NEEDLELESS ELECTROSPINNING OF SILK FIBROIN/POLYCAPROLACTONE BLEND NANOFIBRES

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Abstract

In this study, composite electrospun fibres consisting of silk fibroin and polycaprolactone was fabricated by needleless electrospinning method. The electrospinning of silk fibroin/ polycaprolactone blends with different composition ratios was performed with formic acid as a spinning solvent. The effects of blend ratio of silk fibroin/polycaprolactone in spinning solution is investigated as a function of the properties of spinning solution, the morphology of electrospun fibres and the spinning performance of electrospinning process. Result showed that an increase in the weight ratio of polycaprolactone in spinning solution produces a significant effect on the fibre diameter of the electrospun fibre and the spinning performance of process. With an increase in the amount of polycaprolactone in spinning solution decreasing the fibre diameter and the spinning performance of electrospining process. The silk fibroin/ polycaprolactone blend fibres had diameters ranging from 200 to 1100 nm.

Keywords : needleless electrospinning, silk fibroin, polycaprolactone

1. INTRODUCTION

Electrospinning is a simple but effective method to produce polymer fibres with diameter in the range from several micrometers down to tens of nanometers, depending on the polymer and processing conditions. electrospinning technology can be divided into two branches as needle electrospinning and needleless electrospinning. Needle electrospinning is based on less productive capillary spinners with a low production rate. Needleless electrospinning technologies are based on highly productive jet creation from the surface of free liquid by self-organization [1]. For example, Jirsak et al. [2] invented a needleless electrospinning system using a roller as the fibre generator, which was commercialized by Elmarco Co. (Czech Republic) with the brand name “Nanospider™”. The roller electrospinning device contains a rotating cylinder electrode, which is partially immersed in a polymer solution reservoir. When the roller slowly rotates, the polymer solution is loaded onto the upper roller surface. Upon applying a high voltage to the electrospinning system, a number of solution jets are simultaneously generated from the surface of the rotating spinning electrode, thereby improving fibre productivity [3].

Silk fibroin is a candidate material for biomedical applications because it has good biological compatibility and oxygen and water vapour permeability, in addition to being biodegradable and having minimal inflammatory reactions. Silk fibroin is used in various areas, such as cosmetics, medical materials for human health and food additives [4-6]. Previous studies showed that silk fibroin can be dissolved in a mixture of formic acid and calcium chloride and it can be spun into nanofibres by the needleless electrospinning method [7-8]. The silk electrospun fibre sheet is brittle in the dry state and it would be unsuitable for practical use. However, the properties of the fibre sheet can be can be improved by blending with other synthetic polymers. In this experiment, polycaprolactone was selected for blending with silk solution. This is due to biocompatibility and good mechanical properties of polycaprolactone. The aim of this work is to fabricate a silk/polycaprolactone blend fibres by needleless electrospinning method. The effect of blend ratio of silk/polycaprolactone in a spinning solution is investigated as a function of the properties of spinning solution, the morphology of electrospun fibres and the spinning performance of electrospinning process.

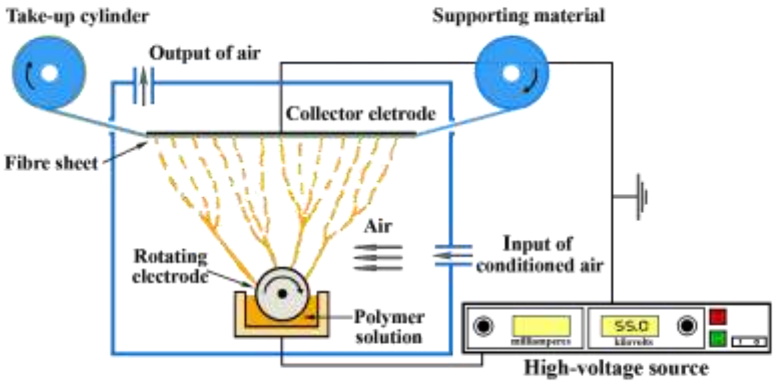
2. MATERIALS AND METHODS

Thai silk cocoons of *Bombyx mori* Linn. silkworms (Nang-Noi Srisakate 1) were obtained from Amphoe Mueang Chan, Si Sa Ket Province, Thailand. Polycaprolactone (Mw 80,000 g/mol) was purchased from Sigma Aldrich. The chemicals used for the preparation of the spinning solutions were calcium chloride (Fluka AG, Switzerland) and 98% formic acid (Penta, Czech Republic). Silk solutions (SF) was prepared by dissolving the degummed silk fibres in a mixture of formic acid and calcium chloride. The silk fibroin concentration was fixed at 12 wt%. Silk fibroin/polycaprolactone blend fibres sheets were prepared by electrospinning the mixture of each silk fibroin solution and 20 wt% of polycaprolactone (PCL), which were dissolved in formic acid. The silk solution was blended with the polycaprolactone solutions in various weight ratios at 9/1, 8/2, 7/3, 6/4 and 5/5 respectively. Subsequently, the blended solution was electrospun at a high voltage of 55 kV. A schematic representation of the equipment used in the experiment is illustrated in Figure 1. The spinning electrode was made of metal wire with 125 mm in length. The electrospun fibres sheets were collected on the backing material moving along the collector electrode by a velocity 10 mm/min. Electrospinning was carried out at a distance of 100 mm; the temperature was 22$\pm$2 ^{O}C and air humidity was 40$\pm$2%.

Conductivity, surface tension and viscosity of the solutions were measured by a CON 510 Bench Conductivity/TDS Meter (Eutech Instruments), a Tensiometer (Krüss K9) and a HAKKE RotoVisco RV1 rheometer. The morphological appearance of the electrospun fibres was observed with a scanning electron microscope (SEM, Vega 3 Tescan). The SEM images were analysed with NIS-Elements AR software. The average fibre diameter and its distribution were determined from 100 random fibres obtained under each spinning condition. The spinning performance of the electrospinning process was calculated from the mass per unit area and width of the electrospun fibre sheets and the velocity of the backing material, the equation is given below [9] :

$$P = \frac{G \times W \ \times V_f}{L_r}$$

Where P is a spinning performance (g/min/m), G is a mass per unit area of electrospun fibres sheet in gram per square metre (g/m^2), W is a width of fibre layer in metre (m), Vf is a take up cylinder speed in metre per minute (m/min) and Lr is a length of spinning electrode in metre (m).



(a)

(b)

Fig. 1 (a) Schematics of needless electrospinning system, (b) a spinning electrode.

3. RESULTS AND DISCUSSION

The results show that the variation of weight ratio of polycaprolactone solution in blend solution had a significant effect on properties of the solution (as shown in Table 1). It is obviously clear that conductivity of spinning solution decrease with increasing ratio of polycaprolactone, while surface tension of the solution was increased. However, all of the silk/polycaprolactone blend solutions still have spinnability with a needleless electrospinning system.

Table 1 Properties of silk/polycaprolactone blend solutions at various weight ratios

silk/polycaprolactone	Conductivity (mS/cm)	Surface tension (mN/m)	Viscosity (Pa s)
10/0	7.45	40.11	0.223
9/1	6.66	42.03	0.231
8/2	6.04	45.53	0.258
7/3	5.30	47.30	0.298
6/4	4.44	49.97	0.349
5/5	3.55	52.07	0.424

SEM micrographs of the electrospun fibre composed of silk fibroin and polycaprolactone at various weight ratios are shown in Fig. 2. Increasing the weight ratio of polycaprolactone in spinning solution influenced fibre diameter of the obtained fibre. The average fibre diameter decreasing from 701 nm to 388 nm with an increase in the weight ratio of polycaprolactone in silk/polycaprolactone solution increased from 10/0 to 5/5, respectively.

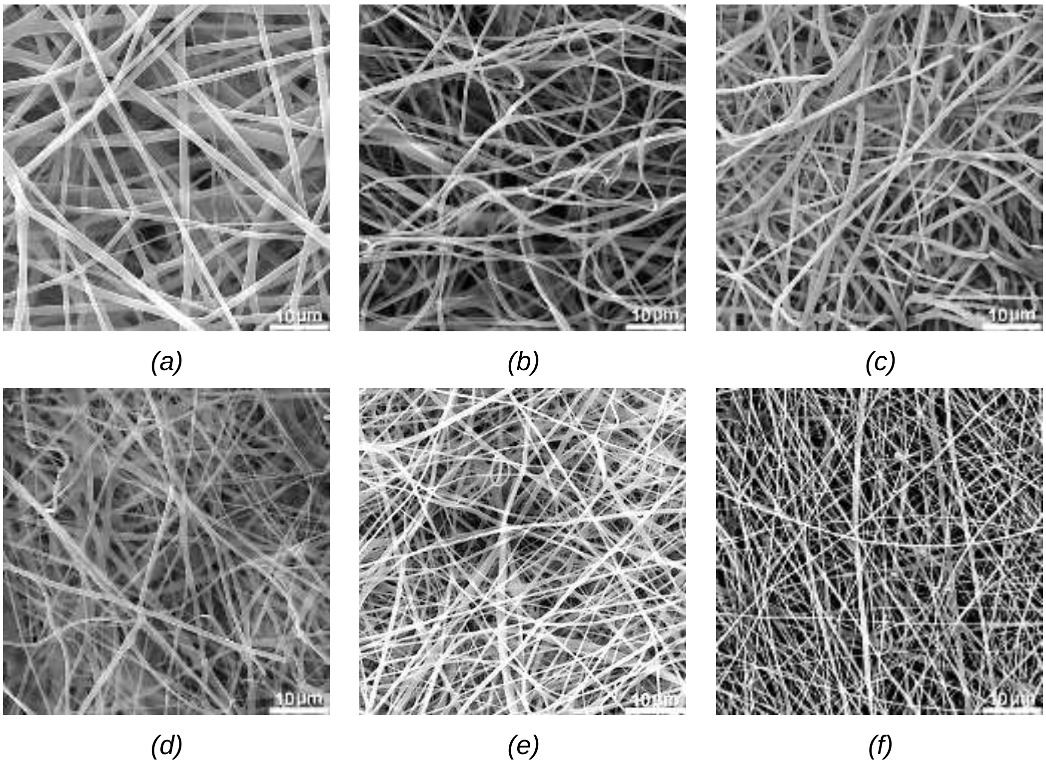


Fig.2 SEM micrographs of SF/PCL blend fibres prepared from SF/PCL solution at various weight ratios. a) 10/0; b) 9/1; c) 8/2; d) 7/3; e) 6/4; f) 5/5

Furthermore, increasing the weight ratio of polycaprolactone affected the spinning performance of the spinning process. The spinning performance of the silk/ polycaprolactone electrospun fibres changed from 1.136 g/min/m to 0.237 g/min/m when the applied voltage was increased (Fig. 3). It is possible that the addition of polycaprolactone cause an increase in surface tension of the solution (as results are shown in Table 1). Thus, the surface tension of the solution might prevent the formation of fibres resulting in a decrease in a spinning performance of the process. However, percent elongations at the breakage of the electrospun fibres sheet increased from 3.50 % to 20.32 %, when the weight ratio of polycaprolactone in silk/polycaprolactone solution increased from 10/0 to 5/5. This indicated that the brittleness of electrospun fibres sheet decrease with increasing ratio of polycaprolactone.

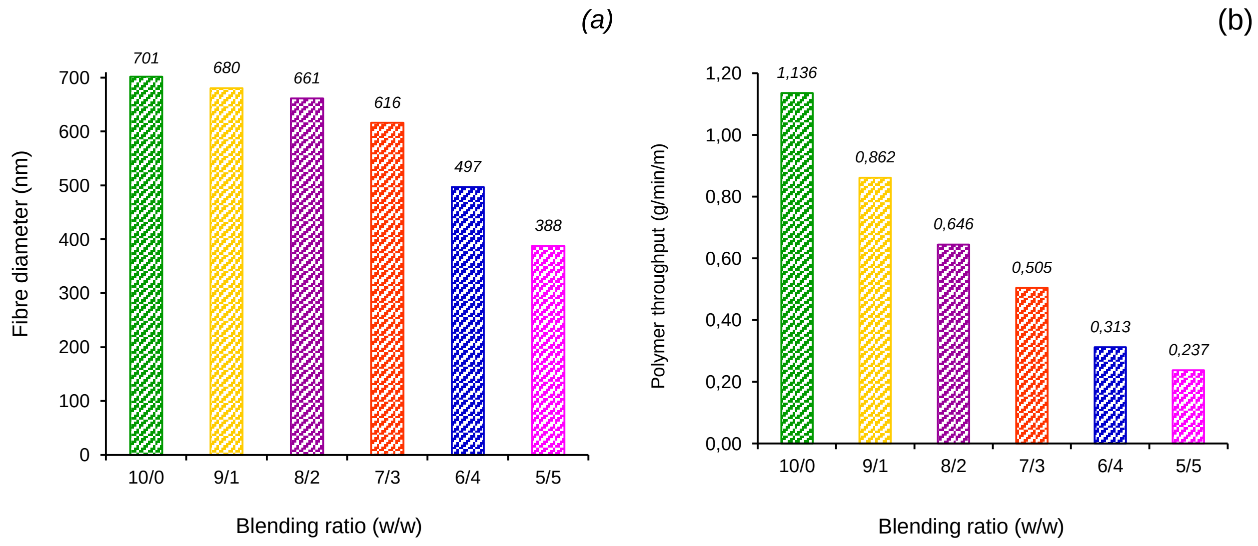


Fig. 3 Effects of blend ratio of SF/PCL on (a) average fibre diameter; (b) spinning performance.

4. CONCLUSION

We prepared silk/polycaprolactone electrospun fibre sheets using needleless electrospinning technique and investigated the effect of blend ratio in the spinning solution on the properties of spinning solution, the morphology of electrospun fibres and the spinning performance of electrospinning process. The results suggested that an amount of polycaprolactone in the blend solution had an effect on the properties of blend solution. Increasing the weight ratio of polycaprolactone in the spinning solution leads to a reduction in the fibre diameter and the spinning performance in the electrospinning process. However, the brittleness of electrospun fibre sheet can be improved by blending with polycaprolactone. About the cytocompatibility and cell behavior onto the blend electrospun fibre sheets will study more in further work.

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LITERATURE

[1] LUKÁŠ, D., SARKAR, A., MARTINOVÁ, L., VODSEDÁLKOVÁ, K., LUBASOVÁ, D., CHALOUPEK, J., POKORNÝ, P., MIKEŠ, P., CHVOJKA, J. and KOMÁREK, M., "Physical principles of electrospinning (Electrospinning as a nano-scale technology of the twenty-first century)", *Textile Progress,* Vol. 41 Issue 2 pp. pages 59-140. 2009.

[2] JIRSAK, O., et al., *A Method of Nanofibers Production from a Polymer Solution Using Electrostatic Spinning and a Device for Carrying Out the Method*, in *EP1673493*. 2005: Czech Republic.

[3] NIU, H., WANG, X. and LIN, T. *Needleless Electrospinning : Developments and Performances*, http://cdn.intechopen.com/pdfs/23290/InTech-Needleless_electrospinning_developments_and_ performances.pdf. Accessed: 2012-05-16.

[4] VEPARI, C., KAPLAN, D.L. "Silk as a biomaterial", *Progress in Polymer Science*, Vol. 32, pp. 991-1007, 2007.

[5] MIN, B-M., LEE, G. KIM, SH., NAM, YS., LEE, TS. and PARK, WH. "Electrospinning of silk fibroin nanofibers and its effect on the adhesion and spreading of normal human keratinocytes and fibroblasts in vitro", *Biomaterials*,Vol. 25 , pp. 1289-1297, 2004.

[6] WANG, Y., KIM, H.J., NOVAKOVIC, G.V. and KAPLAN, D.L., "Stem cell-based tissue engineering with silk biomaterials", *Biomaterials*, Vol. 27, pp. 6064 - 6082 (2006).

[7] ARMATO, U., PRA, I.D., MIGLIARESI, C., MOTTA, A. and KESENCI, K. *Method for the Preparation of a Non-Woven Silk Fibroin Fabrics*. US Patent 7285637, October 23, 2007

[8] SASITHORN, N. and MARTINOVÁ, L., "Effect of Calcium Chloride on Electrospinning of Silk Fibroin Nanofibres", *Proceeding book The 4th RMUTP International Conference,* ISBN 978-974-625-563-9, pp 51-58, 2012.

[9] YENER, F. and JIRSAK, O., "Comparison between the Needle- And Roller Electrospinning of Polyvinylbutyral", *Journal of Nanomaterials*, vol. 2012, 2012.