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Evaluation of the Electrospinning Manufacturing Process based on the Preparation of PVA Composite Fibres

Abstract

Poly (vinyl alcohol) (PVA) is a highly biocompatible, biodegradable and non-toxic synthetic material. Chitosan and gelatin, as well as PVA, have been widely used materials in recent years owing to their excellent biocompatibility, biodegradability, bacteriostasis and other desired characteristics. In this study, PVA/chitosan and PVA/gelatin nanofibrous composite membranes were fabricated using the electrospinning technique. The volume ratios of the PVA/chitosan and PVA/gelatin solutions were varied (90/10, 80/20, 70/30, 60/40, 50/50, 40/60), and the electrical field was increased from 0.5 to 1 kV/cm. The micro-morphology of the composite membranes was examined by scanning electronic microscopy (SEM) to compare the spinnability of PVA/Chitosan with that of the PVA/Gelatin electrospun membrane. Observation results indicate that when the volume ratio of the PVA/Chitosan and PVA/Gelatin solutions was 80/20, an optimal condition was obtained. SEM photographs of the PVA/Chitosan and PVA/Gelatin membranes demonstrate that PVA/Chitosan and PVA/Gelatin exhibited good spinnability.

Key words: electrospinning, PVA, gelatin, chitosan.

the electrical voltage applied, the tip-to-collector distance and flow rate also play important roles in electrospinning.

Poly (vinyl alcohol) (PVA) [3, 4], a hydrophilic polymer, has excellent chemical and thermal stability and can be easily modified through its hydroxylic groups [5]. Notably, PVA is commercially available in a wide range of molecular weights at low prices. Additionally, PVA is also a highly biocompatible, biodegradable and non toxic synthetic material. Easily manufactured by electrospinning, PVA also has good chemical and thermal stability. Since 1950 [6, 7], PVA has been a common commercial product due to its characteristics, namely that it is easily cross-linked, has high water permeability and is non-toxic.

Chitosan [8 - 10] and gelatin have both become popular materials in recent years due to their excellent biocompatibility, biodegradability, bacteriostasis as well as other favourable properties. Chitosan and gelatin are commonly used in clinical applications, such as wound healing, scaffolds for vascular grafts and drug delivery. Unfortunately, gelatin and chitosan in a water system cannot be spun by electrospinning. Since the spinnability of chitosan and gelatin is not high, another synthetic biodegradable polymer, PVA, was utilised in this experiment to improve the spinnability of chitosan and gelatin. Notably, PVA is a biocompatible and biodegradable synthetic material that is non-toxic. It is easily manufactured because it dissolves easily in water at

80 °C. This study attempted to improve the spinnability of chitosan and gelatin by using PVA.

Experimental

Materials

The deacetylation degree of chitosan is 85. The solvent of the PVA ($M_n = 8.0 \times 10^4$) solution was deionised water (DW), and that of the chitosan solution was acetic acid (CH_3COOH) (99 - 100%). Gelatin Type A (approx. ~ 300 Bloom, Sigma) was made from porcine skin. Formic acid was utilised as a solvent in the gelatin solution.

Preparation of the electrospinning solution

The PVA was first dissolved in DW; the concentration of the PVA solution was 3 - 10% at 80 - 85 °C. Chitosan solutions were prepared by dissolving chitosan powder in 1% acetic acid. The PVA solution and the chitosan solution were blended at different ratios (90:10, 80:20, 70:30, 60:40, 50:50 and 40:60) at room temperature.

The PVA solution blended with 8% gelatin solution at different volume ratios (100:0, 90:10, 80:20, 70:30 and 60:40)

Table 1. Electrospinning parameters.

High-voltage power, kV	Collector distance, cm	Flow rate, ml/h
11 - 15	10 - 12	0.75

Introduction

Electrospinning [1, 2] is recognised as an efficient means of fabricating submicron-sized fibres. Up to now various polymers have been electrospun into ultrafine fibres that are as thin as several nanometers. The fibres generated by electrospinning form a porous membrane with a high specific surface area, high porosity and very small pores. Therefore nanofibres are promising materials for use in numerous biomedical applications such as tissue engineering, medical prostheses, wound dressing, drug delivery and artificial organs. Important parameters of the electrospinning process include the properties of the polymer solution such as molecular weight, viscosity, conductivity and surface tension. However,

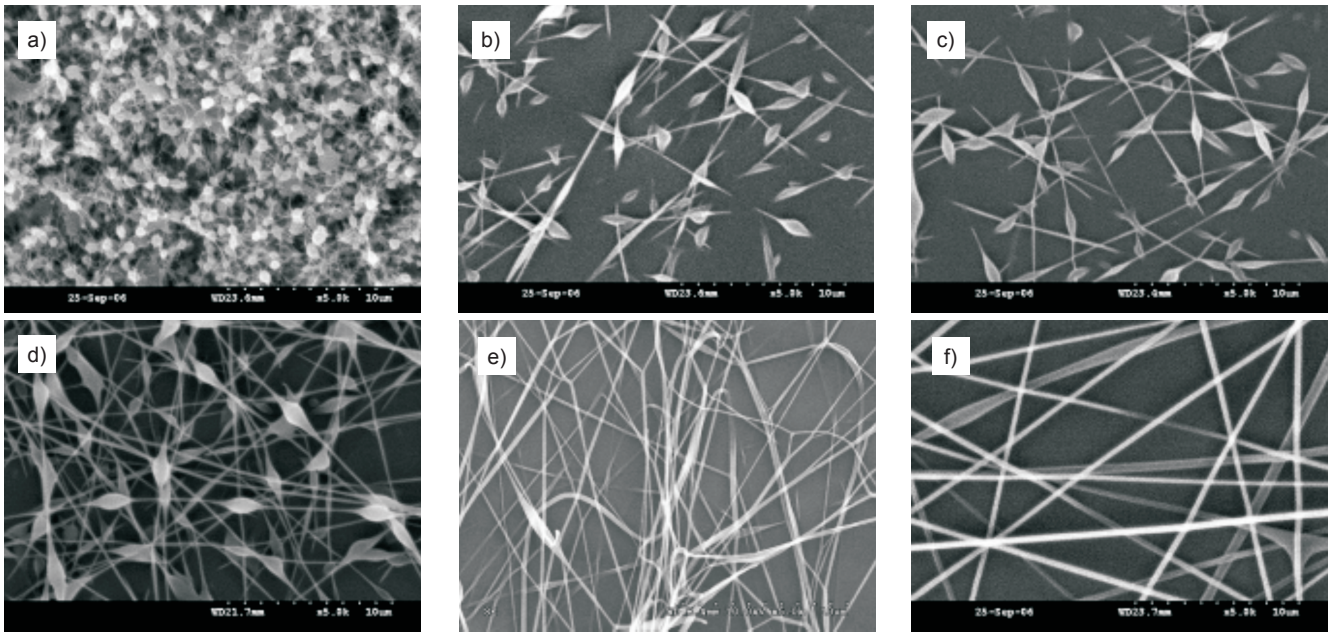


Figure 1. SEM photographs of PVA electrospun membranes at various concent.: 5000×; A) 3%, B) 4%, C) 6%, D) 8%, E) 9% and F) 10%.

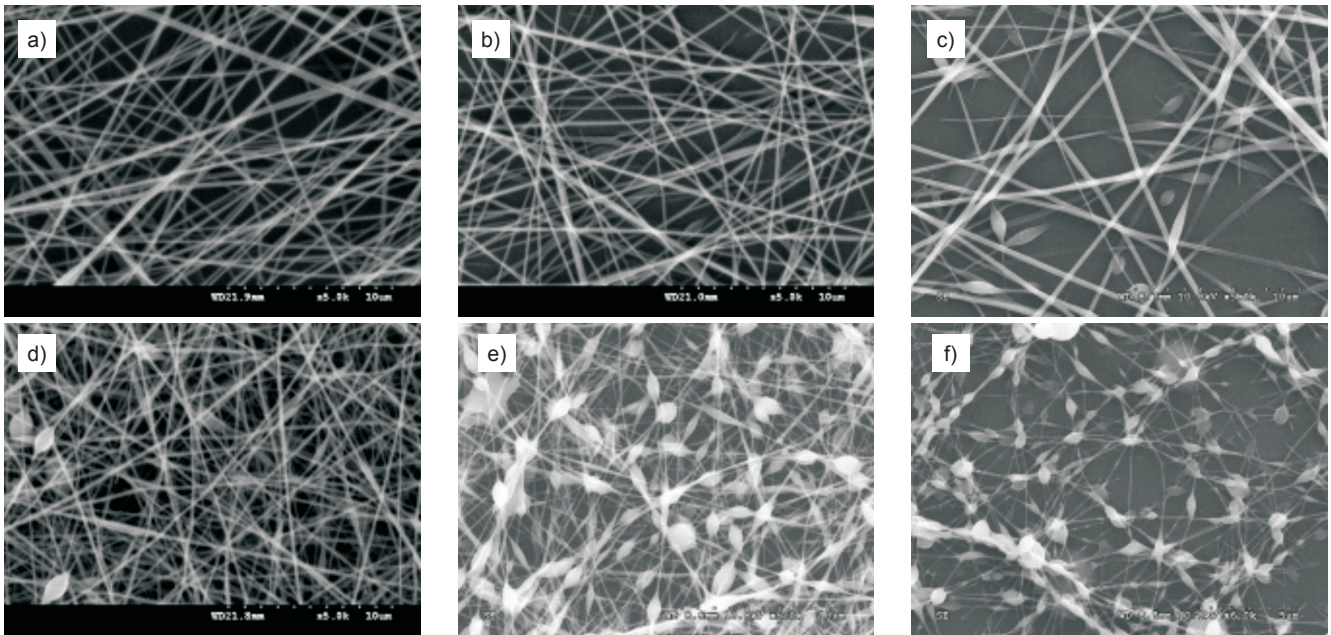


Figure 2. SEM photographs of electrospun PVA/chitosan membranes at various volume ratios: 5000×, A) 90/10, B) 80/20, C) 70/30, D) 60/40, E) 50/50 and F) 40/60.

at room temperature was used to prepare the secondary electrospinning solution.

Electrospinning apparatus

Electrospinning was performed at room temperature. The polymer solution was drawn from a capillary, and the droplet at the tip of the capillary was forced out by a metering pump and electrostatic charge. Fibres formed when the solvent evaporated in air. These dried fibres were collected on a conducting mesh. The collector was placed 10 – 12 cm away from the tips and a voltage of 11 – 15 kV was

applied to the capillary through a high-voltage power supply. The collecting mesh was grounded. The parameters of the electrospinning are shown in **Table 1**.

Results and discussion

Polymer concentration

Figure 1 shows SEM photographs of the PVA solutions at different concentrations (3%, 4%, 6%, 8%, 9% and 10%). The diameters of the electrospun fibre in **Figure 1** (F) were 470 - 660 nm. The beads of electrospun fibre gradually de-

creased when the PVA concentration increased. Additional beads were found in membranes at low concentrations. However, a uniform fibre structure formed at a high PVA concentration because the viscosity of the PVA solution increased as the concentration increased. Therefore, the effectiveness of electrospinning can be improved. When the PVA concentration in the solution was < 3%, beads were easily generated during electrospinning. When this concentration exceeded 10%, a high viscosity was obtained. Hence, the jet would become unstable, and the spinnability of electrospun fibres decreased.

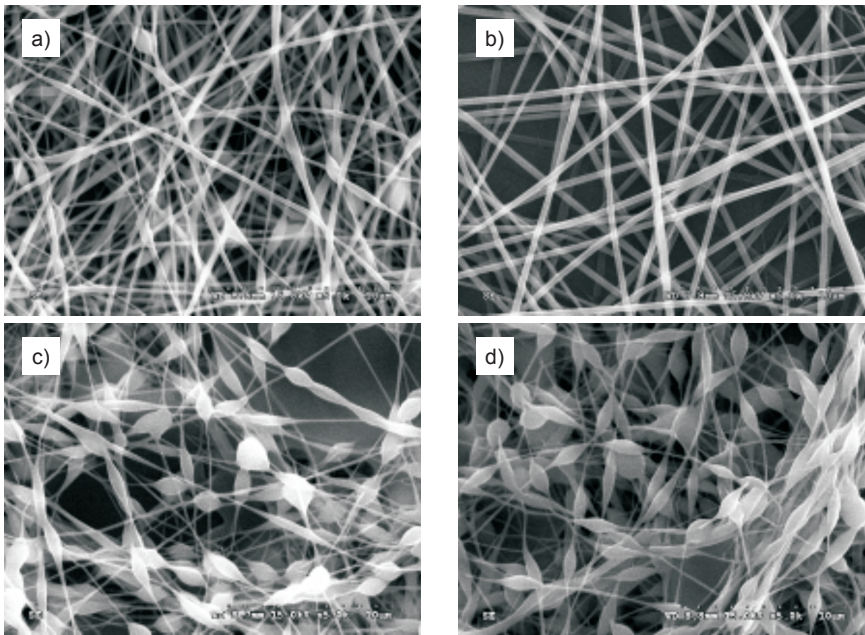


Figure 3. SEM photographs of electrospun PVA/gelatin membranes at various volume ratios: 5000 \times , A) 90/10, B) 80/20, C) 70/30 and D)60/40.

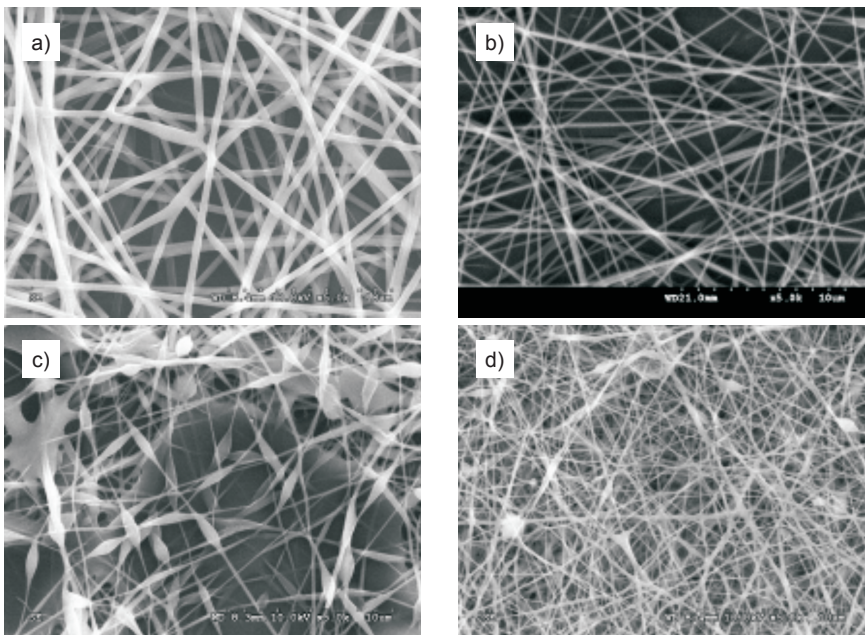


Figure 4. SEM photographs of a nanofibre in various electric fields (PVA/chitosan = 80/20): A) 0.50 kV/cm, B) 0.67 kV/cm, C) 0.83 kV/cm and D) 1.00 kV/cm.

Effect of blend volume ratio

In previous studies, when the addition of cationic and anionic polyelectrolytes increases, the conductivity of a polymer solution increases. Therefore, the traction force of electrospinning increased and the diameter of the electrospun membrane decreased. In this study, the solvent used for electrospinning the PVA/chitosan blend was acetic acid. As chitosan is a cationic polysaccharide with amino groups, it can be dissolved under acidic conditions. **Figure 2** shows SEM images of the PVA/chitosan membranes, whose

diameter was 330 - 600 nm. These images indicate that the diameter of the electrospun membrane declined when the volume ratio of the chitosan solution in the electrospinning solution increased. Chitosan, an ionic polyelectrolyte with a high charge density, was present on the surface of the jet ejected during electrospinning. As the charge carried by the jet increased, the jet became extremely elongated in the electrical field. Excess charges in the jet caused self-repulsion. These phenomena explain why the fibre diameter decreased as the chitosan volume

ratio in the blended solution increased. Thus, as the charge density increased, the diameters of final fibres decreased. Beads were generated by electrospinning when the chitosan volume ratios were increased in the blended solution (**Figure 2**).

Figure 3 presents SEM photographs of the PVA/gelatin membranes at various volume ratios; their fibre diameters were 470 - 630 nm. The PVA/gelatin nanofibre membrane was spun at various volume ratios. As the ratio of the gelatin solution increased, the number of beads and droplets formed increased. At a low volume ratio (< 50/50), the electrospun nanofibres could not be spun by electrospinning. When the ratio of the gelatin solution exceeded 50%, nanofibres could not be spun.

In this work, the optimal electrospinning parameters for PVA/Chitosan and PVA/Gelatin included a blended solution volume ratio of 80/20.

Effect of the electric field

In this investigation, the PVA/chitosan and PVA/gelatin blended solutions were fixed at a volume ratio of 80:20 and subjected to various electrical fields. **Figure 4** shows SEM images of the PVA/chitosan blended solution with various electrical fields. As the electrical field increased, the diameter of fibres decreased. However, beads were easily generated by electrospinning as the electrical fields increased.

Figure 5 shows SEM images of the PVA/gelatin blended solution subjected to various electrical fields; the diameter of electrospun fibres was 310 - 650 nm. The fibre size decreased as the electric field increased. However, when the electrical field exceeded 0.83 kV/cm, the beads and droplets reduced the uniformity of the electrospun nanofibre membranes. Under a high electrical field (> 0.83 kV/cm), the number of beads and droplets increased as the electrical field increased. The optimal electrical field for PVA /chitosan achieved by electrospinning was 0.67 kV/cm, and the best electrical field for PVA/gelatin attained by electrospinning was 0.83 kV/cm.

Conclusions

When the PVA spinning solution had a low concentration (below 3 %), nanofibres could not be spun into fibres. Conversely, this work obtained uniform fibres without beads when the PVA solution was 10%. Thus, PVA improved the

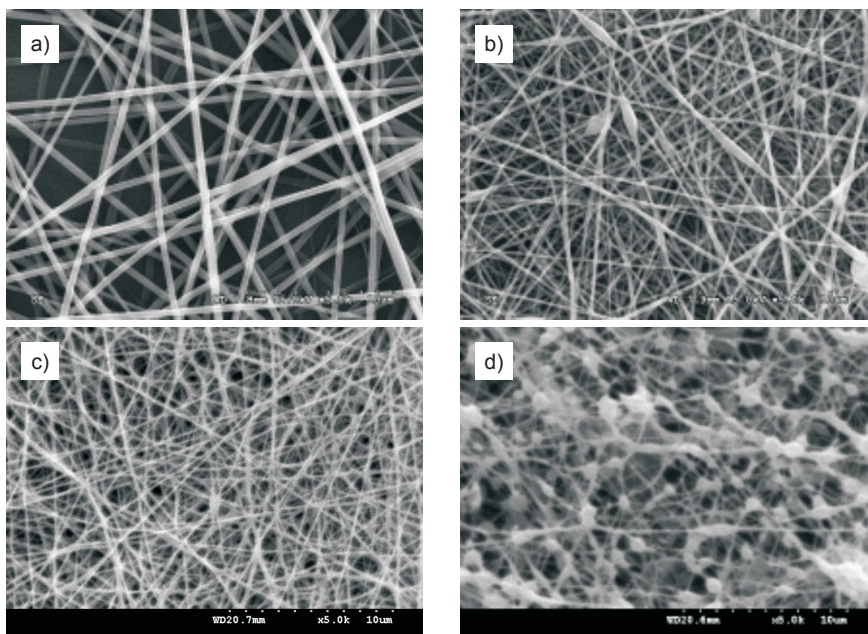


Figure 5. SEM photographs of a nanofibre in various electric fields (PVA/gelatin = 80/20): A) 0.50 kV/cm, B) 0.67 kV/cm, C) 0.83 kV/cm and D) 1.00 kV/cm.

spinnability of chitosan and gelatin. The morphology and diameter of fibres were dominated by the PVA/chitosan blend volume ratio. The diameter of fibres decreased as the chitosan volume ratio in the blended solution increased. Furthermore, beads were generated by electrospinning when the chitosan volume ratios in the blended solution increased. A uniform PVA/gelatin electrospun membrane was obtained at a volume ratio of 80/20. As the electrical fields increased, the diameter of the PVA/chitosan fibres decreased, and beads were easily formed by electrospinning. The size of PVA/gelatin fibres decreased as the electrical field increased. However, for an electrical field exceeding 0.83 kV/cm, beads and droplets reduced the uniformity of the electrospun nanofibre membranes; when the electrical field was increased to a substantial size (> 0.83 kV/cm), the number of beads and droplets increased. This study demonstrates that PVA enhances the spinnability of gelatin and chitosan. The electrospinning of PVA/chitosan and PVA/gelatin is optimised when the volume ratio of either blended solution is 80/20, and when the electrical fields are 0.67 kV/cm and 0.83 kV/cm, respectively.

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Faculty of Textile Engineering and Environmental Protection

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