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Systematic parameter study for ultra-fine fiber fabrication via electrospinning process

S-H. Tan[a], R. Inai[a], M. Kotaki[b], S. Ramakrishna[a,c,d,*]

[a]*Department of Mechanical Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117576, Singapore*
[b]*Molecular and Performance Materials Cluster, Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602, Singapore*
[c]*Nanoscience and Nanotechnology Initiative, National University of Singapore, 9 Engineering Drive 1, Singapore 117576, Singapore*
[d]*Division of Bioengineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117576, Singapore*

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Abstract

Processing parameters effects on the morphology such as fiber diameter and its uniformity of electrospun polymer nanofibers was investigated. A processing map summarized effects of solutions properties and processing conditions on the electrospun nanofiber morphology was obtained. Polymer concentration, its molecular weight, electrical conductivity of solvents were found as dominant parameters to control the morphology. Based on the systematic parameter study, electrospun PLLA fibers as small as 9 nm were successfully produced.

Keywords: Electrospinning; Polymer nanofibers; Systematic parameter study

1. Introduction

Electrospinning is one of the processing techniques to spin polymer fibers with diameter in nanometer scale. This technique, invented in 1934, makes use of an electrical field that is applied across a polymer solution and a collector plate, to force a polymer solution jet out from a small hole [1]. As the solution jet travels, the solvent evaporates and leaves behind a charged polymer fiber, which is elongated by an electrical force and attracted to the collecting plate with an opposing or zero polarity. Till date, many polymers have been successfully electrospun into nanofibers and electrospun polymer nanofibers with diameter as small as 5 nm have been reported in the literature [2]. However, the detailed approach for the achievement was not presented clearly and there still has been a difficulty in electrospinning such ultra-fine nanometer scale polymer fibers. Due to the unusually high porosity in their nanometer scale architecture and large surface area, these ultra-fine polymer nanofibers are of commercial interest, and they are regarded as favorable candidates for many applications such as filtration membrane, tissue engineering scaffolds and protective clothing [3]. As particular interests have been addressed in the tissue engineering, great efforts have been made to study electrospinning of biodegradable polymers [4–11].

It has been found that morphology such as fiber diameter and its uniformity of the electrospun polymer fibers are dependent on many processing parameters. These parameters can be divided into three groups as shown in Table 1. Numerous reports studying the effects of these parameters (solution properties [4,12], processing conditions [12–14], ambient conditions [14]) have been reported and each of the parameters has been found to affect the morphology of the electrospun fibers. Under certain condition, not only uniform fibers but also beads-like formed fibers can be produced by electrospinning. Although the parameters of the electrospinning process have been well analyzed in each of polymers these information has been inadequate enough to support the electrospinning of ultra-fine nanometer scale polymer fibers. A more systematic parametric study is hence required to investigate. In this paper, the solution properties and processing conditions

* Corresponding author. Tel.: +65 6874 6591; fax: +65 6872 5563.
E-mail address: seeram@nus.edu.sg (S. Ramakrishna).

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Table 1
Processing parameters in electrospinning

Solution properties	Viscosity[a]
	Polymer concentration[a]
	Molecular weight of polymer[a]
	Electrical conductivity[a]
	Elasticity
	Surface tension
Processing conditions	Applied voltage[a]
	Distance from needle to collector
	Volume feed rate[a]
	Needle diameter
Ambient conditions	Temperature
	Humidity
	Atmospheric pressure

[a] Processing parameters studied in this paper.

effects on the morphology of electrospun nanofibers were studied to produce ultra-fine polymer fibers without beads.

2. Experimental

The polymers used in the study were poly(L-lactid-*co*-caprolactone) (P(LLA-CL)) (70/30 wt%) with molecular weight (M_w) of 150,000 g/mol, and poly(L-lactid acid) (PLLA) with M_w of 100,000 and 300,000 g/mol. These polymers were dissolved in a few types of solvents, i.e. dichloromethane (DCM), *N*,*N*-dimethylformamide (DMF) and pyridine, with different mixture ratio, at room temperature and atmospheric pressure (Table 2).

The electrical conductivities of the solvents were measured using a conductivity meter (ES-12, Horiba). The viscosities of the polymer solution used in the experiments had also been obtained using a strain controlled rheometer (ARES 100 Force Rebalanced Transducer, Rheometric Scientific).

For the electrospinning process, polymer solution was placed into the syringe with the needle with inner diameter of 0.21 mm. Randomly oriented nanofibers were electrospun by applying the voltage of 10–25 kV to the needle using a high voltage supplier (gamma high voltage research). The grounded plate collector was located at distance from 10 to 15 cm and the polymer solution was loaded at feed rate from 0.1 to 1.5 ml/h by a syringe pump (Fisher Scientific Pte. Ltd).

All electrospun fibers collected were stored in vacuum for at least 24 h to ensure that the solvents were completely vaporized. Finally, in order to determine the morphology of the electrospun fibers, the nanofibers were observed under scanning electron microscope (SEM; JSM-5800LV, JEOL) and transmission electron microscopy (TEM; JEM-2010F FasTEM, JEOL).

3. Results and discussion

3.1. Polymer solution properties

3.1.1. Polymer concentration effect

Five series of polymer solutions with different concentration of PLLA dissolved in DCM/pyridine were prepared as shown in Table 3. Electrospinning results (Fig. 1) showed that the diameter of the electrospun fibers dramatically decreased with decreasing polymer concentration. A minimum polymer concentration to electrospin an uniform fibers was found to be 1.0 wt% and beaded fibers were formed with further decreased polymer concentration. Surface tension effects could be dominant with decreased polymer concentration/solution viscosity and beaded fibers were consequently produced. Hence, despite the capability to shrink the size of the fibers by decreasing the polymer concentration, this success of obtaining finer fibers was compromised by the change of the fiber uniformity.

3.1.2. Molecular weight effect

PLLA with different molecular weights were used in this study, i.e. M_w: 100,000 and 300,000 g/mol. Each of the polymers was dissolved in the pure DCM to determine the minimum concentration to electrospin fibers without beads. Experimental results (Fig. 2) showed that non-uniform fibers were formed more easily with low molecular weight of PLLA (LM-PLLA) than the other. Beads were first observed from LM-PLLA solution at a minimum concentration of 9 wt%, and the diameter of the beaded fibers in a straight portion, not beads portion was 400 ± 50 nm. While

Table 2
Electrical conductivity and viscosity of solvents

Solvents	Mixture ratio of solvents (wt%)	Electrical conductivity (μS/cm)	Dielectric constant	Vapour pressure (at 20 °C) (kPa)	Boiling point (°C)	Viscosity (mPa s)
DCM	–	0.0 (at 22.4 °C)	9.1	47.4[a]	40[a]	0.45
DCM/DMF	70/30	1.7 (at 17.4 °C)	–	–	–	0.64
DMF	–	2.3 (at 17.3 °C)	36.7	0.492[a]	153[a]	0.92[a]
DCM/pyridine	80/20	7.2 (at 22.3 °C)	–	–	–	–
	50/50	13.1 (at 22.2 °C)	–	–	–	0.65
	40/60	13.8 (at 22.1 °C)	–	–	–	–
	20/80	13.2 (at 22.2 °C)	–	–	–	–
Pyridine	–	4.4 (at 22.8 °C)	12.5	2.0[a]	115[a]	0.95[a]

[a] Obtained from Ref. [19–21].

Table 3
PLLA polymer solutions used for processing studies

Polymer	Polymer concentration (wt%)	Solvents	Mixture ration of solvent (wt%)
PLLA	1.25	DCM/pyridine	40/60
	1.75		40/60
	2.5		50/50
	3.5		50/50
	4.0		50/50

with similar diameter, high molecular weight of PLLA (HM-PLLA) solution, at 4.5 wt% in a concentration, was able to produce beads free uniform fibers. In addition, when HM-PLLA was electrospun at a lower polymer concentration of 3.5 wt%, finer uniform nanofibers with diameter of 322 nm were successfully produced.

Molecular weight of the polymer reflects the number of entanglements of polymer chains in a solution, thus solution viscosity. Hence, even when polymer concentration is low, HM-PLLA can maintain enough number of entanglements of the polymer chains, thus sufficient level of solution viscosity to produce a uniform jet during electrospinning and restrain effects of surface tension, which plays a significant role in beads formation on electrospun nanofibers. In summary, polymer molecular weight played an important role in determining the minimum polymer concentration to electrospin fine polymer fibers.

3.1.3. Solvent electrical conductivity effect

For polymer solutions to study effects of solvent electrical conductivity on morphology of electrospun fibers, DCM was used as a main solvent for dissolving P(LLA-CL). DMF or pyridine was also added to increase the conductivity of the polymer solution. Three solvents with different electrical conductivities were used to prepare P(LLA-CL) solution at a fixed polymer concentration of 10 wt%, i.e. DCM with 0.0 μS/cm at 22.4 °C, DCM/DMF (70/30 wt%) with 1.7 μS/cm at 17.4 °C, and DCM/pyridine (50/50 wt%) with 13.1 μS/cm at 22.2 °C (Table 4).

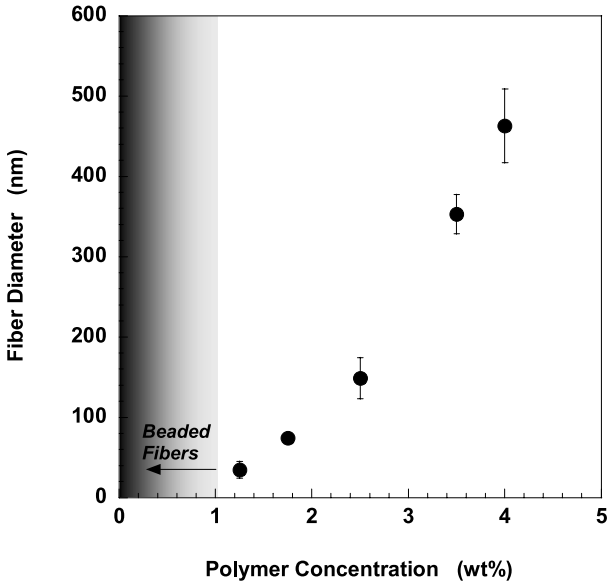


Fig. 1. Polymer concentration effects on the diameter of the electrospun PLLA (M_w: 300 K) fibers.

A comparison of the diameter of the electrospun fibers with the electrical conductivity of the solutions was shown in Fig. 3. There was a significant drop in the diameter of the electrospun polymer fibers when the electrical conductivity of the solution increased. Beads were also observed from solution 1 and this might be due to low conductivity of the solution, which results in insufficient elongation of a jet by electrical force to produce uniform fiber. The beads can be removed using high molecular weight of the polymer. Electrospun polymer nanofibers with the smallest fiber diameter were obtained from solution 3 with the highest electrical conductivity. This interprets that the drop in the size of the fibers was due to the increased electrical conductivity.

To further study conductivity effects, solutions consist of DCM with different ratio of pyridine were prepared (Table 2). Although electrical conductivity increased with an increase of pyridine content, it was saturated when the pyridine ratio is above 50 wt%.

Generally, an electrical conductivity of a solution reflects a charge density on a jet thus elongation level of a jet by an electrical force. Therefore, under the same applied voltage and spinning distance, a solution with a higher electrical conductivity may cause higher elongation of a jet along its axis and thus electrospinning fibers with smaller diameter.

3.2. Processing conditions

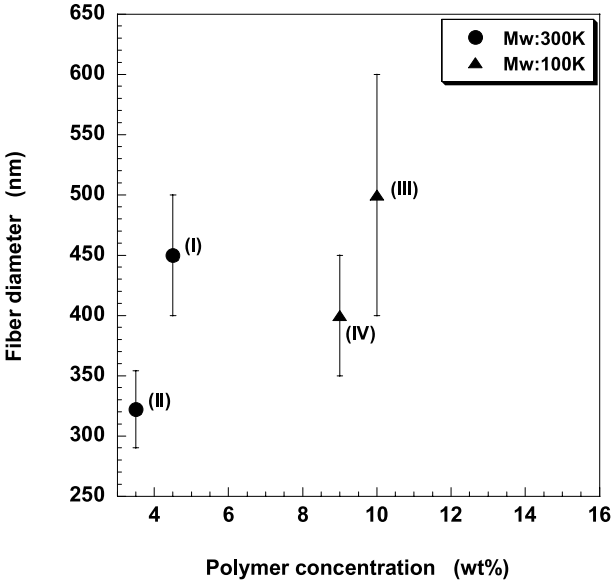
Parameters for processing condition include the voltage and volume feed rate applied during electrospinning. These parameters effects on the morphology of the electrospun fibers were summarized below.

3.2.1. Voltage effect

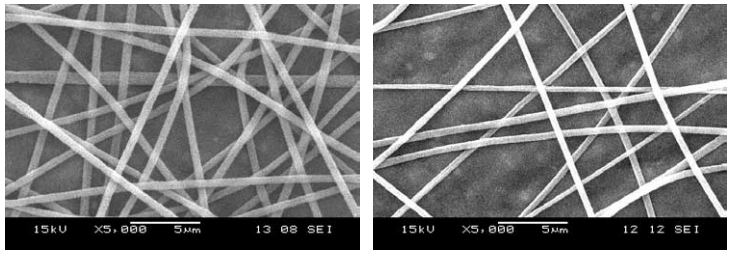
It was already reported that a diameter of electrospun fibers was not significantly affected by an applied voltage [11,14–18]. In this study, in order to confirm the past studies, HM-PLLA solutions was electrospun with two different levels of applied voltage, i.e. minimum and maximum voltage levels to produce a single jet without clogging or splitting. Morphology of electrospun fibers resulted from a single jet, not multiple jets were

Table 4
P(LLA-CL) polymer solutions used for processing studies

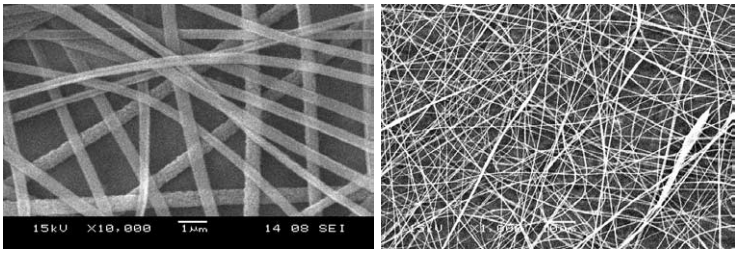
	Polymer	Polymer concentration (wt%)	Solvents	Mixture ratio of solvents (wt%)
Solution 1	P(LLA-CL)	10	DCM	–
Solution 2			DCM/DMF	70/30
Solution 3			DCM/pyridine	50/50



(a)



(I) (III)



(II) (IV)

(b)

Fig. 2. Molecular weight effects on the morphology of the electrospun PLLA fibers.

investigated. Too high voltage is not favorable in this study as it causes multiple jets, which would provide smaller diameter of electrospun fibers, but non-uniform fiber diameter. Fig. 4 clearly shows the trend of voltage effects on morphology of electrospun nanofibers observed using same HM-PLLA solutions used to study polymer concentration effects (Table 3). It was observed that the diameter of the electrospun fibers was not dramatically changed with varied applied voltage. This voltage effects was particularly diminished when the polymer concentration was low. According to past works, higher voltage was reported to induce not only larger diameter but also smaller diameter. Applied voltage may affect some factors such as mass of polymer fed out from a tip of needle, elongation level of a jet by an electrical force, morphology of a jet (a single or multiple jets), etc. A balance among these factors may determine a final diameter of electrospun fibers. It is also noted that beaded fibers have been found to be electrospun

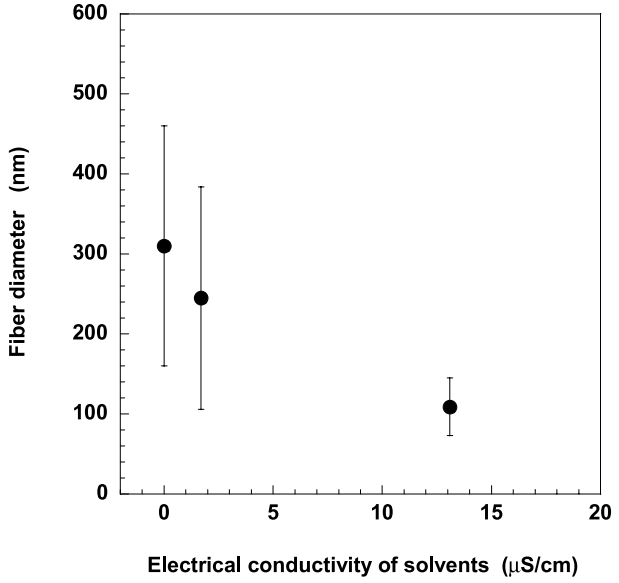


Fig. 3. Solution conductivity effects on the diameter of the electrospun P(LLA-CL) (70/30 wt%) fibers.

with too high level of applied voltage. Although voltage effects show different tendencies, the voltage did not show a significant role in controlling the fiber morphology.

3.2.2. Volume feed rate effect

A similar trend was observed for the effect of volume feed rate on the morphology of electrospun fibers. For the same polymer used, Fig. 5 shows that the diameter of the electrospun HM-PLLA fibers was not significantly changed with varied volume feed rate. The influence due to the volume feed rate also diminished when the polymer concentration is low.

According to parameter studies presented above, polymer concentration, its molecular weight and electrical conductivity of solvents were found to play a significant role in controlling the morphology of the electrospun nanofibers while the voltage and the feed rate were less effective compared to those parameters. Therefore, it can be noted that the morphology of the electrospun nanofibers is primarily affected by polymer concentration, its molecular weight and electrical conductivity of solvents (primary parameters), followed by the voltage and the feed rate (secondary parameters).

3.3. Processing map

Based on the processing parameter studies, all the parameters effects on the morphology of the electrospun nanofibers were summarized in a processing map (Fig. 6). Suitable level of processing parameters must be optimized to electrospin polymers into nanofibers with desired morphology and the parameters levels are dependent on properties of polymers and solvents used in each of electrospinning process. Understanding of the concept how each of processing parameter affect the morphology of the electrospun nanofibers is essential. All the parameters have been divided into two groups; i.e. one with parameters which affect the mass of polymer fed out from a tip of needle, and the other with parameters which affect an electrical force during electrospinning. Polymer concentration, applied voltage and volume feed rate were considered to affect the mass of polymer. Polymer concentration and feed rate directly reflect to the mass of polymer. Increased polymer concentration and feed rate tend to bring more mass of polymer into the polymer jet. It is noteworthy that the minimum polymer concentration to

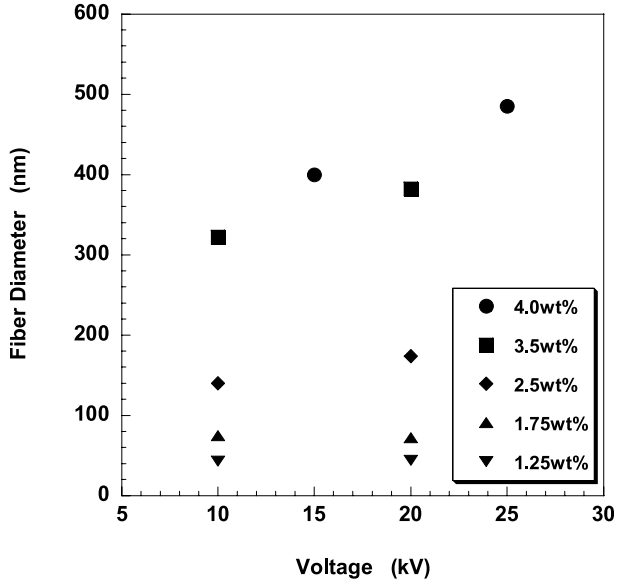


Fig. 4. Applied voltage effects on the diameter of the PLLA (M_w: 300 K) fibers electrospun from solutions with different polymer concentration.

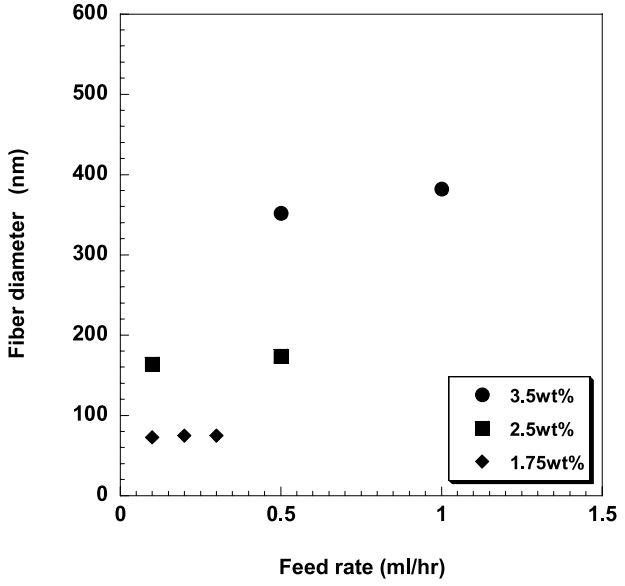


Fig. 5. Volume feed rate effects on the diameter of the PLLA (M_w: 300 K) fibers electrospun from solutions with different polymer concentration.

electrospin uniform fibers was determined by the molecular weight of polymer. High molecular weight of polymer provides enough level of solution viscosity to produce a uniform jet during electrospinning even when polymer concentration is relatively low. Applied voltage reflects to force to pull a solution out from the needle hence higher applied voltage causes more solution coming out. On the other hand, it was considered that solution electrical conductivity and applied voltage affect a charge density thus an electrical force, which acts to elongate a jet during electrospinning. Hence, higher solution electrical conductivity and applied voltage increase the jet elongation. Therefore, it is summarized that electrospun fibers with smaller diameter can be produced with lower polymer concentration, feed rate and applied voltage when the effects of mass of polymer dominates to determine the final diameter of electrospun fibers, while smaller diameter of fibers can be electrospun with higher solution electrical conductivity and applied voltage when the effects of the jet elongation is dominant. For both cases, non-uniformed/beaded fibers were found if the parameters were either too high or too low. In fact, applied voltage affects both the polymer mass and the jet elongation, however, the effects is not as dominant as the other parameters for controlling the morphology of electrospun fibers. It must be noted that polymer concentration, molecular weight and solution electrical conductivity play a primal role in determining the morphology of electrospun fibers. Polymer fibers with smaller diameter can be electrospun with higher electrical conductivity of solution and lower polymer concentration which can be further decreased by higher molecular weight of polymer.

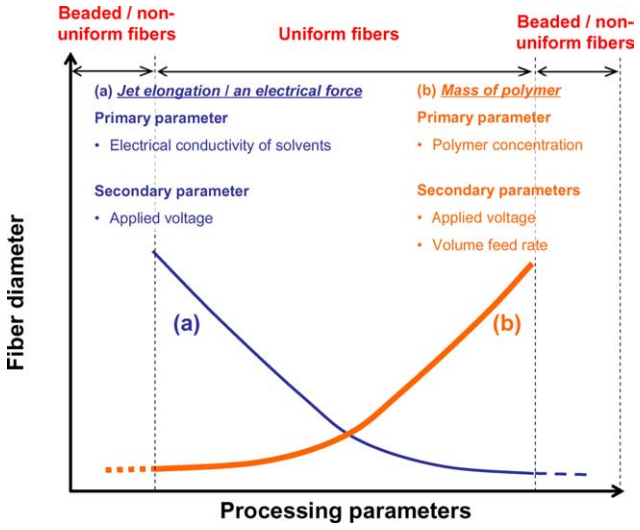
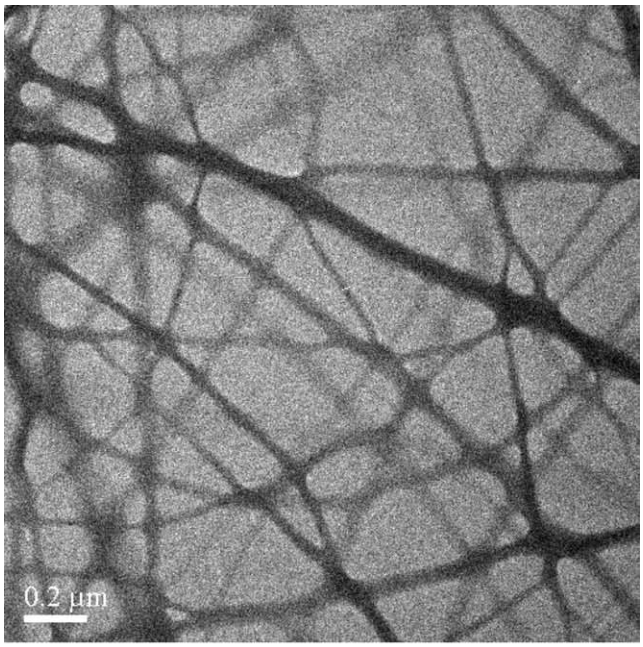


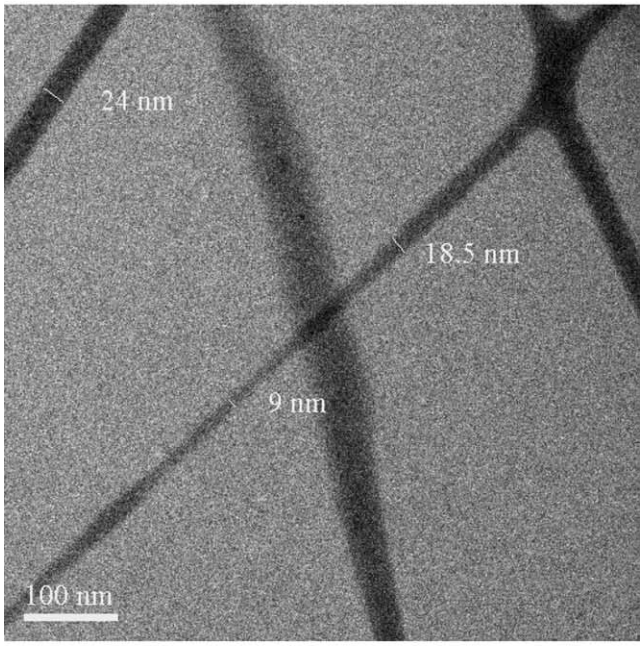
Fig. 6. Processing map obtained based on the systematic parameter study: (a) jet elongation/an electrical force (affected by electrical conductivity of solvents, applied voltage), (b) mass of polymer (affected by polymer concentration, applied voltage, volume feed rate).

3.4. Finest polymer fiber achieved

With the target of electrospinning ultra-fine polymer fibers, all the parameters studied in this paper were optimized in a systematic manner on the basis of the processing map shown in the previous section. As a start,



(a)



(b)

Fig. 7. TEM image of ultra-fine PLLA fibers: (a) at lower magnification, (b) at higher magnification.

HM-PLLA, which can achieve the minimum polymer concentration, was selected and dissolved in solvents with high electrical conductivity which results in a high charge density, thus high elongation of a jet by an electrical force. DCM was used as a main solvent to prepare the polymer solution, and pyridine was added at a proportion to increase the overall conductivity of the solution, giving an overall proportion of DCM/pyridine (20/80 wt%) which allows polymer to dissolve completely and shows maximum range of electrically conductivity (Table 2). The minimum concentration of the polymer to produce a fine solution jet and uniform fibers was then determined at a low concentration of 1 wt%. Finally, when combined with the best processing parameters to electrospin this solution: i.e. smallest available metal needle of inner diameter of 0.21 mm; low volume feed rate of 0.1 ml/h; applied voltage of 10 kV and spinning distance of 100 mm, excellent results were achieved. Ultra-fine polymer fiber as small as 9 nm in diameter was observed under TEM (Fig. 7). The average diameter of these fibers was 19 ± 6 nm.

4. Conclusion

Effects of processing parameters for the polymer solution properties and processing condition on the morphology, i.e. fiber diameter and its uniformity, of electrospun polymer fibers were studied in this paper. As the results, the processing map was obtained, and the polymer concentration, its molecular weight and the solution's electrical conductivity, were found as dominant parameters to control the morphology of electrospun polymer fibers. Based on the systematic parametric study, polymer nanofibers as small as 9 nm in diameter had been successfully produced. This paper has shown the possibility and ease of controlling the morphology of the electrospun polymer fibers.

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References

[1] Formhals A, US Patent 1975504; 1934.
[2] Hou H, Jun Z, Reuning A, Schaper A, Wendorff JH, Greiner A. Macromolecules 2002;35:2429–31.
[3] Hung ZM, Zhang YZ, Kotaki M, Ramakrishna S. Compos Sci Technol 2003;63:2223–53.
[4] Lee KH, Kim HY, Khil MS, Ra YM, Lee DR. Polymer 2003;44:1287–94.
[5] Deitzel JM, Kleinmeyer JD, Hirvonen JK, Tan NCB. Polymer 2001;42:8163–70.
[6] Jaeger R, Schonherr H, Vancso GJ. Macromolecules 1996;29:7634–6.
[7] Buer A, Ugbolue SC, Warner SB. Text Res J 2001;71:323–8.
[8] Zong X, Kim K, Fang D, Ran S, Hsiao BS, Chu B. Polymer 2002;43:4403–12.
[9] Deitzel JM, Kleinmeyer J, Harris D, Tan NCB. Polymer 2001;42:261–72.
[10] Bongnizki M, Czado W, Frese T, Schaper A, Hellwing M, Sterinhart M, et al. Adv Mater 2001;13:70–2.
[11] Mo XM, Xu CY, Kotaki M, Ramakrishna S. Biomaterials 2004;25:1883–90.
[12] Fong H, Chun I, Reneker DH. Polymer 1999;40:4585–92.
[13] Reneker DH, Chun I. Nanotechnology 1995;7:216–23.
[14] Demir MM, Yilgor I, Yilgor E, Erman B. Polymer 2002;43:3303–9.
[15] Buchko CJ, Chen LC, Shen Y, Martin DC. Polymer 1999;40:7397–407.
[16] Katti DS, Kyle W, Robinson KW, Ko FK, Laurencin CT. J Biomed Mater Res Part B: Appl Biomater 2004;70B:286–96.
[17] Kidoaki S, Kwon IK, Matsuda T. Biomaterials 2005;26:37–46.
[18] Fennessey SF, Farris RJ. Polymer 2004;45:4217–25.
[19] Ian MS. Solvent recovery handbook second edition, Blackwell Science, CRC Press, 2002.
[20] Bruno TJ, Svoronos PDN. CRC handbook of basic tables for chemical analysis, CRC Press, 1989.
[21] International programme on chemical safety.