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The effects of solution properties and polyelectrolyte on electrospinning of ultrafine poly(ethylene oxide) fibers

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Abstract

The effects of solution properties and polyelectrolyte on the electrospinning of poly(ethylene oxide) (PEO) solutions were investigated. Ultrafine PEO fibers without beads were electrospun from 3, 4, 7 and 7 wt% PEO solutions in chloroform, ethanol, (dimethylformamide) DMF and water, respectively. At these concentrations, the values of $[\eta]C$ were ~10 for all solutions. The average diameters of PEO fibers were ranged from 0.36 to 1.96 μm. The higher the dielectric constant of solvent was, the thinner PEO fiber was. The average diameters of electrospun PEO fibers from PEO/water solutions were decreased and their distributions were narrowed by adding 0.1 wt% poly(allylamine hydrochloride) (PAH) and poly(acrylic acid sodium salt) (PAA) due to the increased charge density in solutions. The addition of PAH and PAA lowered the minimum concentration for electrospinning of a PEO/water solution to 6 wt%.

Keywords: Poly(ethylene oxide); Electrospinning; Polyelectrolyte

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1. Introduction

The production of ultrafine polymer fibers via electrospinning is a new technology that overcomes the limitation of conventional fibers and non-woven mats [1–6]. Over the fast few years, ultrafine electrospun synthetic and natural fibers having unusual properties of high surface area-to-volume and length-to-diameter ratios have been applied in various areas such as separation filters, wound dressing materials, tissue scaffolds, sensors, etc. [7–15].

In electrospinning, polymer solution is ejected from a capillary by a strong electrostatic force and deposited as a non-woven fibrous mat on an electrically grounded target. As this jet travels through the air, the solvent evaporates, leaving behind ultrafine polymer fibers. As one of the most extensively studied polymers for electrospinning, poly (ethylene oxide) (PEO) has been widely used with/without the addition of another polymer [16–24]. In fundamental studies, PEO solutions were electrospun in order to investigate the effects of process parameters of electrospinning such as spinning voltage, solution flow rate, and the distance between the needle tip and the ground electrode (working distance), and solution properties such as solution viscosity, conductivity, dielectric constant, and surface tension on the structure and morphology of electrospun PEO fibers. It was found that solution properties are the main factors influencing the transformation of polymer solution into ultrafine fibers [19,20]. Above a certain concentration, fibers without beads are electrospun and thinner fibers are obtained from a polymer solution with higher net charge density. Reduced surface tension favors the formation of fibers without beads [16]. In practical studies, solutions of natural proteins with PEO were electrospun into ultrafine fibers in order to improve their processability because they are very difficult to be processed into fibrous forms alone [21,23]. PEO with polyaniliane doped with camphorsulfonic acid was electrospun to produce ultrafine conducting fibers [17].

The electrospinning of polymer in various solvents can provide very useful informations to understand the effects of relevant solution properties. PEO can be dissolved in chloroform, ethanol, dimethylformamide (DMF) and water [25] and most of researches on PEO electrospinning were

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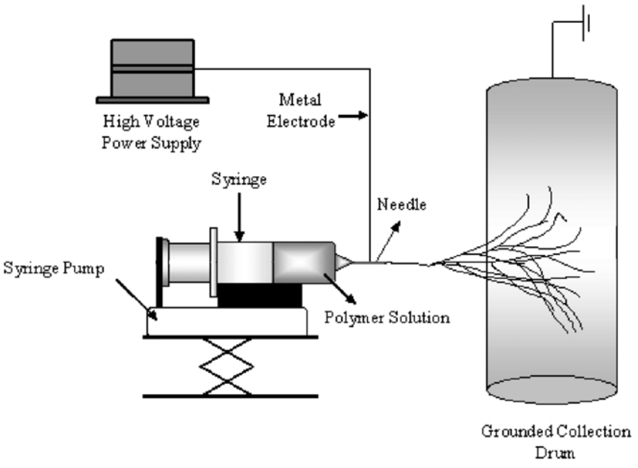


Fig. 1. Schematic diagram of electrospinning set-up.

carried out with one of these solvents [16–24]. In this study, the effects of solution properties and polyelectrolyte on the morphology and diameter of electrospun PEO fibers were investigated by electrospinning PEO solutions in these solvents and PEO/water solutions with small amounts of cationic and anionic polyelectrolytes.

2. Experimental

2.1. Materials

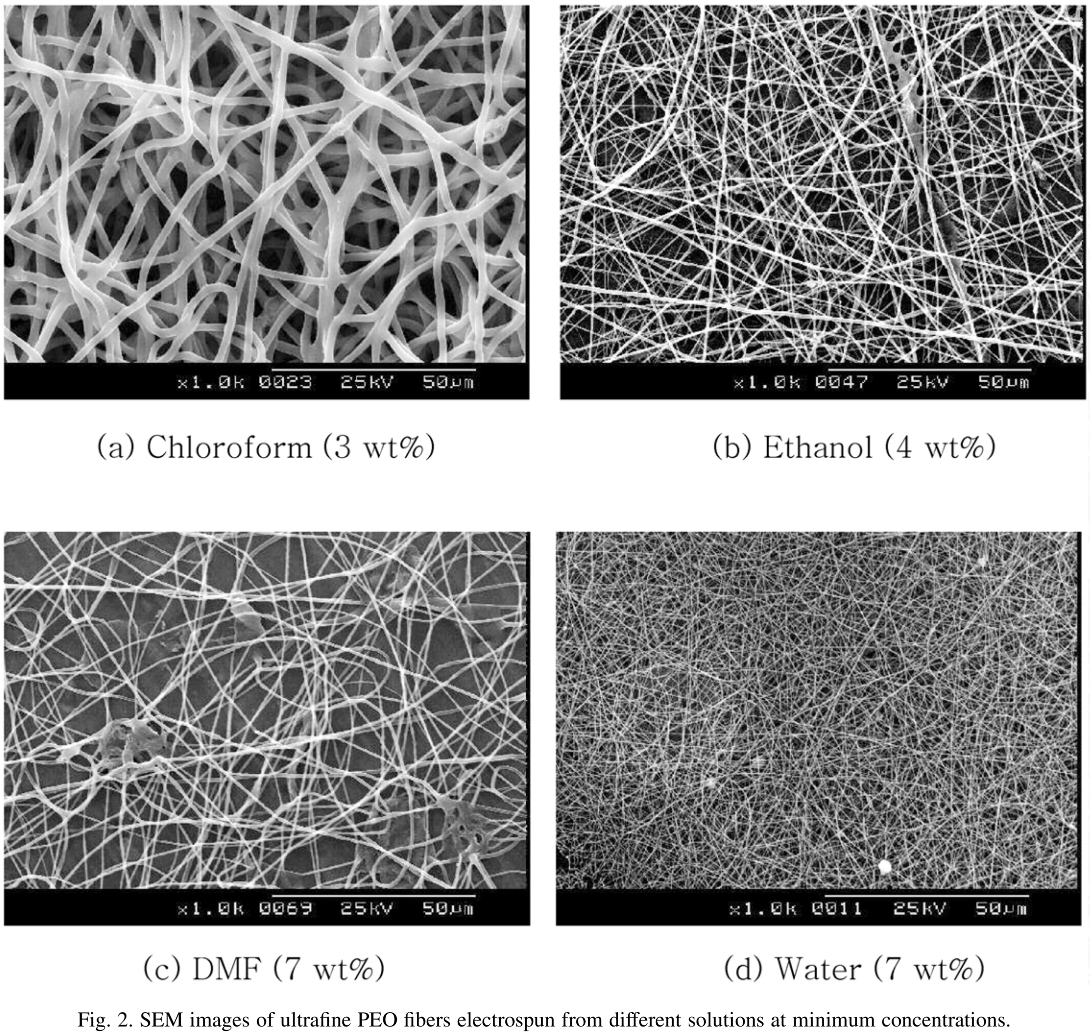
PEO ($M_v = 300,000$) was purchased from Aldrich. Chloroform, ethanol, DMF and water were all reagent grades. Poly(allylamine hydrochloride) (PAH, $M_w = 15,000$) and poly(acrylic acid sodium salt) (PAA, $M_w = 15,000$, 35 wt% solution in water) were purchased from Aldrich and used without further purification.

2.2. Intrinsic viscosity

The viscosities of PEO solutions were measured for a series of concentrations made by successive dilutions by using an Ubbelohde viscometer at 25 ± 0.1 °C. Intrinsic viscosity ($[\eta]$) was determined by the extrapolation of specific viscosity η_{sp} to zero polymer concentration as follows:

$$[\eta] = \lim_{c \to 0} (\eta_{sp}/c) \tag{1}$$

where c is the PEO concentration (g/dl).



(a) Chloroform (3 wt%)

(b) Ethanol (4 wt%)

(c) DMF (7 wt%)

(d) Water (7 wt%)

Fig. 2. SEM images of ultrafine PEO fibers electrospun from different solutions at minimum concentrations.

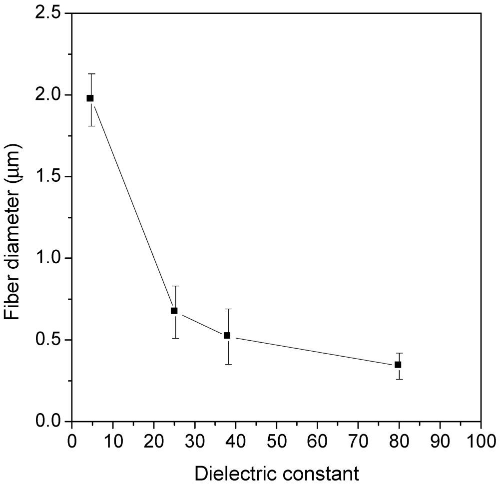


Fig. 3. The relationship between the dielectric constant of solvent and the average diameter of PEO fibers.

2.3. Electrospinning

PEO solutions in chloroform, ethanol, DMF and water and PEO/water solutions with small amounts of polyelectrolyte were electrospun. PEO concentrations were in the range of 1–10 wt%. Fig. 1 shows a schematic diagram of the electrospinning set-up used in this study. It consisted of a syringe and needle (i.d. = 0.84 mm), a ground electrode (d =21.5 cm, stainless steel sheet on a drum whose rotation speed can be varied), and a high voltage supply (Chungpa EMT, CPS-40K03). The needle was connected to the high voltage supply which can generate positive DC voltages up to 40 kV. The working distance was in the range of 6–24 cm. Positive voltage applied to polymer solutions were in the range of 11–27 kV. The solution flow rates were controlled by a syringe pump and ranged from 0.5 to 5 ml/h. All electrospinnings were carried out at room temperature.

2.4. Measurement and characterization

The conductivity and surface tension of PEO solution were measured by using a conductivity meter (Isteck Model 455C) and an interfacial tension meter (Kruss Model K8), respectively, at 25 °C. The viscosities of PEO/water solutions with PAH and PAA were measured on a Brookfield digital viscometer (Model DV-E) at 25 °C. The morphology of electrospun fibers was observed on a scanning electron microscope (SEM) (Hidachi S-2350) after gold coating. The average diameter was determined by analyzing SEM images with a custom code image analysis program.

3. Results and discussion

3.1. Effect of solution properties

Various electrospinning conditions for continuous and steady spinning of PEO solutions in chloroform, ethanol, DMF and water were tested and the results are listed in Table 1. In cases of PEO solutions in chloroform, ethanol and water, they were successfully electrospun at 13 kV positive voltage, 10 cm working distance, and 3 ml/h solution flow rate. The applied voltage was almost two

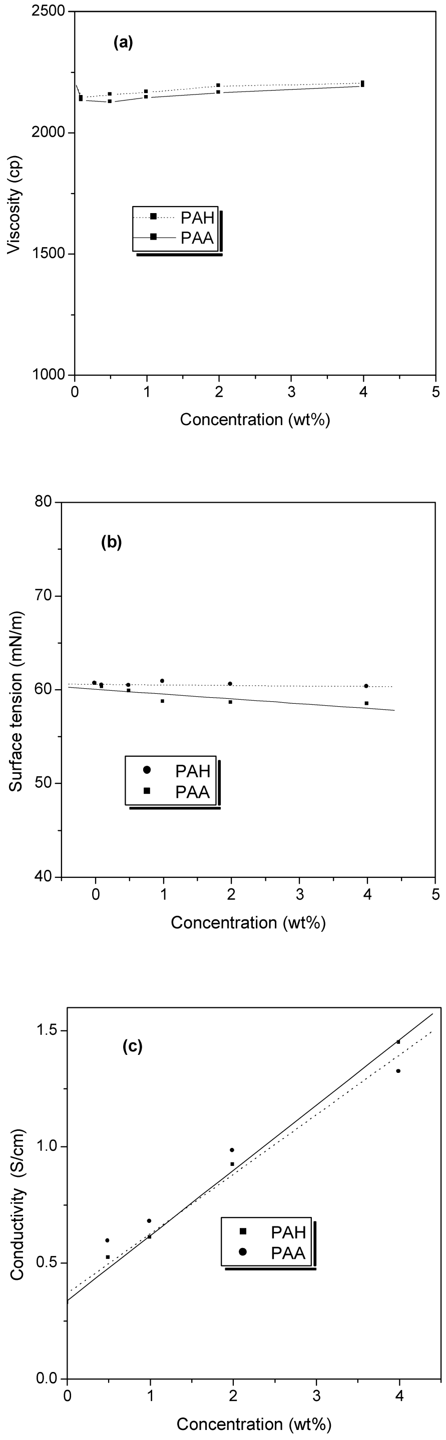


Fig. 4. Changes in (a) viscosities, (b) surface tensions, and (c) conductivities of 7 wt% PEO/water solutions with different amounts of PAH and PAA.

Table 1
The electrospinning conditions in chloroform, ethanol, DMF and water

Solvents	Potential (kV)	Distance (cm)	Flow rate (ml/h)	Concentration (wt%)	Formation
Chloroform	13	10	3	2.0	Beaded
				3.0	Fibers
				4.0	Fibers
				5.0	Fibers
Ethanol	13	10	3	2.0	Droplets
				3.0	Beaded fibers
				4.0	Fibers
				5.0	Fibers
DMF	25	20	3	5.0	Droplets
				6.0	Beaded fibers
				7.0	Fibers
				8.0	Fibers
Water	13	10	3	5.0	Beaded fibers
				6.0	Beaded fibers
				7.0	Fibers
				8.0	Fibers

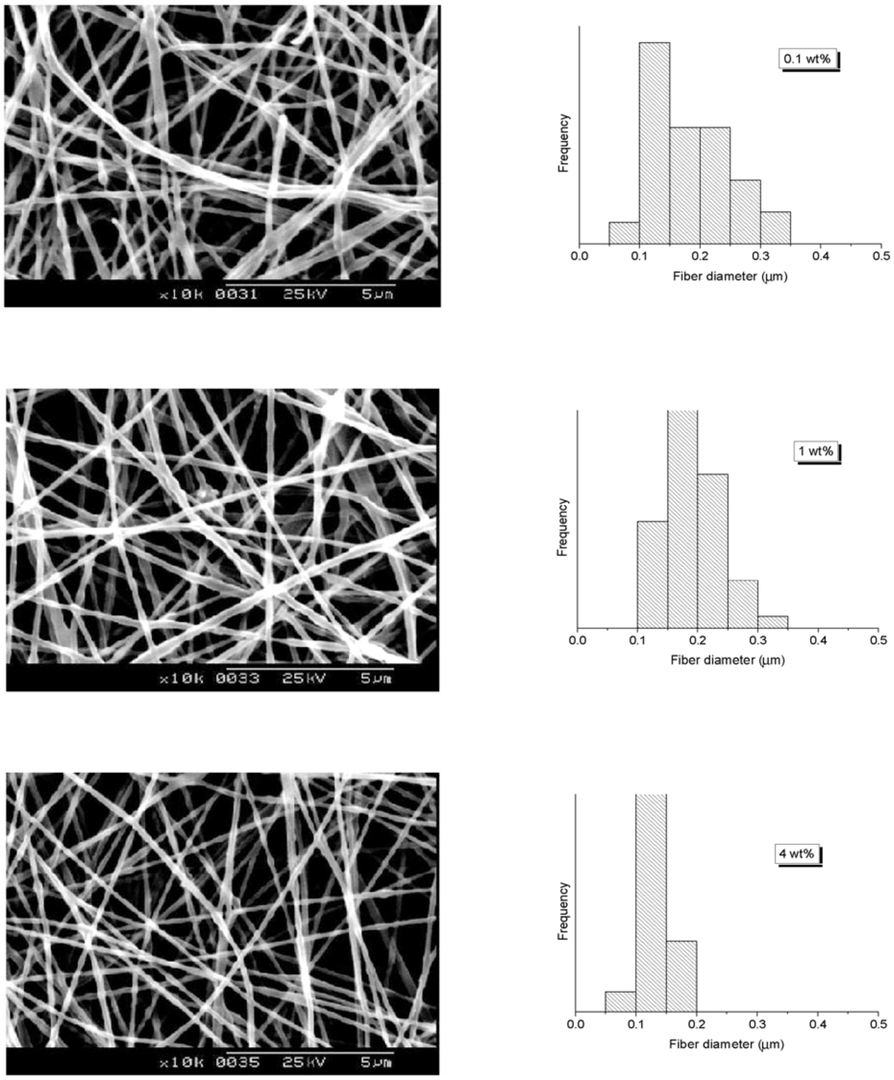


Fig. 5. SEM images and diameter distributions of ultrafine PEO fibers electrospun from 7 wt% PEO/water solutions with different amounts of PAH.

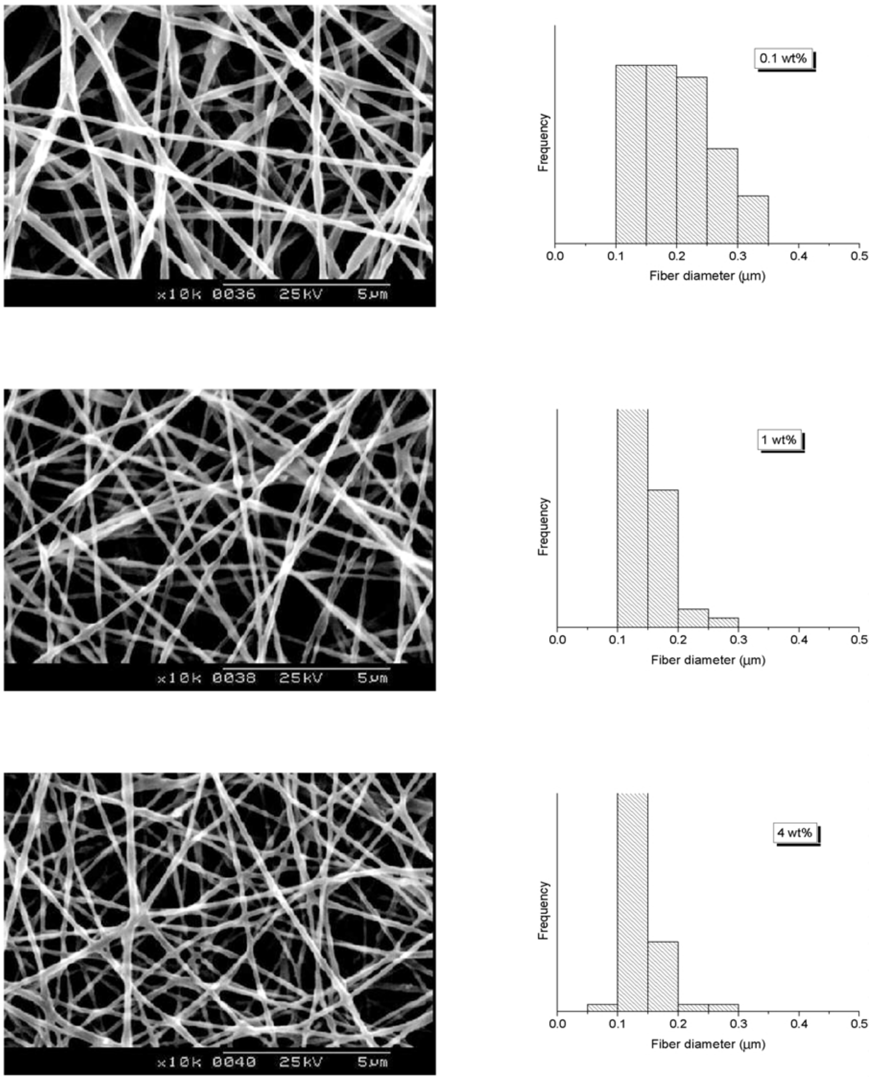


Fig. 6. SEM images and diameter distributions of ultrafine PEO fibers electrospun from 7 wt% PEO/water solutions with different amounts of PAA.

times higher than initial voltages that could overcome the surface tensions of PEO solutions in these solvents. In the case of PEO solution in DMF, the solution was electrospun at 25 kV positive voltage and 20 cm working distance. Much higher positive voltage and longer working distance were needed to obtain ultrafine PEO fibers probably due to its higher boiling temperature. Ultrafine PEO fibers without beads were obtained from electrospinning of 3, 4, 7 and 7 wt% PEO solutions in chloroform, ethanol, DMF and water, respectively. These minimum concentrations were dependent on the type of solvent. Fig. 2 shows SEM images of ultrafine PEO fibers electrospun from chloroform, ethanol, DMF and water solutions at these minimum concentrations. The morphology and average diameter of electrospun fibers was affected by the type of solvent. The average diameters of PEO fibers were ranged from 0.36 to 1.96 μm. The most ultrafine PEO fibers (0.36 μm) were obtained from a 7 wt% PEO/water solution. As reported in our previous study [26], the average diameter of PEO fibers were not significantly changed according to the acceleration voltage, working distance, and solution flow rate for all solvents. However, it was observed that the average

Table 2
The intrinsic viscosity, Martin constant and critical concentration of PEO solutions in chloroform, ethanol, DMF and distilled water

Solvents	Intrinsic viscosity ($[\eta]$)	Martin constant (K_m)	Critical concentration ($C = 10/[\eta]$)
Chloroform	3.39	6.51	2.94
Ethanol	2.63	9.08	3.80
DMF	1.48	27.71	6.76
Water	1.51	14.06	6.62

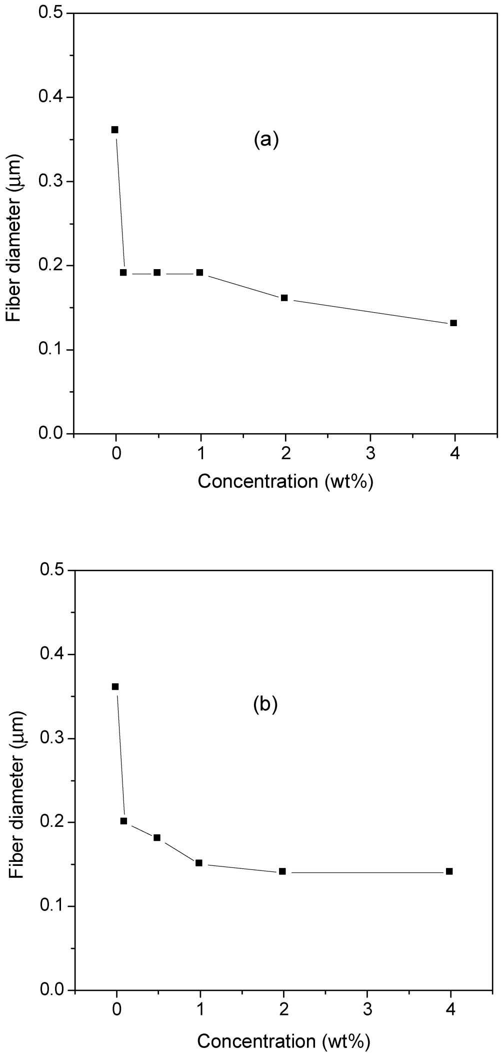


Fig. 7. Average diameters of PEO fibers electrospun from 7 wt% PEO/water solutions with different amounts of (a) PAH and (b) PAA.

diameters of electrospun fibers were increased with increasing the PEO concentration.

In order to understand the solvent effect on the minimum spinning concentration and average fiber diameter, solution properties of PEO were investigated. The intrinsic viscosities of PEO solutions in chloroform, ethanol, DMF and water are listed in Table 2. They were in the range of 1.51–3.39 dl/g, which is directly related to the solubility of solvent (interaction between PEO and solvent). Analogously, the Martin constant (K_m) reflecting interactions between polymers, and polymer and solvent was determined by using the following equation [27]:

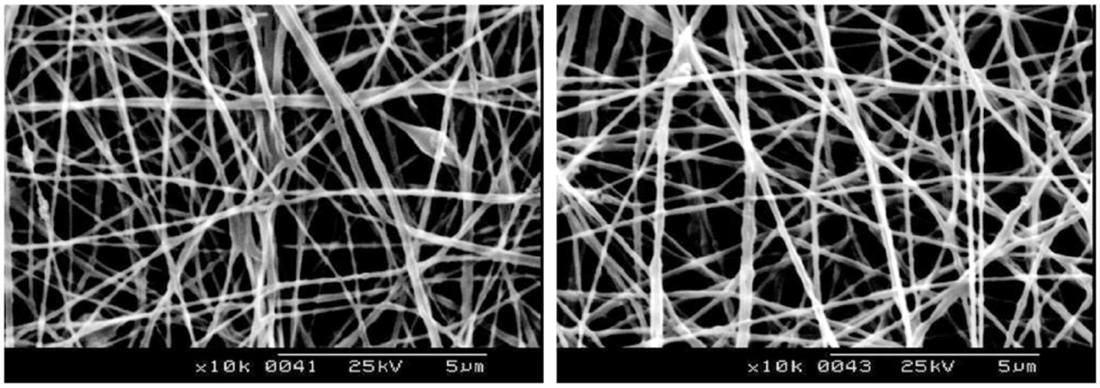
$$\eta_{sp}/[\eta]c = \exp(K_m[\eta]c) \tag{2}$$

A larger value of K_m indicates a greater level of interaction between polymers. As expected, intrinsic viscosities and the Martin constants for these PEO solutions consistently indicate that PEO interacts with chloroform, ethanol, water, and DMF in decreasing order of strength. In other words, PEO has the most expanded conformation in chloroform. Koski et al. [28] investigated the effect of molecular weight of poly(vinyl alcohol) (PVA) on its electrospun fiber structure. Ultrafine PVA fibers ranging from 0.25 to 2 μm in diameter were obtained above a minimum concentration and/or molecular weight ($[\eta]C > 5$). The cross-section of PVA fibers were circular-shaped at $[\eta]C < 9$ and changed to flat fibers at $[\eta]C > 9$. In this study, different minimum concentrations of PEO were observed according to the type of solvents. However, the values of $[\eta]C$ were ~ 10 for all solutions (Table 2). It is considered that the entanglement of PEO occurs when $[\eta]C > 10$ [27]. The solution viscosity would increase sharply from $[\eta]C > 10$.

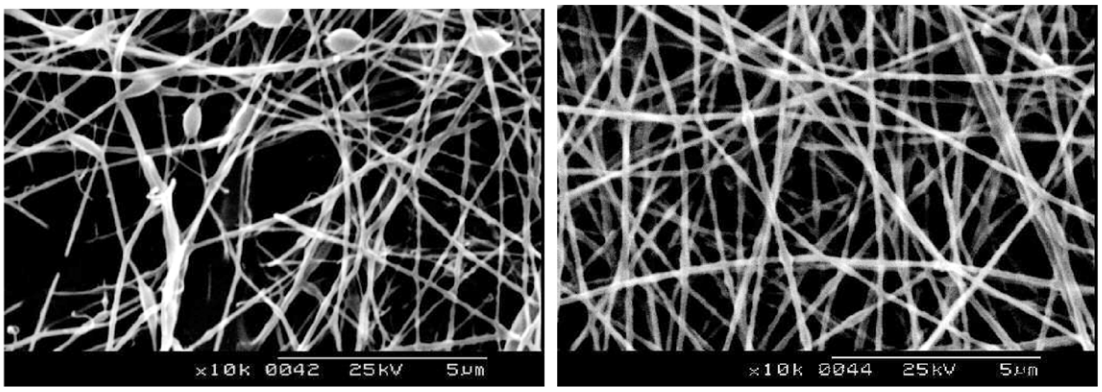
On the other hand, although all PEO solutions were electropsun at $[\eta]C \sim 10$, the resulting PEO fibers exhibited different fiber diameters ranging 0.36–1.96 μm as shown in Fig. 2. In order to interpret this difference, the relationship between the dielectric constant of solvent and the average diameter of fibers is plotted in Fig. 3. The dielectric constants of chloroform, ethanol, DMF and water were 4.8, 25.3, 38.3 and 80.1, respectively, at 25 °C. The higher the dielectric constant of solvent was, the thinner PEO fiber was. The dielectric constant is a measure for the polarity of solvent. Charges have a much greater effect to a polar solvent than to a non-polar solvent. It is considered that solvent with a larger dielectric constant have a higher net charge density in solution. As the charges carried by the jet increased, higher elongation forces were imposed to the jet under the electrical field, resulting in smaller beads and thinner fiber diameters.

3.2. *Effect of polyelectrolyte*

To the best of our knowledge, the effect of polyelectrolyte on the electrospinning of polymer solution has not been reported yet. It is well-known that the addition of salt increases the charge density in ejected jets and thus stronger elongation forces are imposed to the jets due to the self-repulsion of the excess charges under the electrical field, resulting in substantially straighter shape and smaller diameter of electrospun fibers. The addition of salt was found to be relatively more effective on the fiber diameter than other parameters [12]. It is expected that the addition of cationic and anionic polyelectrolytes would increase the charge density in ejected jets and result in thinner fibers. In this study, small amounts of PAH and PAA (0.1–4 wt% to the weight of PEO) were added to a PEO/water solution. Fig. 4 shows changes in solution viscosities, surface tensions, and conductivities of 7 wt% PEO/water solutions when small amounts of PAH and PAA were added. The solution viscosities and surface tensions of the solutions were slightly changed, but their conductivities were significantly increased with the amount of PAH and PAA



(a) 5 wt% (b) 6 wt%



(c) 5 wt% (d) 6 wt%

Fig. 8. SEM images of PEO fibers electrospun from 5 and 6 wt% of PEO aqueous solutions with 2 wt% of PAH and PAA.

added. SEM images and diameter distributions of ultrafine PEO fibers electrospun from 7 wt% PEO/water solutions with different amounts of PAH and PAA are shown in Figs. 5 and 6, respectively. The same process conditions for electrospinning of the PEO/water solutions were used and more than 100 fibers were tested in order to determine the diameter distribution. The surface morphologies of PEO fibers electrospun with/without polyelectrolyte were very similar. The average diameters were decreased and their distributions were narrowed with increasing the amount of PAH and PAA. Usually, the increase of electron charge density diminished the fiber diameter in electrospinning and formed further smooth fibers. The average diameters of PEO fibers electrospun from 7 wt% PEO/water solutions with various amounts of PAH and PAA are shown in Fig. 7. The average diameters were dramatically decreased with the addition of just 0.1 wt% PAH and PAA and leveled off at 4 wt%. The addition of polyelectrolyte increased the charge density of solution and that the electrospun fibers became finer and smoother. However, the effect of conductivity on the fiber diameter might be limited above a critical value because the average diameter of electrospun fibers was not directly related to the magnitude of conductivity.

SEM images of PEO fibers electrospun from 5 to 6 wt% of PEO/water solutions with 2 wt% of PAH and PAA are shown in Fig. 8. PEO fibers electrospun from the 5 wt% solution showed beaded-fiber morphology. Ultrafine fibers without beads were obtained at solution concentrations above 6 wt%. In a PEO/water solution, PEO fibers without beads were produced at concentrations above 7 wt%. Therefore, the addition of polyelectrolyte decreased the minimum concentration of PEO to prepare ultrafine fibers via electrospinning. It is considered that the increased charge density in ejected jets drove thus stronger elongation forces and resulted in straighter shape even at lower PEO concentrations.

4. Conclusions

Ultrafine PEO fibers without beads were obtained from electrospinning of 3, 4, 7 and 7 wt% PEO solutions in chloroform, ethanol, DMF and water, respectively. In the case of a PEO/DMF solution, much higher positive voltage and longer working distance were needed to obtain ultrafine PEO fibers than the other solutions. At these concentrations, the values of $[\eta]C$ were ~ 10 for all solutions, where PEO solutions were in a polymer chain entanglement region. The average diameters were in the range of 0.36–1.96 μm and the most ultrafine PEO fibers (0.36 μm) were obtained from a 7 wt% PEO/water solution. The higher the dielectric constant of solvent was, the thinner PEO fiber was. Solvent with a higher dielectric constant have a higher net charge density in solution. The average diameters of PEO fibers were not significantly changed according to the acceleration voltage, working distance, and solution flow rate for all solvents. When small amounts of PAH and PAA were added to a 7 wt% PEO/water solution, solution viscosities and surface tensions were slightly changed but their conductivities were significantly increased. The fiber diameters were decreased from 0.36 to 0.2 μm with the addition of 0.1 wt% PAH and PAA. The addition of 2 wt% PAH and PAA lowered the minimum electrospinning concentration of a PEO/water solution to 6 wt%.

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