Preparation of Electrospun Porous Ethyl Cellulose Fiber by THF/DMAc Binary Solvent System

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Abstract: Morphological change of electrospun fiber with various solvent was conducted to figure out solvent effect on the surface of ethyl cellulose nanofiber. THF (bp 66 °C) and DMAc (bp 165 °C) binary solvent system was introduced and electrospinning was performed with different ratio of THF/DMAc including each pure solvent at 100 µL/min flow rate of 15 % (w/v) ethyl cellulose dissolved in the solvent. The applied voltage was 10, 13, 15, and 20 kV under 10 cm tip-to-collector distances. Morphology of fibers was evaluated by SEM image through the various magnification. Regular holes were formed on the surface of fiber from pure THF and 80 % THF in DMAc, while smooth surface was observed for the pure DMAc and 80 to 20 % DMAc ratio in THF. As the electric conductivity increased, the diameter of electrospun fiber decreased. In case of binary solvent, the average diameter decreased from 1100 to 500 nm as increased the ratio of DMAc from 20 to 80 %.

Keywords: electrospinning, ethyl cellulose, nanofiber, binary solvent, morphology

Introduction

Cellulose is a naturally occurring polymer of particular interest due to its abundant availability and biodegradability. These properties make cellulose fiber useful in a wide range of area such as filtration, biomedical applications and protective clothing [1]. Unfortunately however, there is a few research article has been reported on the fiber of cellulose and its derivatives produced by the electrospinning method. Ethyl cellulose is a kind of cellulose ether, and it shows good thermostability and electric properties. The film made from ethyl cellulose has quite good permeability, it has been widely used industrial air filter [2].

Electrospinning has been extensively investigated for the preparation of nanofibers exhibiting high surface area-to-volume and length-to-diameter ratios. These characteristics are essential for practical applications such as separation membranes. The characteristic of fiber during electrospinning depends on the solution properties such as viscosity, surface tension, conductivity, boiling point and dielectric constant [3]. The morphology of electrospun nanofibers also depends on the electrospinning parameters such as polymer concentration, spinning distance and solvent properties [4].

Ultrafine porous fibers were prepared by the rapid phase separation during the electrospinning process when a highly volatile solvent was used [5]. Wendorff and coworkers prepared porous fibers from poly-L-lactide, polycarbonate, and polyvinylcarbazole with methylene chloride [6] and these porous nanofibers have potential in applications such as nanofiltration and functional nanotubes by fiber templates [7-9]. Han reported for the preparing the porous fiber and non-porous from cellulose triacetate using methylene chloride and ethanol mixed solvent [5]. At this paper, mixed solvents had low vapor pressure by adding larger amount of ethanol and substantially the solidification of polymer became dominant, resulting in the non porous fiber structure. The dielectric constant of solvent has a significant influence on electrospinning. If a solvent of a higher dielectric constant is added to a solution to improve the electrospinnability of the solution, the interaction between the mixtures such as the solubility of the polymer will also have an impact on the morphology of the electrospun fibers [4].
Table 1. Properties of Solvents used in This Study

<table>
<thead>
<tr>
<th>Solvent</th>
<th>b.p. (°C)</th>
<th>ε(^a)</th>
<th>μ(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>66</td>
<td>7.47</td>
<td>1.7</td>
</tr>
<tr>
<td>DMAc</td>
<td>165</td>
<td>37.8</td>
<td>3.72</td>
</tr>
</tbody>
</table>

\(^a\) Dielectric constant at 20 °C, \(^b\) Dipole moment in Debyes.

DMF added to polystyrene (PS) solution, beads are formed even though electrospinnability should improve due to higher dielectric constant of DMF [10].

In this study, we try to prepare the porous nanofiber from ethyl cellulose dissolved in a THF/DMAc binary solvent system having a different boiling temperature and dielectric constant. Also, we want to find out the role of solvent on the morphology of electrospun ethyl cellulose fiber through observing the magnified images of the fiber prepared with various solvent ratio using THF and DMAc those are having different solvent properties. We expect the more volatile solvent make a hole due to the high evaporating rate during electrospinning.

**Experimental**

**Materials**

Ethyl cellulose, tetrahydrofuran (THF), and dimethylacetamide (DMAc) purchased from Sigma. These chemicals were used without further purification. The basic properties of these solvents are summarized in Table 1.

**Preparation and Characterization of Ethyl Cellulose Solutions**

Ethyl cellulose solutions having a different ratio of binary solvent were prepared with 15 % (w/v) ethyl cellulose dissolved in the THF/DMAc according to volume ratios of 100/0, 80/20, 60/40, 50/50, 40/60, 20/80, and 0/100. The viscosity and the conductivity of the prepared solution were measured by viscometer (LVDV II-, Brookfield Co., USA) and conductivity meter (CM-11P, TOA Electronic Ltd). Surface tension for each solution was measured tensionmeter (K9, Kruss Co., Germany).

**Characterization**

The morphology of electrospun ethyl cellulose fibers such as status of surface, diameter of fiber were observed by Image microscope (Sometech Inc, Korea) and Scanning electron microscope (FE-SEM, Hitachi 8400s, Japan), respectively. The diameter of the electrospun fibers is determined with image analyzer (imageJ).

**Electrospinning Process**

The schematic experimental system used for the electrospinning process is shown in Figure 1. The electrospinning system composed as follows, syringe pump (200 series, KD Scientific Inc., USA) used as injector having plat capillary tip 0.8 mm diameter and connected high voltage DC power supplier generating positive DC voltages up to 50 kV (DC power supply PS/ER 50R06 DM22, Glassman high voltage Inc., USA).

Grounded counter electrode was connected to collector which covered with aluminum foil. Positive voltage applied to polymer solution controlled between 10 and 20 kV with stepwise increase. The concentration of ethyl cellulose solution for fiber formation was fixed with 15 % (w/v). The flow rate were fixed to 100 µL/min and tip to collector distance (TCD) is fixed at 10 cm. All electrospinning were carried out at the room temperature.

**Results and Discussion**

**Effect of Solution**

For the preliminary experiment electrospun of ethyl cellulose performed with each THF and DMAc as a single solvent. We prepare electrospun solution with 15 % (w/v) ethyl cellulose dissolve in the THF or DMAc. Electrospinning carried out at 100 µL/min flow rate, applied voltage was 15 kV under 10 cm tip-to collector distance (TCD). Figure 2 shows SEM images of electrospun ethyl cellulose fiber for the various solvent. The result of electrospinning, both THF and DMAc formed electrospun ethyl cellulose fiber (Figures 2(a) and (c)). In case of THF, hole was formed on the surface of fiber, on the contrary DMAc gave a smooth surface of nanofiber (Figures 2(b) and (d)). For the further study, we evaluate the effect of THF/DMAc binary system according to ratio of solvent.

**Figure 1.** Schematic and photo of electrospinning apparatus.
Effect of Binary Solvent Ratio

From the preliminary experiment, it was found that the morphology of the fibers depends on the solvent significantly. We prepare various solutions with fixed 15% (w/v) ethyl cellulose according to volume ratios of 80/20, 60/40, 50/50, 40/60, and 20/80. Figures 3 and 4 show SEM image of electrospun ethyl cellulose fibers prepared from different ratios of THF/DMAc (v/v). Electrospinning was performed for the various ratio of THF/DMAc including each pure solvent at 100 µL/min flow rate of 15% (w/v) ethyl cellulose dissolved under applied voltage 20 kV applied to 10 cm tip-to-collector distances (TCD). It was found that the addition of DMAc gave the changes not only surface structure of fiber but also the fiber diameter (Figures 3 and 4). Regular holes were formed on the surface of fiber from pure THF (Figure 4(a)) and 80% THF in DMAc (Figure 4(b)), while smooth surface was observed in pure DMAc (Figure 4(g)) and 80 to 20% DMAc in THF (Figures 4(c)∼(e)). We studied about chemical properties of solvent including boiling point and dielectric constant with various THF/DMAc ratios.

Chemical Properties of Ethyl Cellulose Solutions

The chemical properties of the polymer solution have the most significant influence in the electrospinning process and the resultant fiber morphology. The surface tension has a part to play in the formation of beads along the fiber length. The viscosity of the solution and its electrical properties will determine the extent of elongation of the solution. This will in turn have an effect on the diameter of the resultant electrospun fibers [4].

Figures 5 and 6 are plots of viscosity and surface tension of ethyl cellulose solution with different solvent ratio of THF and DMAc. The properties of viscosity and surface tension of binary solvent are less than each single component. Comparing the morphology of electrospun fiber and above results, the properties of viscosity and surface tension did not affect significantly on the poro-
Preparation of Electrospun Porous Ethyl Cellulose Fiber by THF/DMAc Binary Solvent System

Figure 4. High magnified SEM image of the electrospun ethyl cellulose fiber with various solvent ratio; (a) only THF (× 1000), (b) THF/DMAc = 80/20 (× 6000), (c) THF/DMAc = 60/40 (× 3000), (d) THF/DMAc = 50/50 (× 20000), (e) THF/DMAc = 40/60 (× 30000), (f) THF/DMAc = 20/60 (× 40000), (g) only DMAc (× 100000) (ethyl cellulose; 15 % (w/v), applied voltage; 20 kV, flow rate; 100 µL/min, TCD; 10 cm).

Figure 5. Viscosity change of ethyl cellulose solution for the various solvent ratio.

Figure 6. Surface tension change of ethyl cellulose solution for the various solvent ratio.

sity of fiber.
On the contrary the electric conductivity plays the important role on the average diameter and shapes of the fiber. Figure 7 show the electric conductivities of solvent, THF is almost insulator and DMAc is conductor and the conductivities of mixed solvents are increase as
the DMAc ratio increased.

As the electric conductivity increase, the electrospun fiber diameter decreased. For the binary solvent the average diameter decreased from 1100 to 500 nm as increased the ratio of DMAc from 20 to 80%.

The distributions of diameter for the fiber were plotted at Figure 9 as a function of solvent ratio. As DMAc ratio increase, that is increase the electric conductivity, the distribution of the diameter is shift to regular shape.

Such results can be explained by Taylor cone theory [11], as the electric conductivity increased the mobility of solution increased in the high voltage of electric field owe to abundant electric charges in the solution. We could concluded that as DMAc ratio increase caused electric conductivity increase in the mixed solvent, consequently the diameter of fiber are decreased and distribution of the fiber became more regular.

The dielectric constant of a solvent known as a significant property for the electrospinning. Generally, a
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The boiling points of THF and DMAc are 65 and 165 °C, respectively. Because of THF is higher vapor pressure than DMAc, THF evaporate rapidly during electrospinning, while a considerable amount of less volatile solvent remains within ethyl cellulose fiber. Consequently, microhole on the surface of fiber could be formed by electrosprinning of the ethyl cellulose with the high boiling point solvent. Practically only THF was used as a solvent, blockage of tip observed, while DMAc was a single solvent jets appeared to be continuous without a blockage. These phenomena also attributed to mainly from boiling point difference of two solvent [14].

**Effect of Applied Voltage**

A series of experiments was performed with 15 % (w/v) ethyl cellulose solution in 20/80 THF/DMAc volume ratio solvent under applied voltage was varied from 10 to 20 kV and the tip-to-target distance was fixed at 10 cm. The results are shown in Figure 10. There was a slight increase in fiber diameter upon increasing the applied voltage. Also, as the voltage increased, the shape of fiber became more regular electrospun web. Increasing the applied voltage will increase electrostatic repulsion force for fluid jet, which favors thinner-fiber formation. But there was not observed a remarkable difference in the morphology. Corona discharge was occurred over 20 kV applied voltage, and it prevent electrospinning.

Figure 11 show the effect of the applied voltage on 15 % (w/v) ethyl cellulose solution (with a 60/40 THF/DMAc volume ratio) 10 cm tip to collector distance (TCD). With an increasing applied voltage, the diameter of electrospun fibers gradually decreased, and the shape of fiber was become regular. The structure of electrospun ethyl cellulose fiber became the full developed fiber from bead like over 20 kV while mixed shapes observed in the range of 10 to 15 kV of applied voltage. As the applied voltage increased to 10, 13, and 20 kV, the average diameter of fibers decreased 998, 821, and 763 nm respectively.
Conclusion

The morphology of electrospun fiber is very diverse with the kinds and ratio of solvent in the THF/DMAc binary system. The diameter of the ethyl cellulose fibers were influenced by ratio of solvent in the THF/DMAc binary system. Regular holes were formed on the surface of fiber from pure THF and 80 % THF in DMAc, while smooth surface was observed in pure DMAc and 80 to 20 % DMAc in THF. As DMAc ratio increased, the electric conductivity increased almost linearly. For the mixed solvent the average diameter decreased from 1100 to 650 nm as increased the ratio of DMAc from 20 to 80 %. In terms of the applied voltage, the structure of ethyl cellulose electrospun fiber changes at 10 kV from bead like to full developed fiber as voltage increased to 20 kV.

Acknowledgments

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References