Mechanical Engineering, **Reserch Institute of Mechanical Technology, Pusan National University, Busan 609-735, Korea
*Center for Advanced Materials, University of Massachusetts, Lowell, MA 01854. U.S.A.
***School of Nano Engineering, Inje University, Gimhae 621-749, Kyungnam, Korea
(*Received 4 February 2005 • accepted 9 June 2005*)

Abstract–Electrospinning method uses electrical force to produce a polymer nanofiber from a polymer solution. The surface morphology and the pore formation of e-spun fiber have been studied by many variables that are involved in different polymer concentrations and solvent mixing ratios. Another major factor affecting fiber morphology and size distribution is the relative humidity. The interaction between the relative humidity and the solvent evaporation affects the distribution of electric charge on the surface of the e-spun fiber. The higher the electric density, the thinner the fiber that can be produced in low humidity conditions. The relative humidity and solvent evaporation can create pores on the fiber surface. The pores can be formed under the condition of 30% relative humidity using 100% of THF solvent. The boundary of the pores has expanded and becomes formless due to the agglomeration of each pore, which can decrease the evaporating capacity.

Key words: Electrospinning, Nanofibers, Polystyrene, Relative Humidity

INTRODUCTION

In recent years, many researchers have studied and developed nanofibers that have large specific surface area and small pore size. The polymer nanofibers are being used, or finding uses, in filtration; biomedical applications include wound dressings as the structural elements in artificial organs, and reinforced composites [Reneker et al., 1996; Huang et al., 2003]. Although these special needs have stimulated recent studies and renewed interest in the system, quantitatively technical and scientific information regarding process and product characterization are not fully developed [Huang et al., 2003]. Commercial spinning processes depend on the pressure driven extrusion of a viscous polymer and produce fibers which are typically in the range of 5 to 500 μm in diameters [Deitzwl et al., 2001]. On the recent electrospinning researches, nano-scale fibers can be easily produced for many different applications and research fields [Deitzwl et al., 2001; Shawon 2002].

Generally, the suspended drop starts to stretch and to form a Taylor cone in the circumstance of an electric field applied to the solution. The distortion of this solution drop is caused by a balance of the repulsive forces induced on the drop due to the charge distribution and the surface tension of the liquid. When the voltage reaches a critical value, the electric force overcomes the surface tension of the deformed drop in the suspended polymer solution formed at the tip of the syringe, and then a jet can be produced. After the jet travels through the air, polymer fibers are produced by the evaporation of the solvent and are collected at an electrically grounded target. The surface morphology of e-spun fiber is affected by many parameters related to the polymer concentration, the applied voltage, the spinning distance, the air friction, the gravity, the temperature and the ambient parameter [Lee et al., 1995; Deitzwl et al., 2001; Jung et al., 1999]. This study presents the effect of polymer concentration, solvent mixing ratio and relative humidity on the microstructures of the e-spun polystyrene (PS) fiber.

†To whom correspondence should be addressed.
E-mail: ycahn@pusan.ac.kr

EXPERIMENTAL

PS solution is prepared by PS pellets (Aldrich, M.W.: 170,000 g/mol) dissolved with tetrahydrofuran (THF) and dimethylformamide (DMF) (Junsei Co.) in the ultrasonicator. The concentration of the

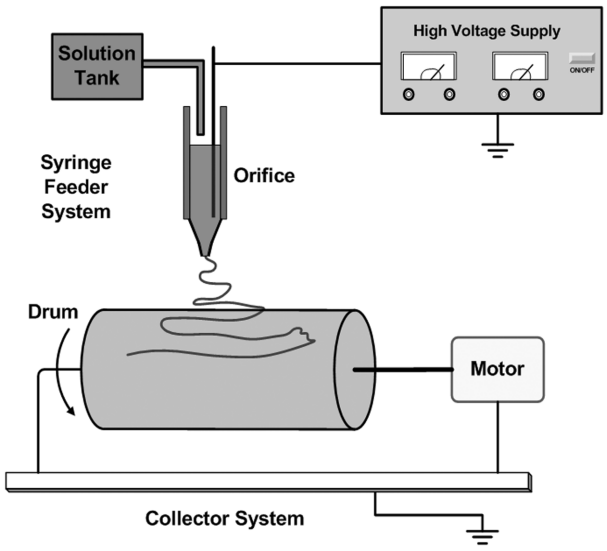


Fig. 1. Schematic diagram of the electrospinning setup.

PS solution is used in the range of 7 to 16 wt% and the solvent mixing ratio of THF : DMF is changed from 100 : 0 to 0 : 100.

Fig. 1 shows the schematic diagram of the electrospinning setup. It consists of three components: syringe feeder, high voltage supply, and collector. The 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 polymeric solution by attaching the lead from the variable high voltage power supply (Chung-pa EMT Inc.). All experiments are conducted with fixed voltage at 20 kV. It is directly connected to the copper wire located inside of the solution. A drum collector covered with aluminum foil is placed in 5-15 cm vertical from the tip of the syringe as a grounded collector. The relative humidity is changed with four steps from 10 to 70%. All experiments are performed at the constant temperature-humidity chamber which can control both the temperature and the humidity automatically. The range of temperature is from 15 to 45 °C and the relative humidity from 10 to 90%.

The viscosity is measured by a Brookfield viscometer (Brookfield, LVDP 1+). The surface morphology of the e-spun fiber is observed with a scanning electron microscope (HITACHI 4200, AMRAY 1400) and an atomic force microscope (XE-100, PSIA Corp.). The sample is prepared on the mica for the atomic force microscopy analysis. The diameter of the e-spun fiber, the size and the depth of the pore are measured by an image processor (GAIA Blue, PSAI XEI) based on SEM and AFM images.

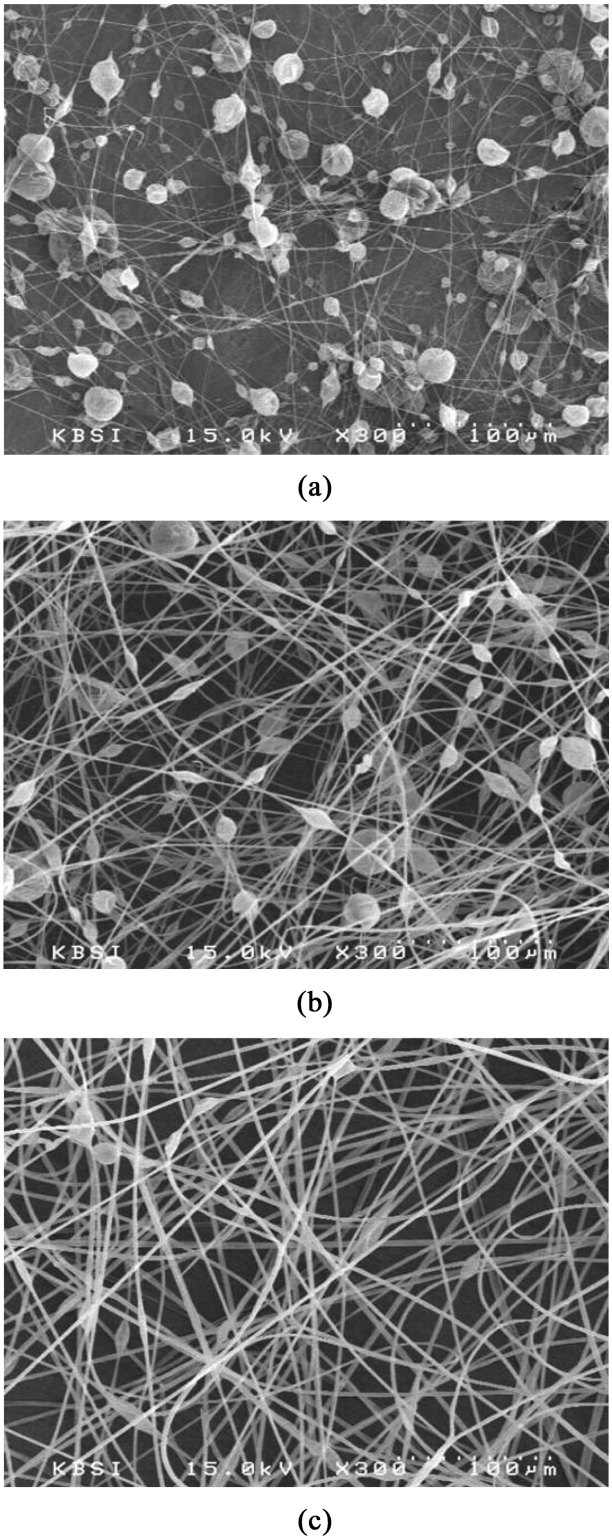


Fig. 2. SEM images of the PS e-spun fibers for the surface morphology as a function of polystyrene concentration of (a) 7 wt%, (b) 11 wt%, and (c) 16 wt%.

RESULTS AND DISCUSSIONS

1. Polymer Concentration

The e-spun fibers are not produced below a PS concentration of 6 wt%. The low viscous polymer solution breaks into droplets due to the surface tension of deformed drops in the suspended polymer solution at the end of the spinneret. The experiments of several PS solutions are conducted at the concentration of 7, 11 and 16 wt%. Fig. 2 shows SEM images of the PS e-spun fibers for the surface morphology as a function of PS concentration. At 7 wt% concentration, e-spun fibers have an average diameter of 340 nm (Fig. 2a). As the concentration of polystyrene increases to 16 wt%, the fiber diameter gradually thickens to 3,610 nm (Fig. 2c). The higher concentration of the polymer solution forms the thicker fibers. The reason is that the polymer viscosity increases with increasing the con-

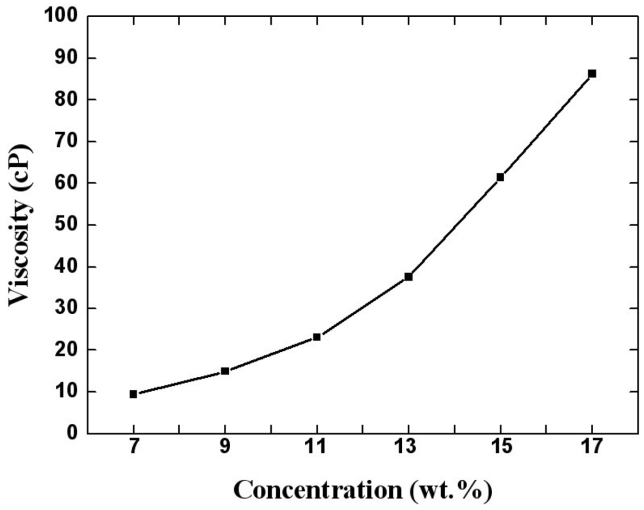


Fig. 3. The viscosity changes as a function of polystyrene concentration (Solvent: THF : DMF=60 : 40).

centration of polymer solution. The high polymer viscosity is preventing the stretching of fibers.

Fig. 3 shows the viscosity changes as a function of the polymer concentration with THF : DMF=60 : 40 measured by the viscometer. The polymer concentration shows an important factor on the viscosity representing the viscoelastic behavior of polymer and the chain entanglement in the polymer solution [Buchko et al., 1999]. A polymer solution with higher viscosity is harder to stretch than the lower viscosity. Such polymeric properties affect the stretch of fiber related to the diameter of fibers.

Polymer concentration has an effect on the bead formation [Fong et al., 1999]. Fibers produced from lower concentrated solution exhibit higher bead density because e-spun fibers are difficult to dry before they reach the collection drum [Kim et al., 2005]. When the solidification process is occurring on the surface of the collection drum, the surface tension makes a bead spherical shape. That is, the surface tension of the solution becomes the dominant influence over viscosity. As the viscosity increases in the solution, the surface tension becomes dominated by viscosity and results in a smaller number of beads [Kim et al., 2003].

2. Solvent Mixing Ratio

Fig. 4 shows SEM images as a function of solvent mixing ratio. When the solvent mixing ratio of THF : DMF is 100 : 0, e-spun fibers have an average diameter of 310 nm (Fig. 4a); as the DMF ratio in the solvent increases to 40%, the fiber diameter gradually thickens to 3,300 nm (Fig. 4d). The fiber diameter steadily increases with increasing DMF concentration and reaches a maximum at a THF : DMF ratio of 60 : 40. It then seems to level off with the sub-

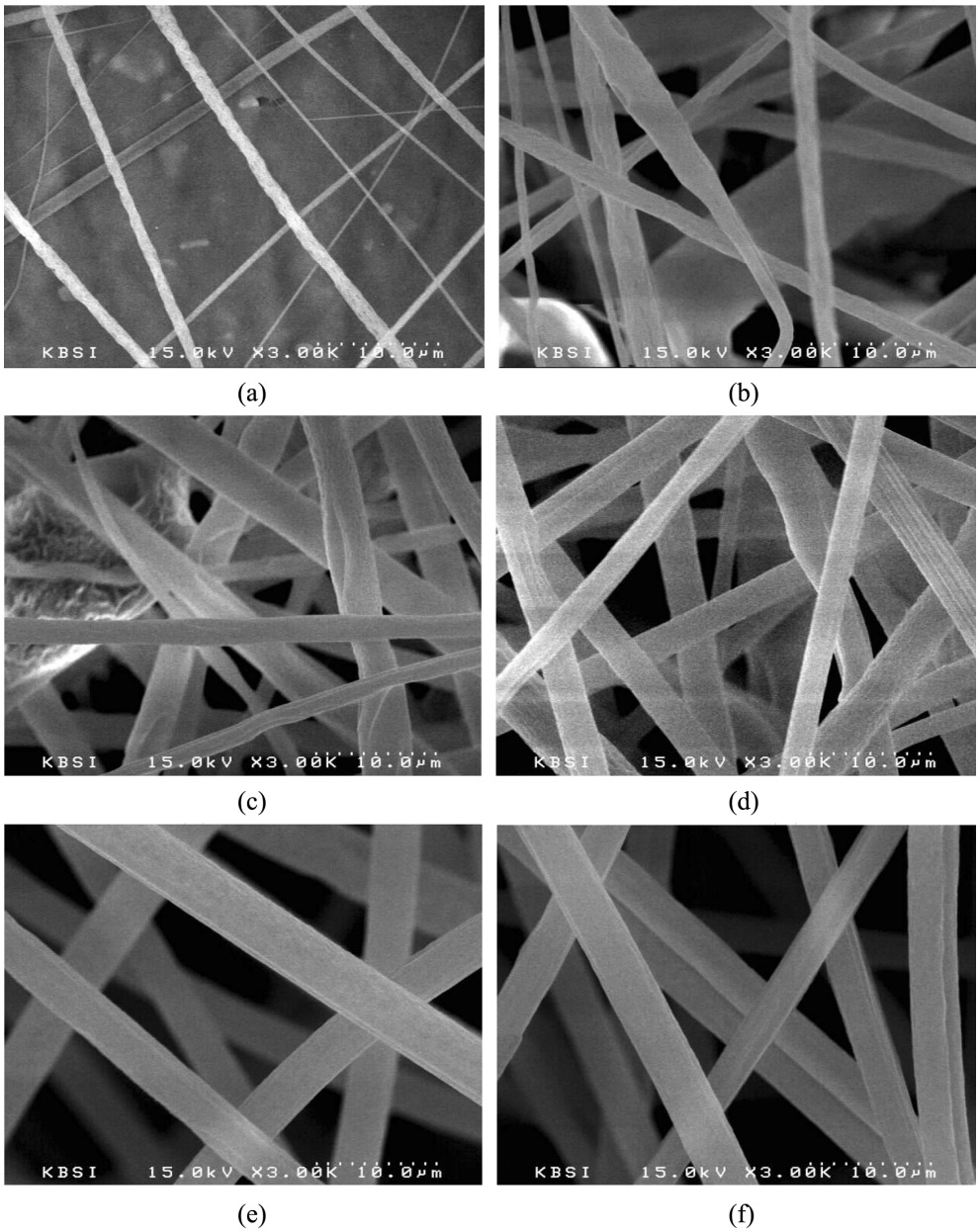


Fig. 4. SEM images of the PS e-spun fibers as a function of solvent mixing ratio at polystyrene concentration 16 wt% and relative humidity 50%; THF : DMF (a) 100% : 0%, (b) 90% : 10%, (c) 80% : 20% and (d) 70% : 30% (e) 60% : 40% (f) 80% : 20%.

sequent increase of DMF concentration. The solvent mixing ratios cause significant changes in the fiber size distribution, shape and overall morphology due to the evaporation of the solvent and the variation of the viscosity. From a concentration of 100 : 0 to 0 : 100 (DMF : THF), the fiber diameter decreases due to the evaporation of the solvent that leads to an increase in the forces from the surface charge density [Shawon, 2002]. 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 as it begins to evaporate from the tip of the

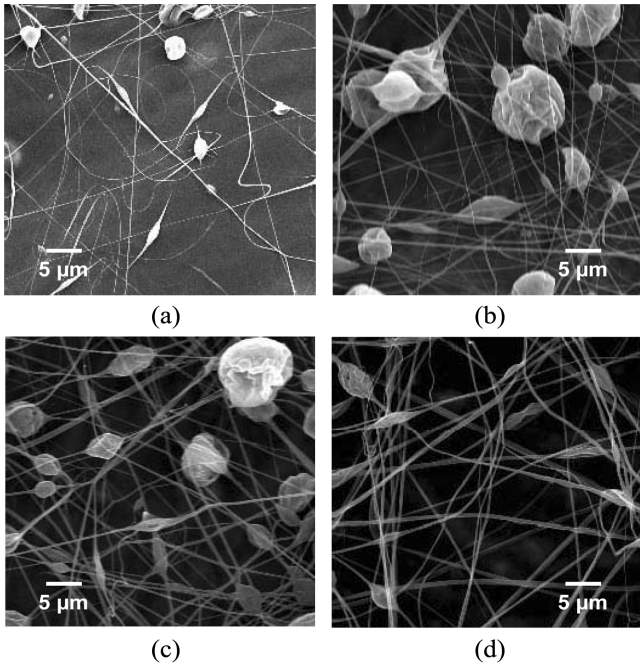


Fig. 5. SEM images of the PS e-spun fibers as a function of relative humidity at 7 wt% polystyrene concentration and solvent mixing ratio of THF : DMF=60 : 40; relative humidity of (a) 10%, (b) 30%, (c) 50% and (d) 70%.

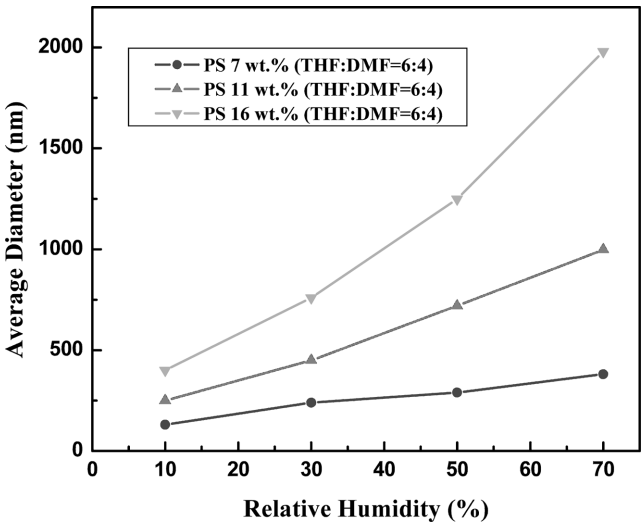


Fig. 6. Average diameters of the PS e-spun fibers as a function of relative humidity at the constant solvent mixing ratio.

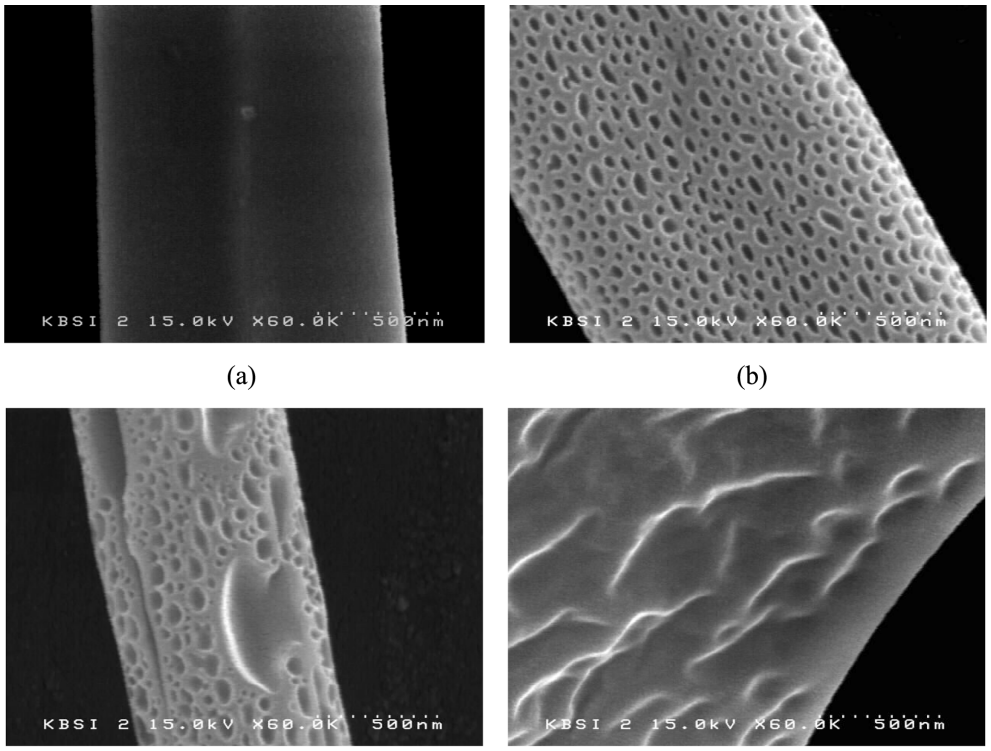


Fig. 7. SEM images of the PS e-spun fibers as a function of relative humidity at polymer concentration 16 wt%, solvent mixing ratio of THF : DMF=100 : 0; the relative humidity of (a) 10%, (b) 30%, (c) 50% and (d) 70%.

syringe. On the other hand, DMF has a lower vapor pressure that is slower than THF. Therefore, at higher ratios of THF to DMF, the solvent evaporation rate from the fiber surface increases due to the large volume of THF in the polymer solution. In terms of applying the voltage on the polymer solution during the electrospinning, the electric charges are distributed on the surface of the fibers. After the solvent is evaporated from the fiber, the charge density per unit mass increases so that it makes the fibers stretch more. According to these phenomena, a higher THF concentration in the solution produces a thinner polymeric fiber. After a mixing ratio of THF : DMF at 60 : 40, a possible saturation point, the fiber diameters are almost the same. Another minor effect to the fiber morphology would be the viscosity of polymer solution. According to the measurement of viscosity, the PS solution dissolved by 100% DMF is more viscous than one dissolved by 100% THF. So the viscosity of PS solution slightly increases with the higher DMF content at the range of 73-82 cP. The higher viscosity of DMF solution creates thicker fiber than the THF solution.

3. Relative Humidity

The humidity and the temperature are fixed at 10-70% and 20 °C by using a constant temperature-humidity chamber. The relative humidity has a great influence on the fiber diameter in terms of the analysis of SEM given in Fig. 5, and the measurement of fiber diameter as given in Fig. 6. When the relative humidity is 10%, the e-spun fibers have an average diameter of 130 nm (Fig. 5a). As the relative humidity increases to 70%, the fiber diameter gradually thickens to 380 nm (Fig. 5d). The lower relative humidity makes thinner fiber because the higher electrostatic charge on the fiber surface has an opportunity to stretch the fibers more. Furthermore, the surface charge of the e-spun fiber is easily discharged at the higher humidity level because the electric charges are captured by the surrounding water vapor that has higher conductivity than air. The greater discharge on the surface of the polymer solution reduces the repulsive force. Thus, it results in producing thicker fibers in the travel of the fibers towards the target. In other words, a system under conditions with more moisture can produce thicker fiber.

When the polymer is dissolved by THF, pores are produced on the surface of e-spun fiber. Fig. 7 shows the SEM images on the surface of e-spun fiber. At 10% relative humidity, pores are not formed on the surface. However, as the relative humidity increases to 30%, many pores are formed on the fiber surface with 48 nm of average diameter and 25 nm of average depth as shown in Fig. 8. As the relative humidity increases, the pore size increases. When the solvent evaporates from the fiber surface to the air, the vaporization for the solvent takes a latent heat of the fiber surface and the surrounding air. When the temperature of both the surface and the atmosphere decreases to the dew point, the relative humidity is increased to 100% and the vapor is saturated. Therefore, fast solvent evaporation at higher relative humidity has more chance to condense the moisture on the surface of e-spun fiber. However, lower relative humidity cannot reach to the dew point of water so that there is no pore distribution on the surface. As the relative humidity increases, bigger water droplets can be formed.

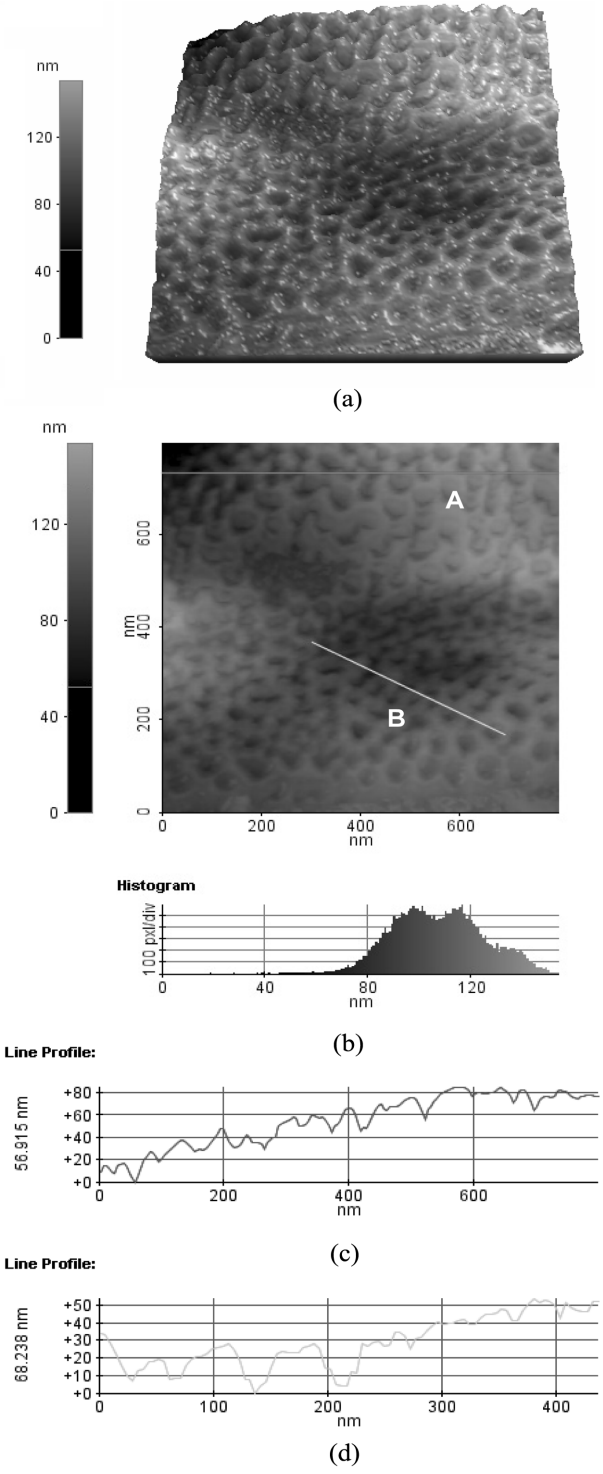


Fig. 8. AFM images for the pores of e-spun fiber on the surface at polymer concentration 16 wt%, solvent mixing ratio of THF : DMF=100 : 0, and relative humidity of 30%: (a) 3 dimensional topography (b) Measuring area and histogram, (c) line profile of location A, and (d) line profile of location B.

CONCLUSIONS

This study investigates the formation of pores on e-spun fiber with respect to the effect of humidity on the surface morphology. The experiments with controlling both polymer concentration and solvent mixing ratio are performed in order to find out the optimum

condition of electrospinning system. According to these experiments, the optimum experimental condition for the uniform e-spun fiber without beads is 16 wt% polystyrene concentration at 2 kV/cm and the fiber with pores is THF(100)/DMF(0) ratio of solvent.

The formation of pores of this experiment is dependent on the humidity. When the THF is evaporated from the surface of e-spun fiber, the latent heat is removed from the e-spun fiber surface. At higher relative humidity, the air surrounding the surface of the e-spun fiber easily reaches the dew point due to the larger amount of moisture in the air.

Pores can be produced at the condition of over 30% relative humidity. The higher relative humidity ratio can produce larger pores. Typical uniform pore sizes are around 46 nm of diameter and 25 nm in depth at the 30% relative humidity. At 70% relative humidity, the pores become formless by agglomeration of expanded pores.

ACKNOWLEDGEMENTS

This study is supported financially by Korea Institute of Science and Technology Evaluation and Planning, and technically by Korea Basic Science Institute. The authors gratefully acknowledge the financial support.

REFERENCES

Buchko, C. J., Chen, L. C., Shen, Y. and Martin, D. C., "Processing and Microstructural Characterization of Porous Biocompatible Protein Polymer Thin Films," *Polymer*, **40**, 7397 (1999).

Deitzwl, J. M., Kleinmeyer, J. D., Hirvoner, J. K. and BeckTan, N. C., "Controlled Deposition of Electrospun Poly(ethylene oxide) Fibers," *Polymer*, **42**, 8163 (2001).

Deitzwl, J. M., Kleinmeyer, J. D., Harris, D. and BeckTan, N. C., "The Effect of Processing Variables on the Morphology of Electrospun Nanofibers and Textiles," *Polymer*, **42**, 261 (2001).

Fong, H., Chun, I. and Reneker, D. H., "Beaded Nanofibers Formed during Electrospinning," *Polymer*, **40**, 4585 (1999).

Huang, Z. M., Zhang, Y. Z., Kotakic, M. and Ramakrishnab, S., "A Review on Polymer Nanofibers by Electrospinning and Their Applications in Nanocomposites," *Composites Science and Technology*, **63**, 2223 (2003).

Jung, H. W. and Hyun, J. C., "Stability of Isothermal Spinning of Viscoelastic Fluids," *Korean J. Chem. Eng.*, **16**, 325 (1999).

Kim, G. T., Ahn, Y. C., Lee, J. K., Kattamuri, N. and Sung, C. M., "Fabrication of Polymer Nanofibers using Electrospinning," *J. Ilass-Korea*, **8**, 31 (2003).

Kim, G. T., Hwang, Y. J., Ahn, Y. C., Shin, H. S., Lee, J. K. and Sung, C. M., "The Morphology of Electrospun Polystyrene Fibers," *Korean J. Chem. Eng.*, **22**, 147 (2005).

Lee, S., Kim, B. M. and Hyun, J. C., "Dichotomous Behavior of Polymer Melts in Isothermal Melt Spinning," *Korean J. Chem. Eng.*, **12**, 345 (1995).

Reneker, D. H. and Chun, I., "Nanometer Diameter Fibers of Polymer, Produced by Electrospinning," *Nanotechnology*, **7**, 216 (1996).

Shawon, J., *Electrospinning of Polycarbonate Fibers with Solvent Mixtures THF and DMF*, M.S. Thesis, University of Massachusetts, Lowell, U.S.A. (2002).