The Effect of Processing Parameters on Formation of Lignosulfonate Fibers Produced using Electrospinning Technology

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Lignosulfonate fibers were produced using electrospinning technology, a method of manufacturing fibrous materials using polymeric solutions, by adding traces of polyethylene oxide to lignosulfonate solutions. Continuous and uniform fibers were obtained under appropriate processing conditions. Solution concentration, applied voltage, flow rate, and syringe-to-collector distance all had effects on fiber formation and diameter. Certain interactive effects among these processing parameters were also observed. Solution concentration was the most significant parameter influencing the diameters of the resulting lignosulfonate fibers. Higher solution concentrations resulted in greater fiber diameters. A broader distribution of fibers was observed as the solution concentration increased. Applied voltage, flow rate, and syringe-to-collector distance had moderate effects on the fiber diameters, and needle gauge had a minor impact on the fiber diameters.

Keywords: Electrospinning; Fiber; Lignosulfonates

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INTRODUCTION

Lignin is a structural component of supporting and conducting tissue in all vascular plants and makes up 15% to 40% of the dry mass of wood. It is not found in its isolated form in nature, but coexists with cellulose as lignin-carbohydrate complex (LCC) in plant cell walls.

Chemicals are traditionally used to extract lignin from plants by breaking the LCC. Alkalis and sulfites are typically used to extract lignin from woody plants. For example, the wood-pulping industry utilizes a sulfite pulping process as one of the ways to remove lignin from the wood pulp before paper is manufactured. This process produces a byproduct called lignosulfonates (Schubert 1965; Crawford 1981; Meister 2002). Different from other types of technical lignin, lignosulfonates are water-soluble.

In recent years, lignin has gained attention in a variety of fields, such as cement manufacturing, ceramics manufacturing, and the production of construction materials. The creation of lignin fibrous materials is one such field of interest. Traditional fiber-producing technology can successfully produce lignin-based fibers with relatively large fiber diameters on the micrometer scale (Kadla *et al.* 2002; Thunga *et al.* 2014; Zhang and Ogale 2014). However, when the fiber diameter decreases to a sub-micron or nanometer scale, the mechanical properties and the surface-area-to-volume ratio of the fibers can increase substantially (Huang *et al.* 2003), and such fibers have the potential to be used in a variety of applications.

With the development and application of nanotechnology, nanofibers have received increased international attention in recent years. Various methods have been developed to produce nanofibrous materials, such as drawing, phase separation, self-assembly, template synthesis, and electrospinning. Among these, electrospinning technology has the ability to produce long and continuous nanofibers while controlling the fiber dimensions. Moreover, this technology is cost-effective and easy to operate (Ramakrishna *et al*. 2005).

Generally, electrospinning is a technique that uses a high-voltage electric charge to draw continuous and uniform micro- or nanoscale fibers from a liquid, such as a polymer solution or melt. A typical electrospinning apparatus includes a high-voltage power supply, a syringe pump, a syringe, and a plate for fiber collection. The polymer solution is first loaded into the syringe and then ejected from the needle of the syringe by the syringe pump to produce polymer droplets at a constant flow rate. High-voltage power is then applied to the needle, causing the surface of the polymer droplets to begin accumulating a positive charge.

As the applied voltage approaches the threshold voltage, the positive charge increases accordingly; when the charge force becomes greater than the surface tension of the droplets, a jet of liquid erupts from the syringe, and the solvent evaporates such that the diameter of the jet drops instantly. The jet then begins to bend and become thinner and longer, leading to the formation of fibers (Yarin *et al*. 2001; Frenot and Chronakis 2003; Subbiah *et al*. 2005; Teo and Ramakrishna 2006).

Various types of polymers have been used in fiber production using electrospinning technology, including natural polymers such as silk fibroin (Min *et al*. 2004), gelatin (Zhang *et al*. 2005), chitosan (Ohkawa *et al*. 2004), lignin (Dallmeyer *et al*. 2010; Ago *et al*. 2012; Teng *et al*. 2013; Salas *et al*. 2014; Poursorkhabi *et al*. 2015), cellulose (Kim *et al*. 2006; Han *et al*. 2008), and hemicellulose (Gan *et al*. 2013). Dallmeyer *et al.* (2010) used seven different types of technical lignin in electrospinning to produce micro- to sub-microscale fibers. Moreover, Jin *et al.* (2014) used lignosulfonates as the raw material to develop carbon nanofibrous web as the electrodes for sodium ion batteries.

During the electrospinning process, a number of parameters influence the formation of fibers, including the following: a) solution parameters such as concentration, molecular weight, viscosity, surface tension, and conductivity; b) process parameters such as voltage, nature of collectors, flow rate, and syringe-to-collector distance; and c) ambient parameters such as humidity and temperature (Subbiah *et al*. 2005; Bhardwaj and Kundu 2010; Li and Wang 2013).

In contrast to kraft lignin, which has been widely studied in developing fibrous materials, using lignosulfonates as the raw material has been less investigated. However, the water solubility of lignosulfonate could reduce the usage of organic solvents and may lead to different applications. Therefore, in this study, lignosulfonates were used as the raw material in the electrospinning process to produce lignin-based fibers from micro- to sub-microscale.

The parameters that affect the fiber production, including concentration, voltage, syringe-to-collector distance, and flow rate were investigated to explore their individual and possible interactive influences on the surface structure and diameter of fibers. A statistical analysis was conducted to tentatively determine the association between electrospinning processing parameters and the resulting diameters of lignosulfonate fibers.

EXPERIMENTAL

Materials

In this study, lignosulfonates (hardwood lignosulfonic acid sodium salt (HLS), Borregaard, Sarpsborg, Norway; weight average molecular weight M_w = 8000 g/mol) were used as the raw material, and polyethylene oxide (PEO, Acros, New Jersey, USA; M_w = 6 × 10^5 g/mol) was selected as the facilitator for HLS fiber formation, based on a previous study (Dallmeyer *et al*. 2010).

Methods

Lignosulfonate solution preparation

Because HLS is a type of water-soluble polymer, deionized water was used as the solvent for this study. The solutions of HLS and PEO were prepared by mixing the appropriate solutes at various weight ratios. Various concentrations of HLS solution were prepared as follows: vials containing the solutions were sealed tightly, vortexed for approximately 1 min, heated in an oil bath at 80 °C until the solutes were dissolved completely, and finally allowed to cool to room temperature before electrospinning.

Electrospinning operation

Electrospinning was carried out in the vertical direction (Fig. 1) using a 1-mL syringe fitted with four different needle gauges. The needle was connected to the positive terminal of a high-voltage power supply, and a wire from the collector was connected to ground. The processing conditions are summarized in Table 1.

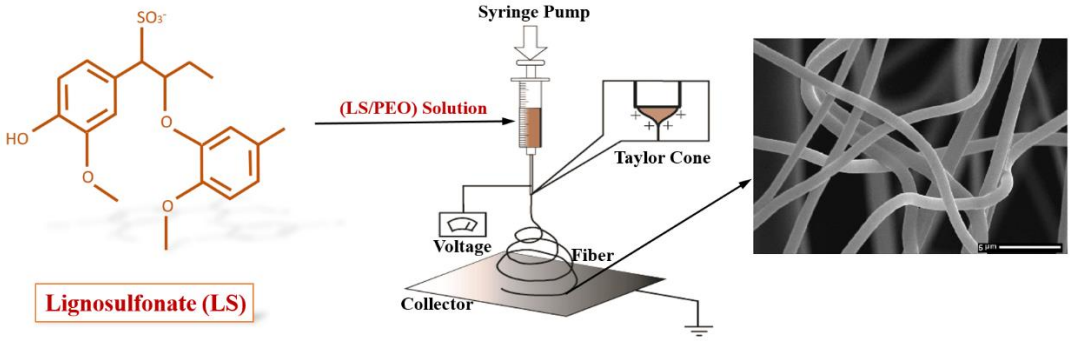


Fig. 1. Schematic of the electrospinning apparatus to produce lignosulfonate fibers

Table 1. Processing Conditions for Electrospinning Operation

Parameters	Range
Concentration of lignin solution	10 to 40%
Applied voltage	5 to 30 kV
Syringe-to-collector distance	15 to 20 cm
Needle gauge	18, 19, 21, and 23 G
Flow rate of solution	0.01 to 0.05 mL/min

Analysis of lignosulfonate fibers

An optical microscope and a scanning electron microscope (SEM, JEOL JSM–5410, Japan) were used to visually inspect the fiber surface structure. The distributions of fiber diameters were obtained by measuring the diameters of 50 HLS fibers for each group. In addition, to investigate the effect of the viscosity of solutions on fiber production, a viscometer (Brookfield AMETEK, USA) was used to measure the viscosity of HLS solutions.

An analysis of variance (ANOVA) ($\alpha = 0.05$) and multiple linear regression analysis were conducted to determine the relationship between the processing parameters and the diameter of fibers using Minitab (Minitab Inc., State College, PA) to gain insight on the individual and correlative effects of the parameters on the fiber diameter.

RESULTS AND DISCUSSION

Lignosulfonate fibers were successfully obtained by electrospinning under appropriate processing conditions. Although various processing conditions were explored, not all of them were suitable for electrospun HLS fibers. The successful results are listed in Table 2, and the effect of each parameter on the diameters of HLS fibers was determined through ANOVA, as shown in Table 3.

According to the ANOVA results, with the exception of the syringe-to-collector distance, each parameter demonstrated a significant effect (p-value $< \alpha = 0.05$) on the fiber diameter. In addition, the solutions not containing PEO failed to produce fibers and instead resulted in electrospray, which is consistent with literature (Dallmeyer *et al*. 2010), and the ratio of HLS: PEO = 97: 3 was found to be the most suitable ratio after preliminary tests. Comparing with other ratios, fibers could be smoothly produced without difficulty by adopting this ratio; therefore, this ratio was used for most of tests in this study.

Fibers were typically obtained when solution concentrations ranged from 10 to 40 wt%, as concentrations below 10 wt% resulted in electrospray and concentrations above 40 wt% produced uneven jetting because of the high viscosity. Because the electropinning with the solution concentration of 15 to 30 wt% enabled smooth fiber production and substantial fiber production compared to the other concentrations. This study primarily emphasized investigating the effects of processing conditions on production of fibers within this range of concentration.

Solution concentrations of 15, 20, 25, and 30 wt% resulted in specific viscosities of 15.9, 32.7, 232.1, and 1370.0, respectively. As shown in Fig. 2(a), a substantial increase in viscosity was observed when the concentration exceeded 25 wt%, which can be attributed to the considerably increasing entanglements in molecular structure (Dallmeyer *et al*. 2010), presenting an exponential trend.

In general, higher concentrations resulted in larger fiber diameters with a power law relationship, as shown in Fig. 2(b), unlike previous work that showed a linear relationship (Dallmeyer *et al*. 2010), in which the formulation and processing conditions were different from this study. Moreover, the distribution of fibers gradually became broader as concentrations were increased, indicating a greater variation in fiber diameter, and also implying less consistent fiber properties.

Table 2. Results of Successfully Electrospun Lignosulfonate Fibers

Concentration of solution (%)	HLS content in solute (%)	Voltage (kV)	Syringe-to-collector dist. (cm)	Needle gauge (G)	Flow rate (mL/min)	Average fiber diameter (μm)	Coefficient of variation (%)
15	97	10.0	15	18	0.01	0.77	36.3
20	93	15.0	15	18	0.01	0.85	27.7
20	95	15.0	15	18	0.01	1.00	26.1
20	97	10.0	10	18	0.01	1.09	41.3
20	97	10.0	15	18	0.01	1.31	40.3
20	97	10.0	15	18	0.03	1.04	37.4
20	97	10.0	20	18	0.03	0.74	31.1
20	97	10.0	20	18	0.05	1.21	26.8
20	97	12.5	15	18	0.01	0.95	49.4
20	97	12.5	15	19	0.01	0.92	42.3
20	97	12.5	15	21	0.01	0.88	32.5
20	97	12.5	15	23	0.01	0.75	36.0
20	97	15.0	15	18	0.01	1.08	31.9
20	97	15.0	15	18	0.03	1.00	31.1
20	97	15.0	15	18	0.05	1.30	26.5
20	97	15.0	20	18	0.03	0.70	26.6
20	97	20.0	10	18	0.01	1.76	41.0
20	97	20.0	15	18	0.01	1.09	41.3
20	97	20.0	15	18	0.03	1.42	36.4
20	97	20.0	15	18	0.05	1.09	41.3
20	97	20.0	20	18	0.01	1.02	28.5
20	97	20.0	20	18	0.01	1.09	29.8
25	97	10.0	15	18	0.01	1.61	31.8
25	97	10.0	15	18	0.03	1.08	21.4
25	97	10.0	20	18	0.01	2.34	31.3
25	97	12.0	15	18	0.01	0.97	56.7
25	97	15.0	15	18	0.01	1.96	28.6
25	97	15.0	15	18	0.03	1.21	21.3
25	97	15.0	15	18	0.05	1.45	37.0
25	97	15.0	20	18	0.01	1.63	43.5
25	97	20.0	20	18	0.01	2.41	28.4
30	97	13.0	15	18	0.01	5.01	20.8
30	97	15.0	15	18	0.01	4.63	33.1
30	97	15.0	20	18	0.01	4.49	25.9
30	97	17.5	15	18	0.01	3.75	35.6
30	97	17.5	20	18	0.01	2.26	19.9
30	97	20.0	15	18	0.01	5.83	11.4
30	97	20.0	20	18	0.01	2.85	15.8

Table 3. Results of ANOVA for Each Parameter

Parameter	p-value
Concentration of HLS solution	< 0.001
Applied voltage	< 0.001
Syringe-to-collector distance	0.879
Needle gauge	0.006
Flow rate of solution	< 0.001

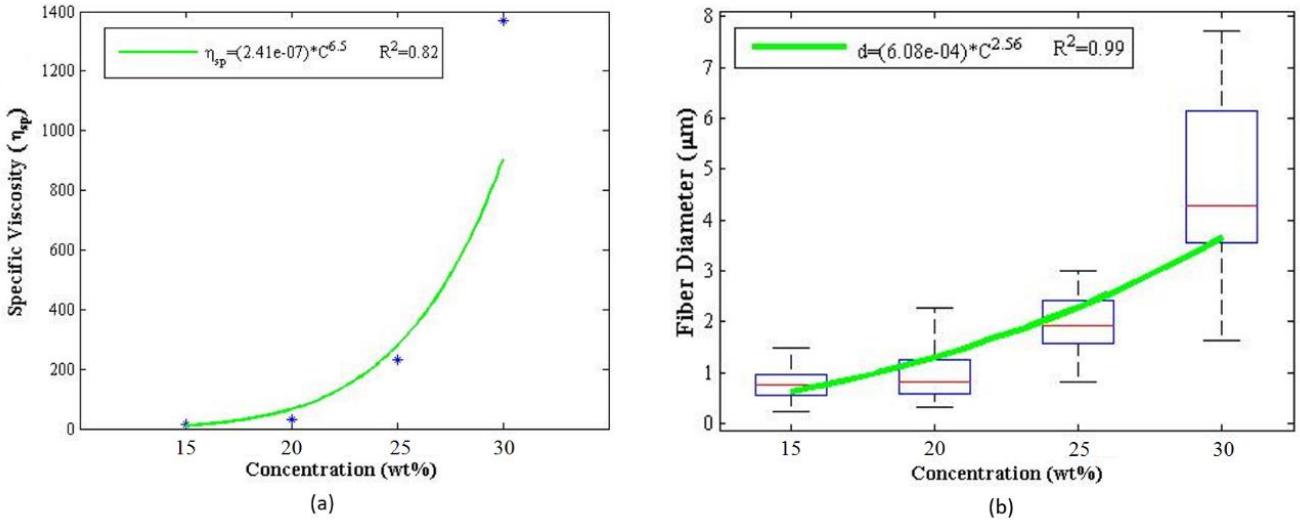


Fig. 2. (a) Plot of the specific viscosity for various solution concentrations; (b) Plot of the fiber diameter for various concentrations (syringe-to-collector distance of 15 cm, flow rate of 0.01 mL/min, and applied voltage of 15 kV)

In addition to solution concentration, the addition of PEO played an important role in fiber formation, which was consistent with previous research (Dallmeyer *et al*. 2010). The amount of added PEO should be adjusted in accordance with the solution concentration, *i.e.*, more PEO content is needed with a lower solution concentration. As the PEO content increased, the fusion of fibers was more commonly observed.

As mentioned in other studies, fibers fuse together when the PEO content is greater than 5% in solution (Kadla *et al*. 2002). Consequently, to obtain smooth fibers with a relatively low percentage of PEO, HLS solution concentrations ranging between 15 and 30 wt% is recommended based on the results of this study. Some speckles were observed on the HLS fiber surfaces; however, further investigation is needed to determine the cause of these speckles.

Other parameters, such as applied voltage, flow rate of solution, and syringe-to-collector distance, also affect the fiber formation (Li and Wang 2013). In particular, a steady applied voltage is crucial during electrospinning (Thompson *et al*. 2007; Yördem *et al*. 2008; Li and Wang 2013), and a specific threshold voltage is essential for the successful formation of fibers. As previously noted, when applying a threshold voltage, the surface of the polymer droplets begins to accumulate a positive charge, gradually forming a Taylor cone and ultimately a jet, leading to the formation of nanofibers (Taylor 1969; Yarin *et al*. 2001; Subbiah *et al*. 2005; Kakade *et al*. 2007). In this study, it was determined that lower solution concentrations required a relatively high threshold voltage, and a longer syringe-to-collector distance required a higher threshold voltage at a concentration of 20 wt%. When the voltage was higher than 20 kV, the jet emitted sparks and the fiber was occasionally scorched. With a higher voltage in these conditions, the initial jet formed a tapered shape instead of a cone shape.

However, according to previous studies, increasing the applied voltage may result in rough fiber surfaces and an increase in beads (Deitzel *et al*. 2001; Reneker and Yarin 2008). The effect of the applied voltage on the diameter of electrospun fibers has remained controversial among researchers.

Although Reneker and Chun (1996) demonstrated that the effect of applied voltage on electrospun PEO fibers is not significant, other researchers have suggested that larger diameter fibers would be produced with higher voltages (Zhang *et al*. 2005). Most researchers suggest that higher voltages would facilitate the formation of smaller diameter fibers (Demir *et al*. 2002; Jun *et al*. 2003; Yuan *et al*. 2004; Kim *et al*. 2006; Gan *et al*. 2013). On the other hand, some researchers believe that the influence of voltage on fiber diameters is correlated with the concentrations of polymer solutions and the distance between the tip and the collector (Yördem *et al*. 2008; Li and Wang 2013).

With applied voltage, the flow rate of solution seemed to have the same effect on fiber formation, in that higher flow rates required higher threshold voltage. However, a flow rate higher than 0.05 mL/min would result in many droplets, as the electrostatic force is not able to draw fibers quickly enough. Nevertheless, HLS fibers could be produced at the flow rate of 0.05 mL/min, with a solution concentration of 20 wt% and a syringe-to-collector distance of 10 cm.

The flow rate influenced the generation of beads during HLS fiber formation: as the flow rate increased, more beads were formed. When the flow rate was 0.05 mL/min and the solution concentration was 25 wt%, a higher number of beads were generated than with a 0.03 mL/min flow rate. No beads were observed with the 0.01 mL/min flow rate. Lower concentrations resulted in more beads at the same flow rates (Fig. 3).

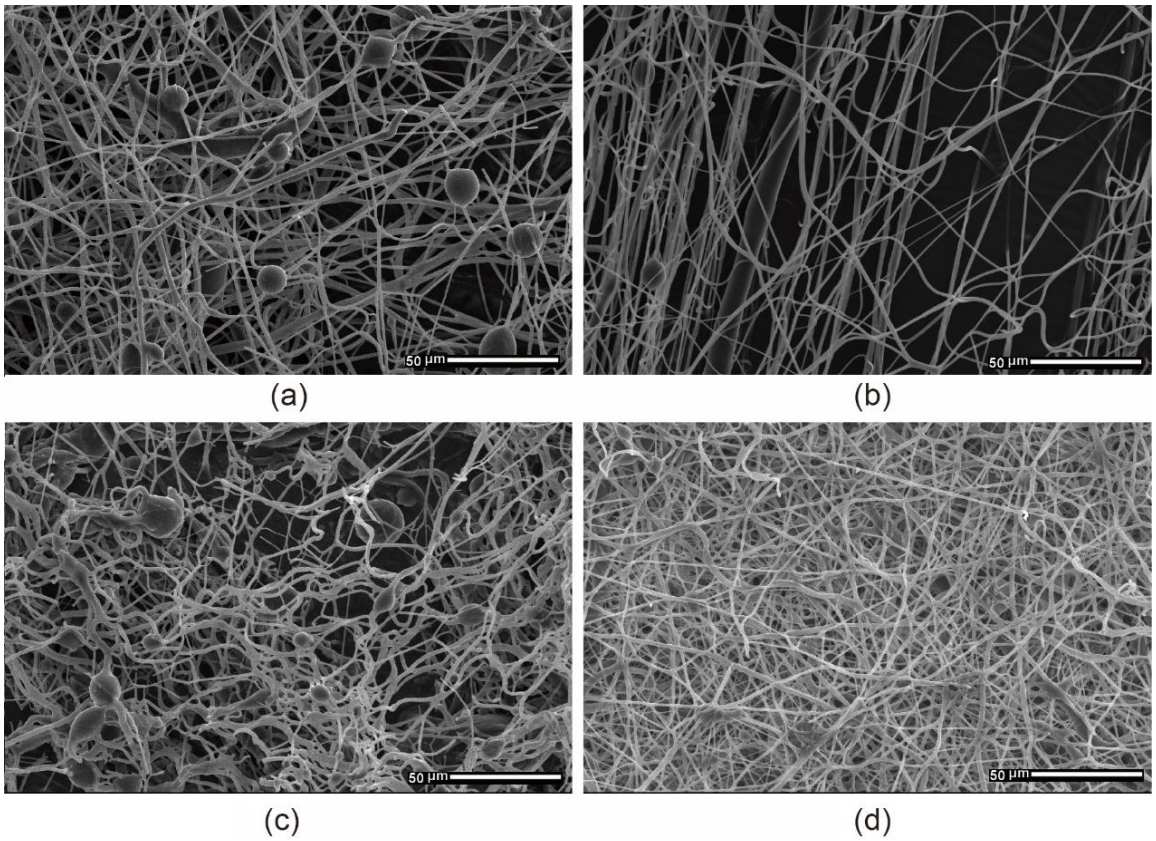


Fig. 3. Fibers made with various processing conditions. (a) and (b): concentration of HLS solution: 25 wt%, HLS: PEO = 97: 3, syringe-to-collector distance of 15 cm; applied voltage of 15 kV; and flow rates of 0.05 mL/min (a) and 0.03 mL/min (b). (c) and (d): concentration of HLS solution: 20 wt%, HLS: PEO = 97: 3; syringe-to-collector distance of 15 cm, applied voltage of 15 kV and flow rates of 0.03 mL/min (c) and 0.01 mL/min (d).

It should be noted that, in this study, the only syringe-to-collector distances that were tested were 15 and 20 cm; and not all adjustments to syringe-to-collector distances resulted in fiber production. The limited available data did not show a significant effect on the diameters of HLS fibers. However, it was previously determined that the syringe-to-collector distance influences the jet radius and the resulting diameters of electrospun fibers for other materials (Thompson *et al*. 2007).

The results from this study indicate that a short syringe-to-collector distance is unsuitable for HLS fiber formation, unless the solution concentration and flow rate are adjusted accordingly. Fibers could not be produced at a short syringe-to-collector distance when a high solution concentration (> 30 wt%) was used. On the other hand, long syringe-to-collector distances created difficulty with fiber collection, as the fibers tended to fall outside of the collector. Unlike the effect of applied voltage, under the same processing conditions, a shorter syringe-to-collector distance resulted in the initial jet forming a tapered shape, which may be attributed to the stronger electrostatic force of the shorter syringe-to-collector distance.

The electrospinning process and the resultant products were very sensitive to the applied operating parameters, such as applied voltage, flow rate of solution, and syringe-to-collector distance; one modified condition required considerable adjustments to other parameters. As a result, some interactive effect could be expected among those processing parameters. According to previous studies, the influence of voltage on fiber diameters is correlated with the concentration of polymer solution and the distance between the tip and the collector (Yördem *et al*. 2008; Li and Wang 2013).

In Fig. 4, HLS fibers of relatively different diameters were produced using various combinations of solution concentrations and applied voltages, implying an interactive effect for these two parameters. However, as shown in Fig. 5, there was no clear trend observed for the interactive effects of voltage, flow rate, and syringe-to-collector distance on the fiber diameters.

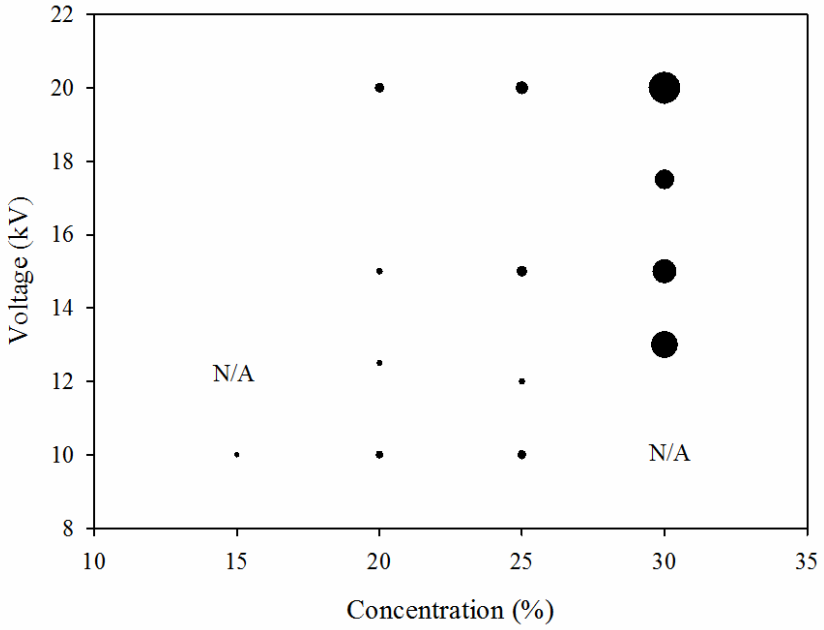


Fig. 4. Resultant fiber diameters from different combination of solution concentration and applied voltage. The larger area indicated larger diameters of fibers.

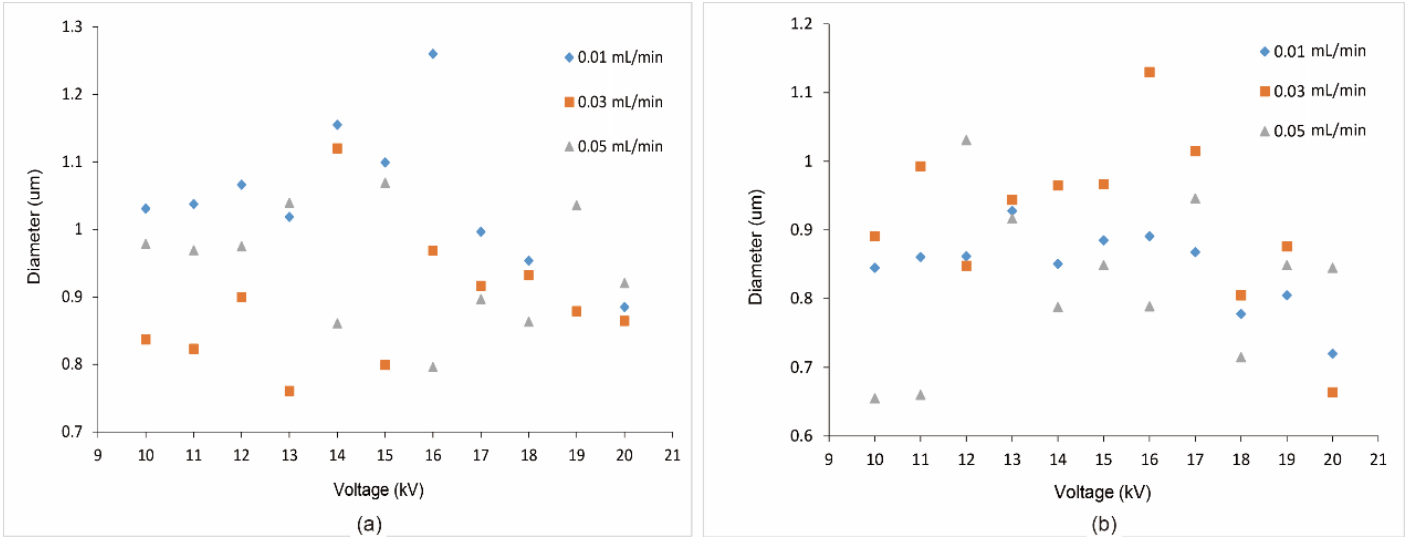
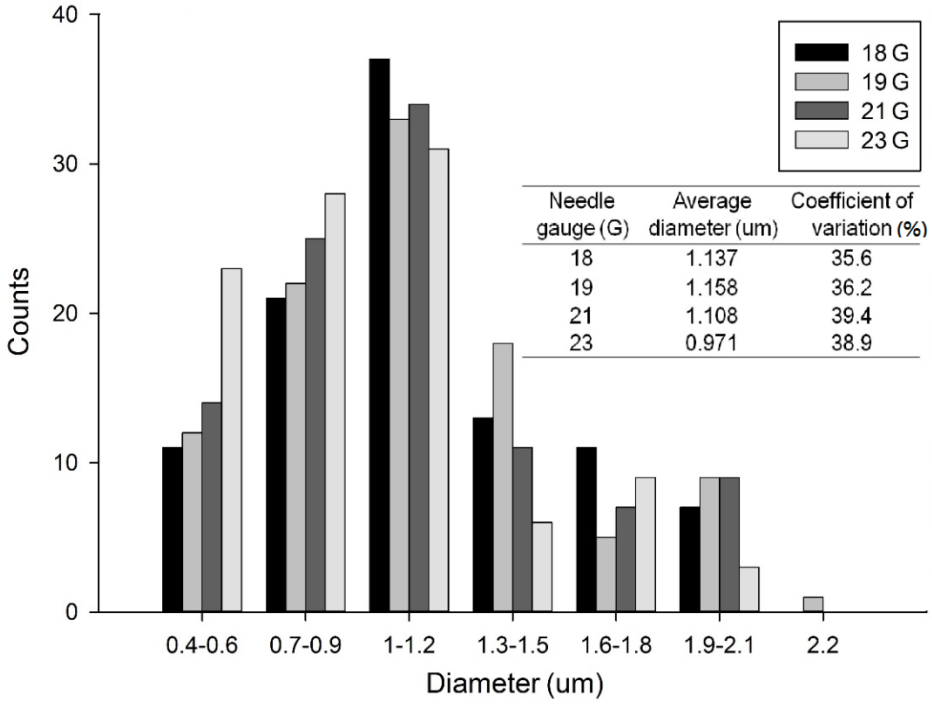


Fig. 5. Effect of applied voltage and flow rate on fiber diameter. (HLS solution concentration of 20 wt%, HLS:PEO = 97:3. (a) syringe-to-collector distance of 10 cm and (b) syringe-to-collector distance of 15 cm.

The diameter distribution of fibers for each group varied using different needle gauges (Fig. 6). As the needle diameter was decreased, the fiber diameter also decreased. The ANOVA results show that, significant differences among groups of different needle gauges were observed, and there were no significant differences between 18, 19, and 21 gauges, but significant difference was found between 23 gauge and any others. This result implies that the needle gauge is only relevant when the size of the inner diameter of the needle is quite small. However, compared with other parameters, needle gauge has a relatively minor effect on fiber diameter.



Needle gauge (G)	Average diameter (um)	Coefficient of variation (%)
18	1.137	35.6
19	1.158	36.2
21	1.108	39.4
23	0.971	38.9

Fig. 6. Distribution of fiber diameters obtained at different needle gauges at solution concentration of 20 wt%

The summarized multiple linear regression formula used in the statistical analyses took the following form,

$$\text{Ln(diameter)} = -3.121 - 0.943X_1 + 1.749X_2 + 0.035(X_1)^2 + 0.079(X_2)^2 - 0.014(X_3)^2 - 0.085(X_1)(X_2) + 0.029(X_1)(X_4) - 0.101(X_2)(X_4) - 1.510(X_2)(X_5) + 0.035(X_3)(X_4)$$

where X_1 is the weight concentration of the HLS solution, X_2 is the applied power voltage, X_3 is the needle gauge, X_4 is the syringe-to-collector distance, and X_5 is the flow rate of the HLS solution. The coefficient of determination (R^2) of this equation is 0.80, showing a good agreement.

Different effects were noted between processing parameters and the fiber diameter. Some parameters, such as HLS concentration and applied voltage, may have a quadratic effect on the fiber diameter; moreover, some processing parameters may show interactive effects. These complicated combinations would cause some difficulties for electrospinning operation and quality control of the electrospun products. The coordination of every parameter is, therefore, critical for successful fiber production using electrospinning technology.

It should be noted that ambient parameters, such as humidity and room temperature, could not be controlled in this research; however, unstable ambient parameters may affect the process of electrospinning operation and fiber formation (Li and Wang 2013). Because the environmental conditions were not controlled in this study, further research is needed to study the effects of climate conditions and to determine the optimal processing conditions.

CONCLUSIONS

In this study, lignosulfonate-based fibers were produced through electrospinning; however, the results have underscored the fact that fiber production using electrospinning technology is sensitive to processing parameters, affecting the formation, surface structure, and diameter of fibers. The conclusions of this study are as follows:

1. Lignosulfonate fibers could be produced through electrospinning when the concentration of lignosulfonate solution was between 15 and 30 wt% with the addition of PEO; however, fiber fusion was also observed with higher PEO content. Moreover, the larger diameter and broader diameter distribution of fibers were found with higher concentrations of lignosulfonate solutions.
2. Overall, concentration had the strongest effect on the diameter of fibers formed, whereas applied voltage, flow rate, and needle gauge had moderate effects on the diameter of fibers.
3. As the solution concentration decreased, a higher threshold voltage was needed to form fibers.
4. The syringe-to-collector distance also influenced the formation and collection of fibers. Higher concentrations of solution required a slower flow rate to produce fibers.

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