

## Electrospinning of Poly(L-lactide-co-D, L-lactide)

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**Abstract:** Electrospinning method was used to fabricate poly(L-lactide-co-D,L-lactide) (PLDLA) nanofiber non-woven membranes. The structure and morphology of the electrospun membranes were investigated by a scanning electron microscope (JEOL) after a gold coating. The diameter of the electrospun fiber was measured by Adobe Photoshop 5.0 software from the SEM pictures. SEM images showed that the fiber diameter and the nano-structured morphology depended on the system and processing parameters such as the solution concentration, applied electric field strength, needle tip diameter and humidity.

**Keywords:** *electrospinning, nanofiber, PLDLA, morphology*

### Introduction

A wide variety of biodegradable and biocompatible polymers have been developed for medical applications including synthetic polymers, such as poly(lactide) (PLA), poly(glycolide) (PGA) and their copolymers, poly( $\epsilon$ -caprolactone), poly(ethylene-co-vinyl alcohol), and natural polymers, such as collagen, protein, and fibrinogen [1-7]. Among them, poly(L-lactide-co-D,L-lactide) (PLDLA) has been widely studied for biomedical applications including surgical sutures, substrates for tissue regeneration and carriers for drug and gene delivery due to its good biodegradability and biocompatibility.

Many different techniques have been investigated to produce nanostructured biodegradable articles such as foam, film, microspheres and fibers [8-11]. It has been demonstrated that the molecular structure and morphology of PLA, PGA and their copolymers can play a major role in the degradation and mechanical properties of the final products. Recently, electrospun non-woven nanofiber membranes have been demonstrated in multiple biomedical applications. Electrospinning is recognized as a unique and useful technique to prepare non-woven mats of polymer fibers with diameters ranging from several microns down to less than 100 nm [12]. Medicated ultra-fine fibers can be fabricated by electrospinning a mixture

solution of a drug and a polymer. They are expected to be promising in future biomedical applications, especially postoperative local chemotherapy, because they have numerous advantages, such as improved therapeutic effect, reduced toxicity, convenience and so on.

In general, the process of electrospinning is affected by system parameters, such as polymer molecular weight, molecular weight distribution and solution properties (viscosity, conductivity, surface tension, etc.), process parameters, such as flow rate, electric potential, distance between capillary and collector, motion of collector, etc [13-15]. Therefore, these parameters should be carefully optimized while controlling fiber diameter and its alignment.

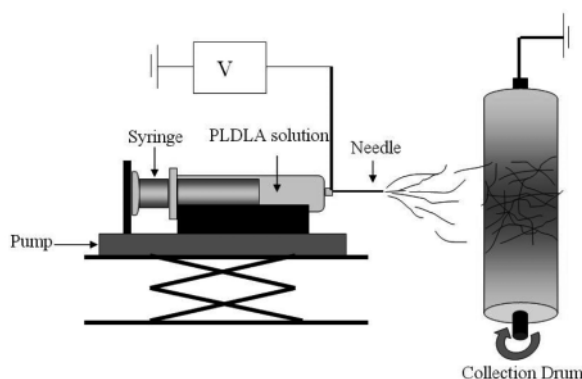
In this work, we have systematically evaluated the effects of the instrument parameters on the morphology of electrospun PLDLA nanofibers, including the solution concentration, applied electric field strength, needle tip diameter, and humidity.

### Experimental

#### Materials

PLDLA (L-lactide:D,L-lactide=70:30, inherent viscosity : 3.3 ~ 4.2 dl/g) was obtained from Boehringer Ingelheim Pharma GmbH & Co. and used without any further purification. Chloroform (Aldrich) was used as a solvent and it was used as received.

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**Figure 1.** Schematic diagram of the electrospinning apparatus.

### Preparation and Characterization of the PLDLA Solutions

PLDLA solutions were prepared by dissolving a measured amount of PLDLA in chloroform at room temperature. The concentrations of the PLDLA solutions were from 0.5 to 3 wt%. The solution viscosity was determined by using a Brookfield DV-II viscometer.

### Electrospinning of the PLDLA Solutions

A schematic diagram of electrospinning device for manufacturing fibers of small diameters is shown in Figure 1. In electrospinning process, a high electric potential was applied to a droplet of PLDLA solution at the tip (ID 0.017~0.045 mm) of a syringe needle. The electrospun PLDLA nanofibers were collected on a target drum which was placed at a distance of 8 cm from the syringe

tip. A voltage of 5~25 kV was applied to the collecting target by a high voltage power supply. The flow rate of polymer solution was 0.002~0.005 mL/min. The relative humidity was varied using a humidifier placed inside of electrospinning box.

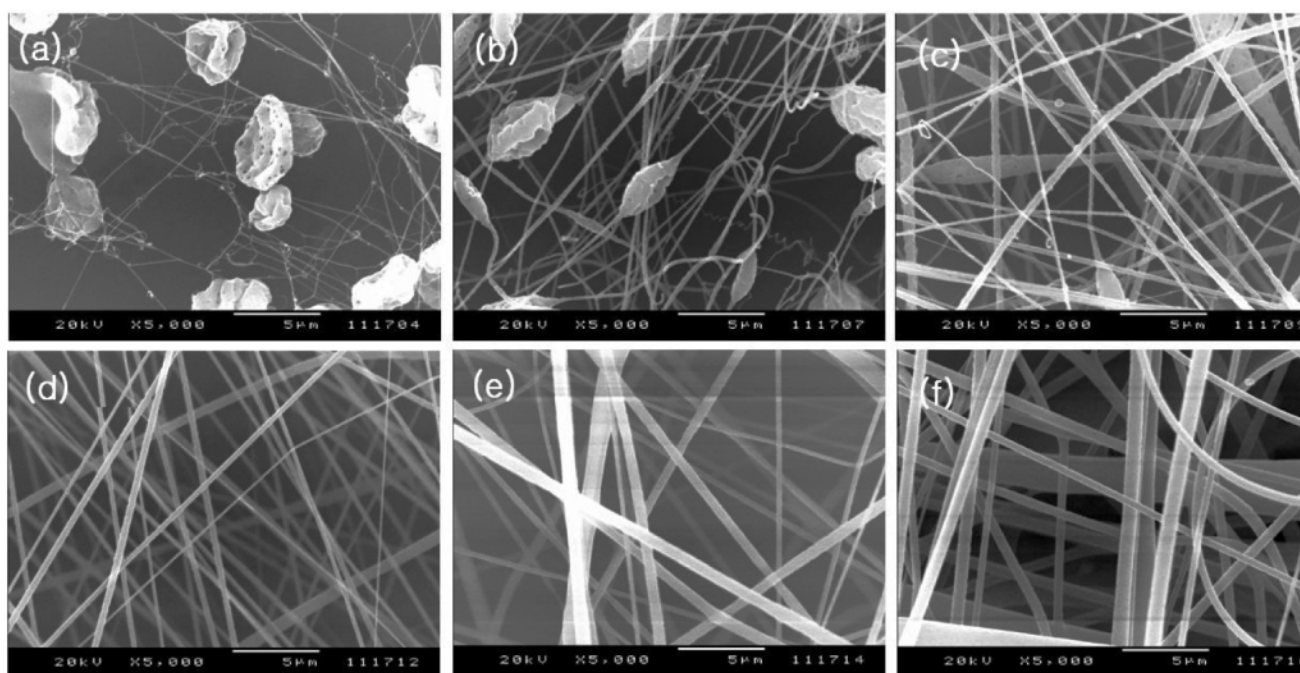
### Characterization

The morphology of the electrospun PLDLA fibers was observed with a scanning electron microscope (JSM-5200) after a gold coating. The average fiber diameter of the electrospun fibers was measured by Adobe Photoshop 5.0 software from the SEM.

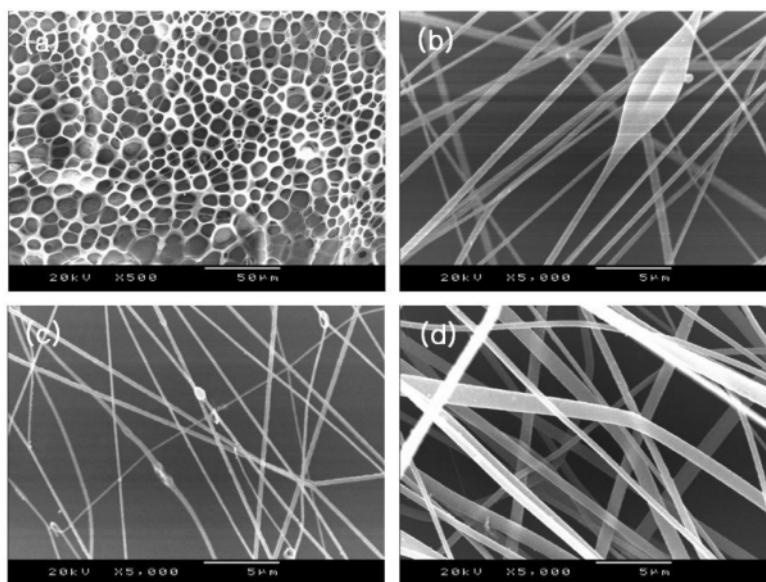
## Results and Discussion

### Effect of Solution Concentration

Changing the polymer solution concentration change the solution viscosity. The viscosity of the 0.5, 1, 1.5, 2, 2.5, and 3 wt% PLDLA solutions in chloroform were found to increase from that of the pure solvent to be 5, 17, 55, 149, 325, and 700 cP respectively. As shown in Figure 2, with an increasing concentration, the morphology was changed from a beaded fiber to a uniform fiber structure, and the fiber diameter was also increased gradually. Thin fibers having big droplets were obtained at a 0.5 wt% solution concentration (Figure 2(a)). Uniform and bead-free fibers were obtained at over 2 wt% concentrations. The average diameter of fiber at 3



**Figure 2.** SEM images of the electrospun fibers from the PLDLA solution with different solution concentrations (voltage=20 kV, flow rate=0.005 mL/min): (a) 0.5 wt%, (b) 1 wt%, (c) 1.5 wt%, (d) 2.0 wt%, (e) 2.5 wt%, and (f) 3.0 wt%.



**Figure 3.** Effects of electric voltage of the 2.0 wt% PLDLA solution on the fiber morphology (flow rate=0.002 mL/min): (a) 5 kV, (b) 10 kV, (c) 15 kV, and (d) 20 kV.

wt% was much larger than that of the fibers spun at the lower concentrations. In electrospinning, the coiled macromolecules in the solution were transformed by an elongational flow of the jet into oriented entangled networks that persisted with a fiber solidification. Below this concentrations, chain entanglements were insufficient for stabilizing the jet and the contraction of the diameter of the jet driven by a surface tension caused the solution to form beads or beaded fibers. At a high concentration, a viscoelastic force which resisted rapid changes in the fiber shape resulted in a uniform fiber formation. However, it was impossible to electrospin the solution if the concentration or the corresponding viscosity was too high due to the difficulty of a liquid jet formation.

#### Effect of Electric Voltage

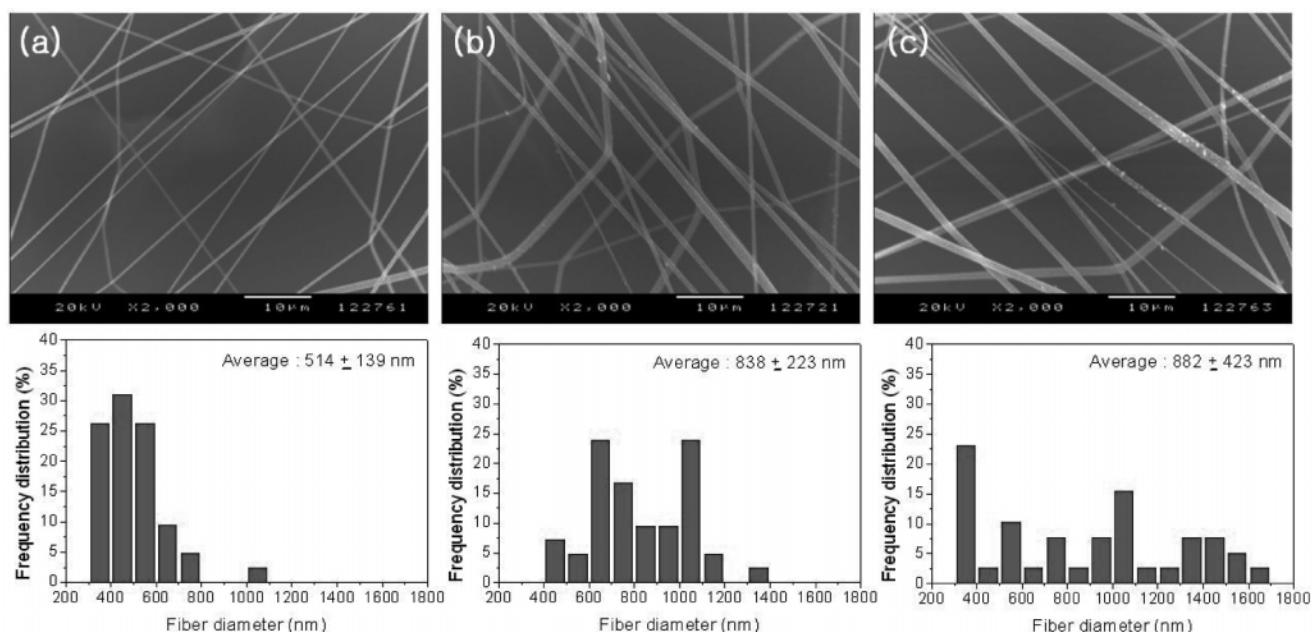
A series of experiments were carried out when the applied voltage was varied from 5 to 25 kV. Results are shown in Figure 3. Weaker voltage, such as 5 kV, was not strong enough to overcome the surface tension and viscoelastic forces of the polymer solution, but at higher voltages at this distance, an electrical discharge would occur. Increasing the applied voltage, i.e., increasing the field strength will increase the electrostatic repulsion force on the fluid jet, which favors a thinner-fiber formation. On the other hand, the solution will be removed from the capillary tip more quickly as the jet is ejected from the Taylor cone. This results in an increase of the fiber diameter. A Corona discharge was observed at a voltage above 25 kV, making electrospinning impossible.

#### Effect of Needle Tip Target Distance

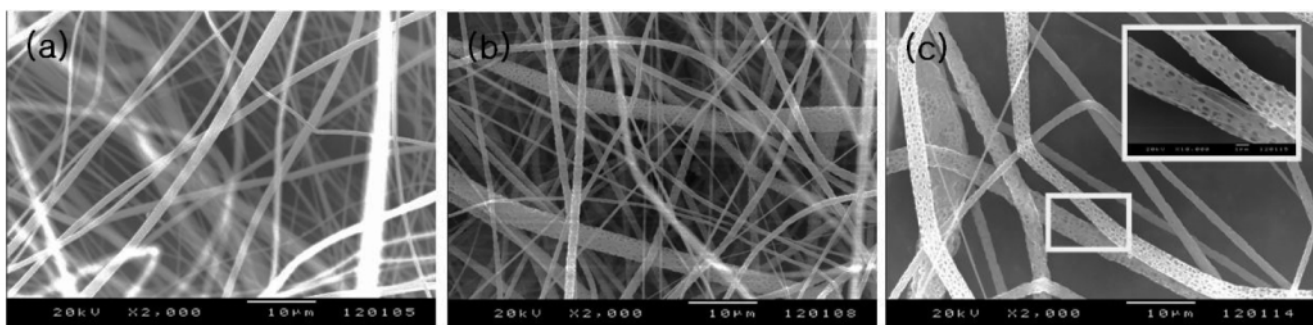
The morphological structure can be changed by changing the needle tip diameter as shown in Figure 4. At the needle tip diameter of 0.045 mm, a uniform fiber structure was observed. But by increasing the needle tip diameter, the average fiber diameter was much larger than that of the fibers spun at a larger needle tip diameter and the fiber diameter distribution was also increased. The change of the needle tip diameter could change the flow rate, and the flow rate could affect electrospinning process. When the flow rate exceeded a critical value, the delivery rate of the solution jet to the capillary tip exceeded the rate at which the solution was removed from the tip by the electric forces. This shift in the mass-balance resulted in a sustained but unstable jet and fibers with a broad distribution for the fiber diameter were formed.

#### Effect of Humidity

The influence of the relative humidity on the morphology of the electrospun PLDLA fiber is shown in Figure 5. At a humidity of 30 %, the fibers were smooth, featureless, and non-porous as shown in Figure 5(a). Increasing the humidity to more than 50 % caused a visible difference in the surface morphology of the fiber. Figures 5(b) and 5(c) show that the fiber surface contains a number of pores randomly distributed on the surface of the fiber, and with increasing the humidity the pores are abundant on the surface of the fiber leaving little space between adjacent pores. The pores are not circular in shape due to the coalescence of smaller pores into larger, non-uniform shaped structures. Figure 5(c) shows that



**Figure 4.** Effect of needle tip diameter of the 2.5 wt% PLDLA solution on the fiber morphology (flow rate=0.005 mL/min, electric voltage=20 kV, tiptarget distance=10 cm): (a) 0.045 mm, (b) 0.025 mm, and (c) 0.017 mm.



**Figure 5.** Effect of humidity of the 2.5 wt% PLDLA solution on the fiber morphology (flow rate=0.005 mL/min, electric voltage=20 kV): (a) 30 %, (b) 50 %, and (c) 70 %.

the pores obtained from the highest achievable humidity, 70 %, are also non-uniform in shape and are slightly larger than those obtained from the 50 % humidity level. Also it is evident that the number of pores on the surface of the fiber increases with increasing humidity. It is concluded that increasing the amount of humidity causes an increase in the number of pores on the surface, the pore diameter, and the pore size distribution.

## Conclusions

PLDLA fibers have been successfully prepared by electrospinning of PLDLA solutions. The morphology of the electrospun fibers was strongly affected by parameters such as polymer concentration, applied voltage, needle tip diameter, and humidity. By increasing the concentration of the PLDLA solution, the morphology was

changed from a beaded fiber to a uniform fiber structure and the fiber diameter was also increased. There was an increase in the average fiber diameter with an increase of the applied electric field and needle tip diameter. Increasing the amount of humidity caused an increase in the number of pores on the surface, the pore diameter, and the pore size distribution.

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