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Preparation of nylon 6/PLA blend nanofibers by needleless electrospinning

Maneerat Charoenchan[1], Tanapak Metanawin[1] and Siripan Metanawin[2,3*]

[1]Department of Materials and Production Technology Engineering, Faculty of Engineering, King Mongkut's University of Technology North Bangkok, Bangkok 10800, THAILAND

[2]Department of Textile Engineering, Faculty of Engineering, Rajamangala University of Technology Thanyaburi, Pathum Thani 12110, THAILAND

[3]Materials Design and Development (AMDD) Research Unit, Faculty of Engineering, Rajamangala University of Technology Thanyaburi, Pathum Thani 12110, THAILAND

[*]Corresponding author: siripan.m@en.rmutt.ac.th

ABSTRACT

The nylon 6/PLA blend nanofibers have been prepared for the first time by needleless electrospinning. The formic acid (FA) was found to be the co-solvent with dichloromethane (DCM) at a ratio of 3:1 for dissolving nylon 6/PLA blend. The nylon 6/PLA blend solutions in various ratios of PLA (8, 10, and 12 wt%) were studied to prepare nanofiber at the applied voltage range of 25 kV to 30 kV. The morphology images of the fibers were shown by scanning electron microscope (SEM). It was found that the average diameter of the nylon 6/PLA blend fibers became smaller as the applied voltage increased from 25 kV to 30 kV and as the PLA content increased from 8 to 12 wt%. The morphology of the fibers became finer with increasing the PLA content. The morphology of the nylon 6:PLA (20:10) nanofibers presented a smooth surface without the formation of beads with an average diameter of 157 nm at the applied voltage of 25 kV. The high PLA content (12 wt%) at a low applied voltage (25 kV) exhibited the bead formation. In contrast, the bead was formed at the medium PLA concentration (10 wt%) at the applied voltage of 30 kV. Therefore, the high PLA content (12 wt%) at a high applied voltage (30 kV) presented a ribbon-like nanofiber of nylon 6/PLA without bead formation. The particle size distribution obtained from SEM images of the nylon 6/PLA nanofiber was narrow at low PLA contents and became broader at higher PLA concentrations.

Keywords: Nylon 6/PLA blend, Needleless electrospinning, Nanofibers, Nanoweb

INTRODUCTION

A nonwoven web or nanoweb is a sheet or mat of fibers connected by physical entanglements or adhesion between individual fibers without knitting or stitching [1]. Several methods can be used to produce nonwoven or nanoweb, for instance, electrospinning, wet spinning, and molding. Electrospinning (ES) is the most common method used in the fabrication of nanofibers and has found uses in both scientific research work and industrial applications. Furthermore, electrospinning is an effective method as it is a versatile, low-cost, and easy method of producing nanoweb membranes [2, 3]. In recent years, some progress has been made to increase the production rate of ES by exploiting multi-needle spinnerets. However, multi-needle spinnerets also present challenges and do not resolve the problem of needle clogging [4]. For this reason, needleless electrospinning (NLES) systems have been developed to increase nanofiber production rates and overcome the needle-associated challenges of the conventional ES process [5].

Poly(lactic acid) or polylactide (PLA) is a biodegradable, bioabsorbable, and biocompatible thermoplastic aliphatic polyester with good thermal performance. These characteristics, including non-toxicity for humans, make it an ideal material for bioengineering applications. However, the mechanical performance of PLA depends on its shape, molecular weight, and process. For example, the mechanical properties of nanowebs from needleless electrospinning techniques depend on the thickness [6]. Therefore, some researchers were using other polymers to improve the mechanical performance of the nanoweb. Jia Xu et al. [6], study the chitosan/PLA blend micro/nanofibers by electrospinning. It was noticed that the average diameter of the chitosan/PLA blend fibers became larger, and the morphology of the fibers became finer

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with the increase in the content of PLA. Nylon-6 is a versatile material because easily spun (electrospinning) and can dissolve in polar and nonpolar solvents [7]. Nylon 6 nanofiber membranes have been widely used as aerosol filtration media and filters because they can produce uniform fibers and have good mechanical properties, low density, and high porosity [8].

Therefore, in this study, the nylon 6/PLA blend micro/nanofibers have been prepared for the first time by needleless electrospinning. Formic acid (FA) was found to be the co-solvent for electrospinning. The nanoweb morphology was studied using a scanning electron microscope (SEM).

MATERIALS AND METHODS

Materials

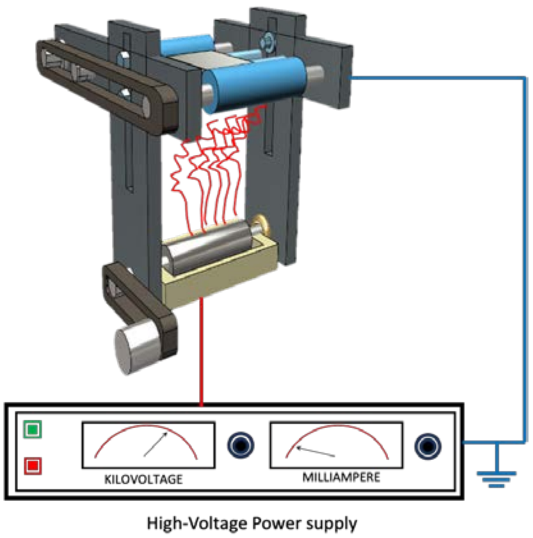
Poly(lactic acid) (PLA, $\bar{M}_w$ of 55.4 kg/mol [9], Ingeo™ Biopolymer 3251D, NatureWorks LLC), nylon 6 (UBE 1013NW8, $\bar{M}_n$ of 13.0 kg/mol [10] Chemicals Asia), dichloromethane (DCM, 99.5%, QRëC™), formic acid (FA, 90%, KemAus™), span bond (75 grams) were used as received.

Table 1 The experimental details of the preparation of the nylon 6:PLA solution.

Sample name	Nylon 6 (wt%)	PLA (wt% of nylon)
Nylon 6:PLA (20:8)	20	8
Nylon 6:PLA (20:10)	20	10
Nylon 6:PLA (20:12)	20	12

Preparation of nylon 6:PLA solution

8.0 g of nylon 6 and difference wt% of poly(lactic acid) (8, 10 and 12 wt%) polymer were dissolved in a 20 cm^3 solution of dichloromethane and formic acid at a ratio (1:3) with a magnetic stirrer at 50 °C for 2 h. The experimental details are shown in Table 1.



Schematic 1 Needleless electrospinning apparatus.

Needleless Electrospinning

The polymer solution was poured into the polymer bath. High voltage was supplied by attaching a clip to the bath. The collector was wrapped with a layer of 75 grams of span bond sheet. The collector-to-bath distance was fixed at 8 cm, as seen in Schematic 1. The electrospinning voltage was applied at 25 and 30 kV. The temperature was 25 °C.

Characterization

The morphology of the nanowebs was observed using a scanning electron microscope (SEM) model SEM-JSM-5410LV from Jeol, Japan. The nanoweb was cut in 9 mm diameter. The substrate was removed and placed on an SEM stub. All the samples were coated with palladium prior to use. The nanowebs diameter was measured with ImageJ software version 1.53e with Java 1.8.0_172.

RESULTS AND DISCUSSION

The effect of the polymer concentration on the nylon 6:PLA nanofibers.

The nylon 6:PLA nanofibers with different PLA ratios were produced by the electrospinning technique. The nylon 6:PLA was dissolved using DCM:FA 3:1. Figure 1 demonstrated SEM images of the nanofiber with the polymer ratios of nylon6:PLA (20:8, 20:10, and 20:12) and their size distribution at the applied voltage 25 kV. It was found that the nanofibers of nylon 6 blended with PLA at the concentration 20:10 presented the uniform fiber size and shape length across the whole region of the spinning area after the electrospinning process, as seen in Figure 1c. In addition, the average diameter of nanofiber nylon 6:PLA (20:10) was 157 nm, which showed a smooth morphology surface without forming beads, as seen in Figure 1d. In contrast, the nylon 6:PLA (20:8) demonstrated the nonuniformity of the nanofibers across the whole spun area, as presented in Figure 1a. Figure 1b presented the average particle size distribution of nylon 6:PLA (20:8), which was 193 nm and broader than the others. However, the bead formation was found at a high concentration of nylon 6:PLA (20:12), as displayed in Figure 1e. Therefore, the average diameter distribution of the nanofibers decreased with increasing the PLA concentration. The viscosity of the polymer blend solution increased by raising the PLA concentration [11]. The Taylor cone is generally generated and stabilized through the strong interactions between polymer molecules in the solution, resulting in the Taylor cone being stretched into a fine jet. However, increasing the PLA concentration caused

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the instability of the Taylor cone [12], resulting in bead formation and a decrease in fiber diameter [11].

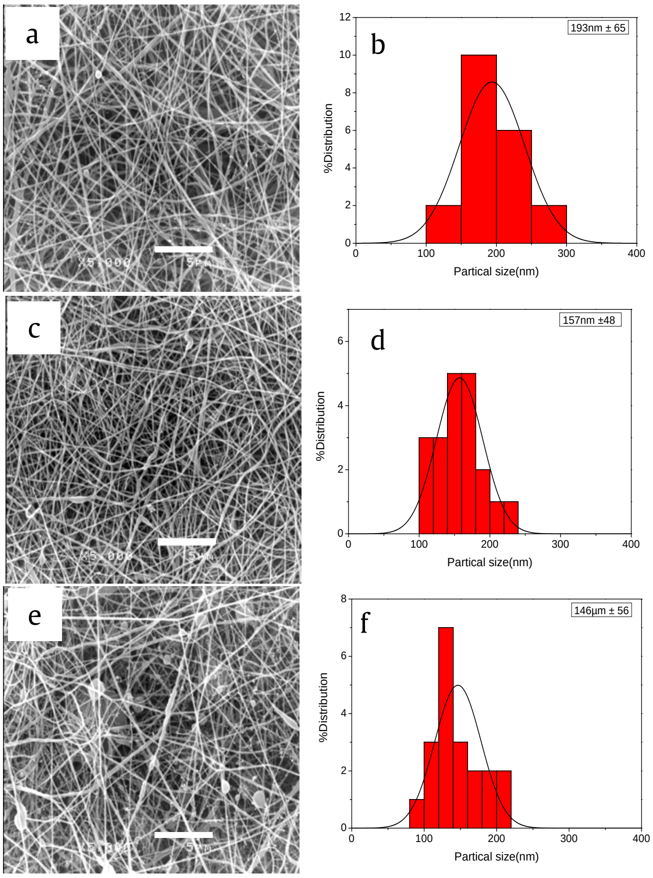

Figure 1 The SEM images of electrospinning nanofiber and their size distribution of (a-b) nylon 6:PLA (20:8) (c-d) nylon 6:PLA, (20:10) (e-f) nylon 6:PLA (20:12) using the solvent ratio DCM:FA (1:3) at the applied voltage 25 kV. The scale bar was 5 μm.

The effect of applied voltage on the nylon 6:PLA nanofibers.

The morphology of nylon 6:PLA with different concentrations of PLA to nylon (20:8, 20:10, and 20:12) and their size distribution at 30 kV were displayed in Figure 2. It was found that the diameter of the nylon 6:PLA (20:8) nanofibers decreased from 193 nm to 143 nm with increasing the applied voltage from 25 kV to 30 kV, as seen in Figures 1a and 2a, respectively. Higher voltage can provide stronger driving forces, facilitate jet formation, promote solution jet elongation, and reduce fiber diameter [13]. However, the diameter of the nylon 6:PLA (20:12) nanofibers was increased from 146 nm to 285 nm when the applied voltage was increased from 25 kV to 30 kV, respectively, as seen in Figure 1e and 2e, respectively. Moreover, the morphology of this nylon 6:PLA (20:12) nanofibers was a ribbon-like shape. A few beats occurred for nylon 6:PLA (20:10) at 30 kV. Therefore, the diameter of nylon 6:PLA (20:10) at 30 kV decreased with the increase in bead formation. The bead was created with increased polymer blend concentration due to the nonlinear interaction of polymer components, resulting in a changing viscosity [11].

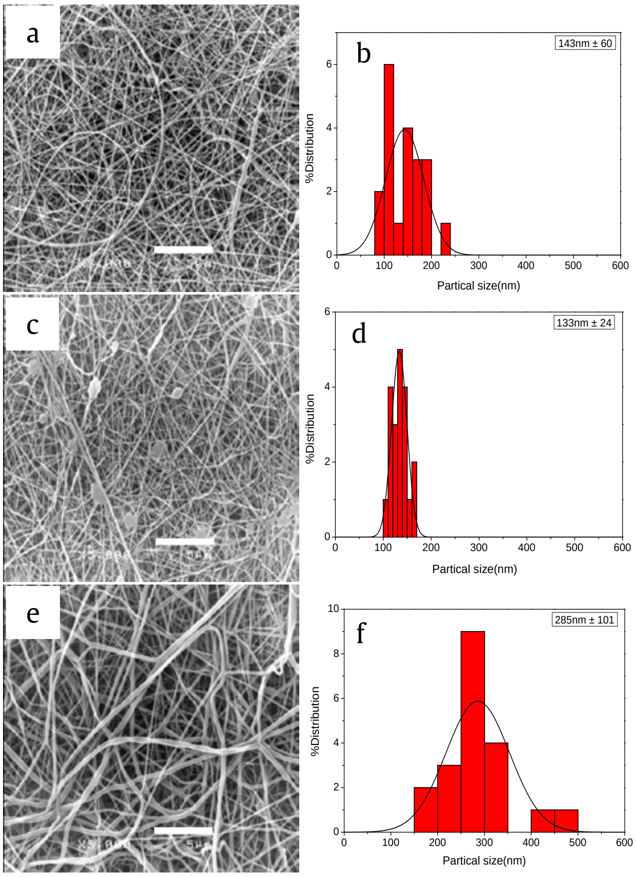

Figure 2 The electrospinning nanofiber mat of (a-b) nylon 6:PLA (20:8) wt% (c-d) nylon 6:PLA, (20:10) wt% (e-f) nylon 6:PLA (20:12) using the solvent ratio DCM:FA (1:3) at the applied voltage 30 kV. The scale bar was 5 μm.

CONCLUSIONS

The nylon/PLA blend micro/nanofibers have been successfully prepared by needleless electrospinning. The mixture of formic acid (FA) and dichloromethane (DCM) at a ratio (1:3) was used as the solvent for electrospinning. The morphology of the fibers was shown by scanning electron microscope (SEM). To study the effect of the polymer concentration of nylon 6:PLA, the conditions of the mixtures are as follows; 20:8, 20:10, and 20:12 at 25 kV. It was found that nanofibers of nylon 6 blended with PLA at the concentration 20:10 presented uniform fiber size and shape length across the whole region of the spinning area after the electrospinning process. The average diameter of nanofibers was 160 nm. Therefore, the diameter of the nanofibers decreased with increasing the PLA concentration. The high concentration of PLA increased the bead formation. The effect of applied voltage on the nylon 6:PLA nanofibers was also studied. It was found that the diameter of the

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nylon 6:PLA nanofibers decreased when increasing the applied voltage from 25 kV to 30 kV, respectively.

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