The Effect of Relative Humidity on Electrospinning of Poly-(vinyl alcohol) with Soluble Eggshell Membrane

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Received 12 September 2011; accepted for publication 17 January 2012

Abstract

Electrospinning of poly-(vinyl alcohol) (PVA) with soluble eggshell membrane (S-ESM) in aqueous media was carried out under 20\%\textendash70\% relative humidity (RH). The S-ESM/PVA spinning dope was 11.66 wt\% solutes concentration with weight ratio of S-ESM:PVA = 40:60. Fiber morphology and fiber diameter were determined using field emission scanning electron microscopy (FE-ESM). A RH of 40\% was found to be optimal for obtaining a sufficient fiber collection of S-ESM/PVA fibers. S-ESM particles were appeared on the surface of the fibers at 20\%-30\% RH. It was also found that the diameter of S-ESM/PVA blend fiber decreased with increasing the RH.

Key Words: Soluble eggshell membrane, Electrospinning, Processability, Relative humidity

1. Introduction

In recent years, electrospinning process has been widely used to produce the fibers with nano scale diameter. Despite the apparent simplicity of the electrospinning principle, the jet formation of spinning dope is influenced by the electrospinning conditions including the spinning parameters and ambient conditions, which resulting in different fiber formation and fiber properties. Therefore, to achieve the intended fiber characteristics, the spinning parameters and ambient conditions have to be carefully designed during electrospinning. A number of reports have already been published on the fundamental processing conditions which include applied voltage, flow rate, and distance between needle and collector to produce nanofibers [1\textendash4]. Ambient parameters, such as relative humidity (RH) and temperature also influence the fiber formation. It is reported the bead formation, rather than cylindrical-beads fibers, occurs under high RH for several polymers such as poly (ethylene oxide) (PEO) [5] and poly (vinyl alcohol) (PVA) [6]. It is also found varying RH can affect the presence of pores by electrospinning poly (methyl methacrylate) (PMMA), polystyrene (PS) and polyvinyl chloride (PVC) [7, 8].

Eggshell membrane (ESM), which contains collagen types I, V, and X is natural protein. ESM exhibits unique properties, such as appropriate moisture retention and air permeability, which are suitable characteristics for medical applications [9]. However, the further application of ESM is limited by its insolubility, therefore, rather than employing natural ESM, water-soluble ESM (S-ESM) from natural hen ESM has been considered to produce the regenerated ESM nanofibers. Recently, several studies reported that S-ESM fibers can be successfully fabricated by blending supporting polymers PEO and PVA [10, 11], because S-ESM itself can not be electrospun due to the low molecular weight resulting in insufficient viscosity for spinning. Further improvement in this type of processing is necessary for electrospinning of S-ESM/PVA blends in aqueous media. It has been reported that pure PVA fibers are obtained by electrospinning at a RH of 20\%\textendash80\% [6]. Adding S-ESM to PVA solution is expected to change the processing ability at various humidity, because the hydrophilic S-ESM could absorb amount of water and have effect on the fiber formation.

In this study, the processability for producing the S-ESM/PVA nanofibers was examined at various RH levels. We tried to determine the link between ambient moisture during electrospinning and fiber shape and fiber surface of PVA/S-ESM blend nanofibers.

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2. Experimental

2.1 Materials

S-ESM powder (Mₜ=6000, Idemitsu Technofine Co., Ltd. Tokyo, Japan) was used as a starting material. PVA (degree of hydrolysis: 98 mol%, Kuraray Poval, Kuraray Co., Ltd. Tokyo, Japan) was used as the supporting polymer for blending with S-ESM. Purified distilled water is used as the solvent.

2.2 Measurement of Moisture regain for S-ESM and PVA powders

The S-ESM and PVA powders were stored in oven at 50°C for 24 hr, then the dried S-ESM and PVA powders were put in 20% and 70% RH for 3 hr, respectively. After 3 hr’s water absorption, the water content of the S-ESM and PVA powders were measured by the infrared moisture determination balance (FD-720, Kett electric laboratory, Japan).

2.3 Solution Preparation

The PVA spinning dope was prepared by dissolving PVA resin in water at 7 wt% under 90°C. The S-ESM/PVA blend dope was prepared by adding S-ESM powder to 7 wt% PVA aqueous solution at weight ratio of S-ESM:PVA = 40:60 according to the previous finding [11]. The total solutes concentration of S-ESM/PVA blend was 11.66 wt%.

2.4 Electrospinning

An electrospinning apparatus was set up by placing a 3-mL syringe capped with a 22-G needle in a syringe pump. The syringe was mounted to enable control of solution flow rate. A copper plate (8 × 8 cm) covered by aluminum foil was used as a collector. First, electrospinning conditions were examined for the pure PVA solution to produce fibers. The obtained electrospinning condition is listed in Table 1. In the case of the PVA/S-ESM blend solution, the electrospinning condition was changed accordingly as also shown in Table 1. The humidity was maintained in all experiments.

2.5 Characterizing

The morphology of the nanofibers was examined by field emission environmental scanning electron microscope (FE-SEM, Hitachi S4200, Hitachi, Japan). Average fiber diameter and distribution of 50 fibers was determined for every sample by analyzing microscopy images using Image J software.

3. Results and Discussion

Table 2 shows the moisture regain of S-ESM and PVA powders in both 20% and 70% RH. The S-ESM powders absorbed more water than PVA powders both at 20% and 70% RH. Furthermore, with increasing the humidity, the moisture regain of S-ESM powders was significantly increased compared to the increase of PVA powders. This preliminary result was considered as key point to understand the effect of RH on S-ESM/PVA fiber formation.

The morphology of PVA nanofibers electrospun under 20% and 70% RH was shown in Fig. 1. The fiber diameter which obtained under 20% RH was 345 ± 59 nm, and it slightly decreased to 304 ± 43 nm when the humidity was increased to 70%. It has been reported that the discharge of fiber can be occurred at high RH [12], therefore the jet could be more stretched and resulted in lower fiber diameter.

Processability of the S-ESM/PVA blend solution was described in Table 2. The moisture regain was shown in a graph. The water content under 20% RH and 70% RH was determined for S-ESM and PVA powders.

Table 2 The moisture regain of S-ESM and PVA powders.

<table>
<thead>
<tr>
<th>Water content (%)</th>
<th>Water content (%)</th>
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<tr>
<td>under 20% RH</td>
<td>under 70% RH</td>
</tr>
<tr>
<td>S-ESM powder</td>
<td>5.90</td>
</tr>
<tr>
<td>PVA powder</td>
<td>1.65</td>
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</tbody>
</table>

Fig. 1 FE-SEM photograph of electrospun PVA fibers under (a) 20%RH and (b) 70%RH.
by drawing at various RH levels in Table 3. At 20% RH, the fiber jet was interrupted almost every 7 minutes because the needle tip was clogged due to high concentration. The impulsive force generated by voltage supply could not overcome the surface tension of high viscosity dope. At 30% RH, the fiber jet contacted the collector continuously but sometimes droplets occurred as illustrated in Table 3. At 40% RH, electrospinning of S-ESM/PVA solution looked promising and fibers were formed continuously. At this humidity, the S-ESM could absorb water from surrounding air and may decrease the viscosity of solution. Therefore the impulsive force could overcome the surface tension and results in a stable jet formation.

When electrospinning was carried out at 50% RH, the single stable jet formed fibers continuously, however, many fibers were released into the air and only a few fibers ended up on the collector. At 60–70% RH, the stable jet was directed onto the collector but many fibers returned toward the needle tip. Therefore, no fibers were deposited on the collector. When the RH became higher and higher, the S-ESM absorbed more and more water resulting in significantly decrease of concentration and viscosity. The impulsive force could be easy to overcome the surface tension, thus the jet was stretched too much and also the fiber discharge leaded the fiber to flowing. Figure 2 shows scanning electron micrographs of S-ESM/PVA blend fibers electrospun at RH of 20–50%. All fibers were uniform and without beads. Particles were present on the surface at low RH. With increasing the RH, the particles were gradually invisible. Three fiber morphology factors were considered to be influenced by the humidity. The absorption of moisture from the surrounding air, the evaporation rate of water and viscosity change occurred by moisture uptake. When the S-ESM/PVA solution was spun at low RH, the S-ESM could only absorb little amount of water from the surrounding air, so that the concentration might not be changed during electrospinning. In this condition, the evaporation rate of water is high and solidification of fiber occurred quickly. S-ESM which is low molecular weight, may not generate molecule entanglement thus the S-ESM remained as particles on the fiber. Therefore, the faster water evaporates, the more S-ESM particles will be released onto the surface of the fibers.

Table 4 shows the average fiber diameter (mean ± SD) of S-ESM/PVA fibers at different RH levels measured on the SEM images. The decrease in standard deviation is more obvious at higher humidity levels. S-ESM/PVA fiber diameter of 300 ± 156, 272 ± 112, 274 ± 76, 256 ± 50 nm was observed at RH of 20%, 30%, 40%, and 50%, respectively. This result confirmed when the S-ESM/PVA solution was spun at high RH, the S-ESM absorbed
water easily so that the viscosity of the solution decreased and generate small fiber diameter. Comparing with the diameter of pure PVA fibers, the adding of S-ESM decreases the diameter of blend fiber due to ions effect. It has been reported the conductivity of spinning dope was increased due to the protein formed ions in water [12]. The jet could be more stretched when the conductivity of spinning solution was increased resulting in small fiber diameter. Therefore, the fiber diameter of S-ESM/PVA blend fibers showed smaller values than that of pure PVA at same RH.

Conclusions

S-ESM/PVA fibers were collected sufficiently at 40% RH at the same temperature from the S-ESM/PVA spinning solution with 11.66 wt% solutes concentration, weight ratio of S-ESM:PVA = 40:60. The stable jet and continuous spinning of S-ESM/PVA was not observed at 20% RH. When the S-ESM/PVA solution was spun at 50%–70% RH, the jet became unstable, probably because the S-ESM absorbed more moisture from the surrounding air and also the discharge of fiber leaded the fiber flowing. The morphology observation showed the S-ESM particle was formed on the surface of fiber at the relative humidity lower than 30%. The diameter of S-ESM/PVA blend fiber was decreased with increasing the RH which could be the moisture absorption by the S-ESM. The further experiment needs to be carried out for the S-ESM/PVA solution with different solutes concentration and weigh ratio of S-EM:PVA. The results obtained here can be used to design suitable spinning condition for the production of regenerated ESM nanofibers.

References