

## Notes

### Unique Surface Morphology of Electrospun Polystyrene Fibers from a *N,N*-Dimethylformamide Solution

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#### Introduction

Electrospinning<sup>1-3</sup> is a well known technique to fabricate organic<sup>4-8</sup> and/or organic/inorganic hybrid fibers<sup>9,10</sup> with a broad range of fiber diameters ranging from a few nm to several  $\mu\text{m}$  by applying a high electric field to polymer solutions or melts. When an electrical force is applied to a polymer droplet, which is formed at the end of a spinneret, the surface tension force is overcome and a charged jet is ejected.<sup>2,3</sup> The jet then is further stretched via a whipping process and is eventually deposited on a collector.<sup>3</sup> The final morphology of the electrospun fiber is determined by the viscoelasticity and the polymer concentration as well as by the processing parameters including the applied voltage and the flow rate of solution or melt.<sup>2-23</sup> In particular, the solvent properties, such as the boiling point (b.p.), conductivity, and surface tension, are key factors that determine the fiber morphology in the electrospinning of a polymer solution.<sup>11-23</sup> Polystyrene has been used as a model polymer to investigate the solvent effect on the morphology of an electrospun fiber owing to its transparency and broad solubility window in common organic solvents. Jarusuwannapoom<sup>11</sup> and Wannatong<sup>12</sup> investigated the solvent effect on the electrospinning of polystyrene in various solvents and concluded that the morphology of an electrospun fiber be dependent on the b.p. and the dipole moment value of the solvent used. Meanwhile, an irregular fiber morphology was observed in an electrospun polystyrene fiber from a highly viscous solution in *N,N*-dimethylformamide (DMF) or from a solution in a mixed (or volatile) solvent.<sup>13-17</sup> For example, Koombhongse

*et al.*<sup>13</sup> reported the formation of flat fibers with a wrinkled surface by a jet collapse phenomenon during the electrospinning of a viscous 30 wt% polystyrene solution in DMF. Moreover, interesting ribbon-like electrospun polystyrene fibers were observed in a mixed solvent containing DMF and toluene. According to Lee *et al.*,<sup>14</sup> the number of irregular beads in electrospun polystyrene fibers in a tetrahydrofuran (THF)/DMF mixed solvent increased with increasing DMF concentration. In the case of electrospinning of polystyrene in a volatile solvent, a porous fiber surface was obtained when the volatile THF (b.p.; 66 °C, vapor pressure; 129 mmHg at 20 °C) was used as the solvent.<sup>15,16</sup> The pores on the surface of the fiber were produced by the rapid evaporation of THF molecules, and the shape and size of the pores were determined by the evaporation rate of the solvent and the relative humidity during electrospinning. Wendorff *et al.*<sup>17,23</sup> reported similar result in the electrospinning of other polymers in a volatile solvent such as dichloromethane (b.p.; 40 °C, vapor pressure; 351.6 mmHg at 20 °C), which yielded polymer fibers with regular pores or pit structure in the 100 nm range. They claimed that the structure formation should be apparently controlled by a rapid phase separation induced by the evaporation of the solvent and a subsequent rapid solidification.

Until now, most studies on the solvent effect on the morphology of electrospun fibers have focused on volatile solvents, e.g. THF, or its mixture. Therefore, the control of the polymer concentration in volatile solvents for electrospinning was limited due to the rapid evaporation of the solvent. In this study, DMF (b.p.; 153 °C, vapor pressure; 2.6 mmHg at 20 °C), which is a non-volatile solvent, was selected to dissolve the polystyrene (190,000 g/mol) and the concentration of the polystyrene solution (~40 wt%) was maximized to retard the evaporation of the solvent in an electrospinnable condition. Unlike the porous morphology observed on the surface of the fibers electrospun from the polystyrene solution in THF,<sup>15,16</sup> an intriguing surface morphology of electrospun polystyrene fibers with numerous protuberances was obtained from the highly viscous solution of polystyrene in DMF.

#### Experimental

**Materials.** Polystyrene ( $M_w$ ; 190,000) and DMF (HPLC grade) were purchased from Scientific Polymer Products and Aldrich, respectively, and was used as received. Different polystyrene concentrations in DMF (20, 25, 30, 35 and 40 wt%) were prepared in a warm water bath (~40 °C) with 1.5-2 h of mild stirring.

**Electrospinning.** The electrospinning apparatus was composed of several components; a high voltage supplier

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(Gamma High Voltage Research, E3 30P-5W, USA), a capillary tube with a stainless steel needle (16 gage), a syringe pump (Hardvard Apparatus, USA), and a stainless steel collecting plate (diameter  $\approx 10$  cm), as described elsewhere.<sup>7</sup> Electrospinning was carried out using a 10 mL syringe with a 1.2 mm diameter spinneret at an applied voltage difference of 16.0 and 19.5 kV over a distance of 21 and 30 cm ( $E=0.76$  and  $0.65$  kV/cm), respectively. The syringe pump was set to deliver the solution at a flow rate of 50 to 150  $\mu\text{L}/\text{min}$ . All the spinning processes were carried out at ambient conditions (relative humidity  $< 30\%$ ).

**Characterization.** The shear viscosity of the polystyrene solution in DMF was measured at room temperature via a rotational rheometer (MCR-300, Paar-Physica, Germany) equipped with a cone/plate-type measuring unit. The fiber morphology and its surface structure were observed by field emission scanning electron microscopy (FESEM, S-4300, Hitachi, Japan). The samples were platinum coated for 45 s to minimize the charging effect. The acceleration voltage and the working distance for each image were 15 kV and 6 mm, respectively. Optical microscopy (OM) (BX51, Olympus, Japan) was used to examine the internal structure of the electrospun fibers as well as the fiber diameters. The fiber diameters were measured using the electronic OM and SEM images using the image analysis software. The cross-sections of the fibers were observed by transmission electron microscopy (TEM) (CM 200, Philips, Netherlands). The fibers were placed in an epoxy resin and hardened in an oven at  $60^\circ\text{C}$  for 2 days. A microtomed slice of a fiber embedded in an epoxy resin was placed on a copper grid and observed by TEM.

## Results and Discussion

Table I summarizes the zero-shear viscosity of the polystyrene solution in DMF as a function of the polystyrene concentration. As the polystyrene concentration was increased from 20 to 40 wt%, the zero shear viscosity of the polystyrene solution increased approximately 40 times from 136 to

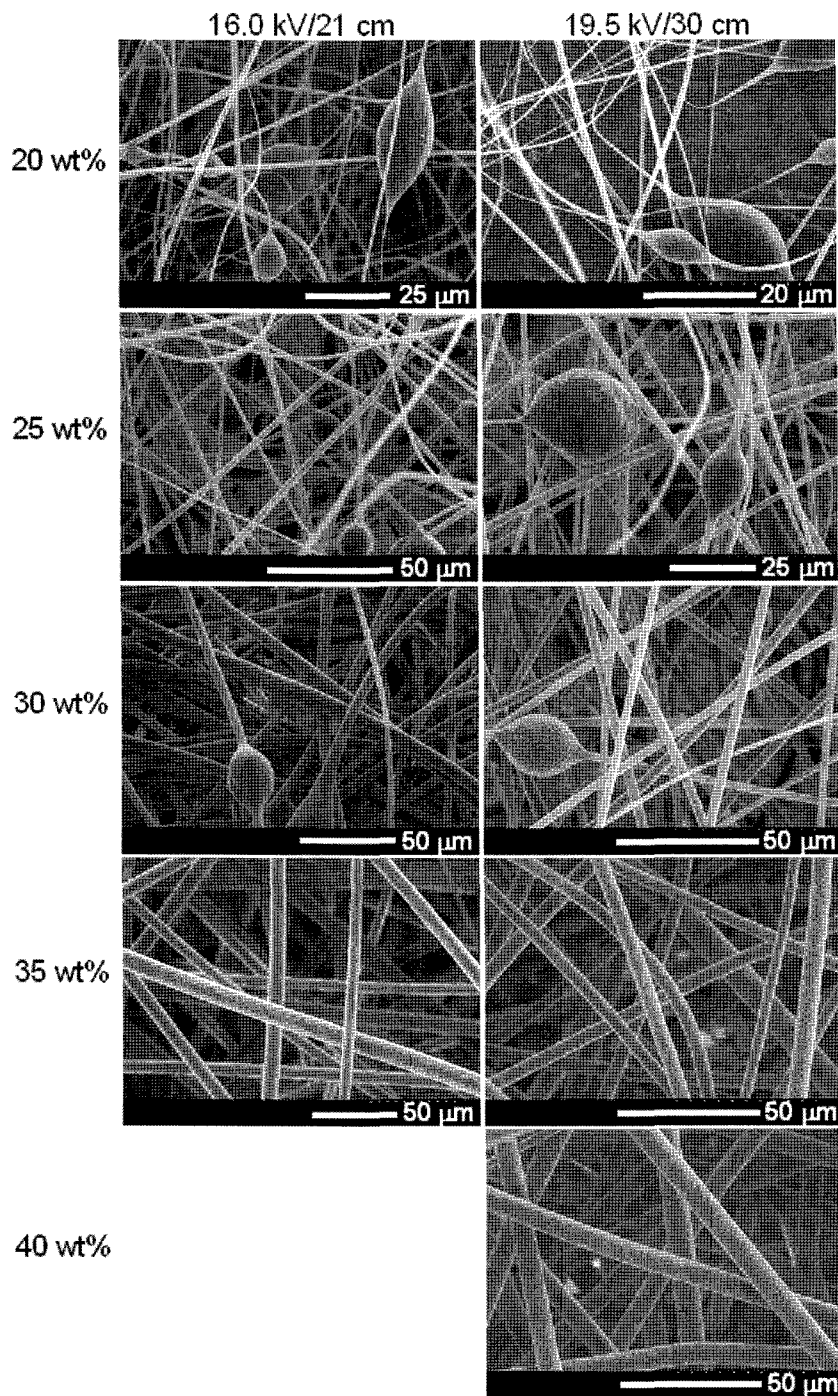
5,148 cP. Although the zero-shear viscosity of the 40 wt% polystyrene solution was much higher than that of the a polymer solution for electrospinning, the solution was still successfully electrospun due to the high b.p. and dipole moment of the DMF.<sup>11</sup>

The surface structure of the electrospun polystyrene fibers with different polystyrene concentrations were examined by optical microscopy. Here, both the applied voltage and the distance between the spinneret and collector were 16.0 kV and 21 cm ( $E=0.76$  kV/cm), respectively, for each solution. When the polystyrene concentration was less than 30 wt% in DMF, beaded string structures along with fibers were obtained. The beaded string structure disappeared at above 30 wt%. However, the diameter of the electrospun polystyrene fiber gradually increased up to  $9.7\pm 1.9$   $\mu\text{m}$  as a result of the insufficient stretching of the highly viscous polystyrene jet with increasing polystyrene concentration. Table I and Figure 1 summarizes the changes in the fiber diameter and morphology as a function of the polystyrene concentration. The distance between the spinneret and the collector with the applied voltage was altered to examine the stretching effect on the fiber morphology. The more stretched fiber has a relatively smaller fiber diameter at the same concentration. The polystyrene fibers electrospun from 30 and 35 wt% polystyrene solutions (16.0 kV and 21 cm,  $E=0.76$  kV/cm) are shown in Figures 2(a) and (b). It is very interesting that there are protuberances on the fiber, which were oriented to the direction of the fiber stretching. In particular, when the distance between the spinneret and the collector was longer (30 cm), the density of these surface protuberances increased at the same concentration, as shown in Figures 2(b) and (c). This suggests that the inherent low vapor pressure of DMF and the large diameter of the fiber retarded the evaporation of DMF during spinning, and the residual solvent entrapped inside the fiber caused an extrusive force, which yielded the unique surface structure. This peculiar morphology on the electrospun polystyrene fiber was totally different from those reported by Megelski<sup>15</sup> and Casper.<sup>16</sup> They obtained porous electrospun polystyrene

**Table I. Zero-Shear Viscosities of the Polystyrene Solution in DMF and the Average Fiber Diameters of the Electrospun Polystyrene Fibers (N; 100, average $\pm$ standard deviation)**

Polystyrene Solution in DMF	Zero-Shear Viscosity (cP)	Fiber Diameters ( $\mu\text{m}$ )		Morphology of Fibers
		16.0 kV/21 cm <sup>a</sup>	19.5 kV/30 cm <sup>a</sup>	
20 wt%	136	1.1 $\pm$ 0.2	0.9 $\pm$ 0.3	Beaded string
25 wt%	379	2.4 $\pm$ 0.6	1.8 $\pm$ 0.5	Beaded string
30 wt%	895	4.8 $\pm$ 1.2	3.3 $\pm$ 0.6	Mostly fibers with many small protuberances
35 wt%	2,066	9.7 $\pm$ 1.9	6.1 $\pm$ 1.7	Fibers with many small protuberances
40 wt%	5,148	-	9.8 $\pm$ 1.7	Fibers with many small protuberances

<sup>a</sup>Strength of the electric field (Applied voltage/Distance between the spinneret tip and the collector).

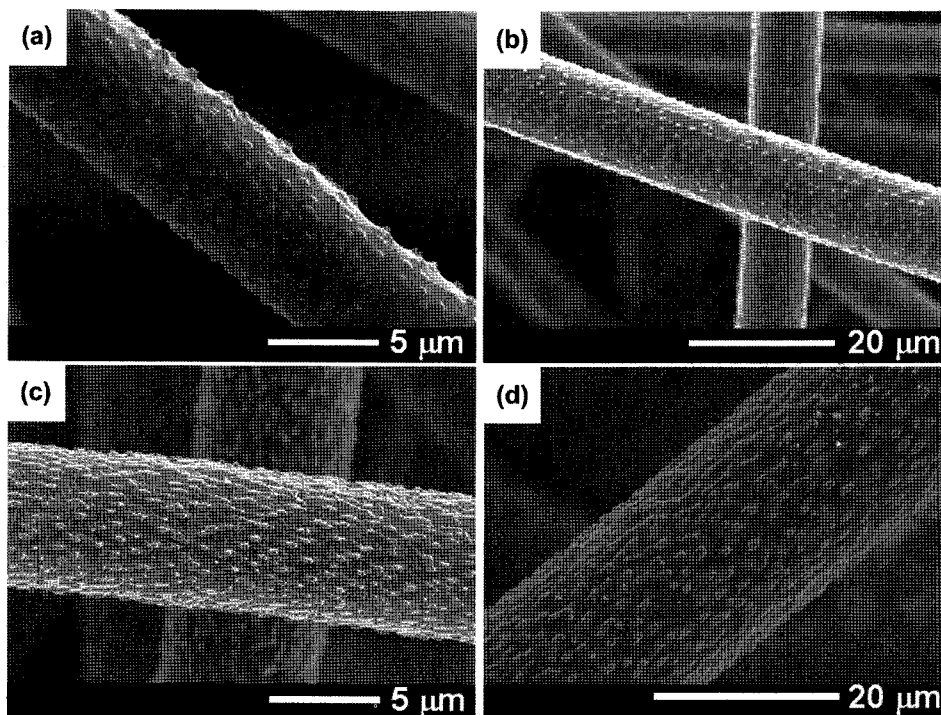


**Figure 1.** FESEM images of the polystyrene fibers electrospun from DMF at different polystyrene concentrations, and different applied voltages and collection distances.

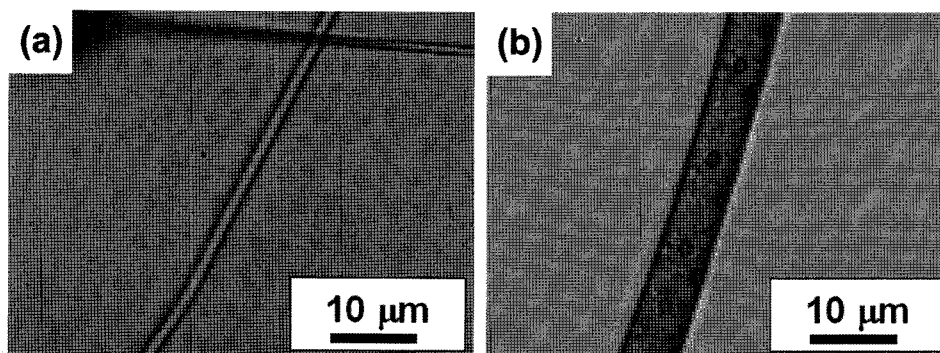
fibers by accelerating the solvent evaporation using volatile THF as the solvent.

The solvent entrapment inside the fibers was observed by optical microscopy in order to confirm our hypothesis. As shown in Figure 3, submicron-size bubbles were observed inside the single fiber electrospun from 30 wt% polystyrene

solution. However, they were not present in the lower concentration (20 wt%). Furthermore, TEM of the cross-section of the polystyrene fiber electrospun from the 30 wt% polystyrene solution clearly shows several solvent bubbles of various diameters (Figure 4).



**Figure 2.** FESEM images of the polystyrene fibers electrospun from DMF at different polystyrene concentrations: (a) 30 wt% and (b) 35 wt% (16.0 kV/21 cm); (c) 35 wt% and (d) 40 wt% (19.5 kV/30 cm).



**Figure 3.** Optical microscopy images (1,500 magnification) of the electrospun polystyrene fibers from (a) 20 wt% and (b) 30 wt% DMF solutions (16.0 kV/21 cm).

## Conclusions

Highly concentrated polystyrene (190,000 g/mol) solutions (30 to 40 wt%) in DMF were electrospun, and the surface morphology of the electrospun polystyrene fibers was investigated. Unlike the porous morphology observed on the surface of the PS fibers electrospun from a volatile solvent such as THF, numerous tiny protuberances were observed on the surface of the fibers electrospun from a non-volatile solvent, DMF. This unique surface morphology was formed due to the residual DMF solvent entrapped inside the electrospun polystyrene fiber. By forming fibers with large

diameters ( $3.3 \pm 0.6 \sim 9.8 \pm 1.7 \mu\text{m}$ ) from highly viscous polystyrene solutions, DMF could not evaporate completely from inside the fibers during electrospinning. Therefore, the extrusive force of the residual solvent inside the fiber would induce a unique surface morphology, which could increase the surface area of the electrospun fibers. The bubbles of residual solvent inside the electrospun fiber were observed by both optical microscopy and TEM.

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**Figure 4.** TEM image of a cross-section of a polystyrene fiber electrospun from the 30 wt% DMF solution (16.0 kV/21 cm).

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