Development of Electrospun Lignin-based Fibrous Materials for Filtration Applications

Chia-Yuan Chang and Feng-Cheng Chang*

Lignin is a valuable biomaterial. It is both naturally abundant and readily available as a byproduct of the pulping processes, and the proper reprocessing of lignin is an effective way to achieve waste recovery. Lignin fiber mats with web structures can be produced using electrospinning techniques. Such fiber mats are a promising material for use in the production of filter products. This study focused on the development of filter media using electrospun lignin fiber mats. A series of tests were conducted (*e.g.*, particle penetration and pressure drop) to evaluate the filtration efficiency of the proposed filters. The results indicated that the unfavorable mechanical properties of filters solely comprised of a single layer of the lignin fiber mat would have a negative impact on the filtration efficiency of such filters. However, lignin-based composite filters developed with polyethylene oxide (PEO) fiber mats and surgical mask filter layers exhibited a filtration efficiency comparable to filter products that filter out 95% of small particles (N95). Therefore, the proposed lignin-based composite filter has the potential for air filtration applications.

Keywords: Lignin; Fiber; Electrospinning; Air filtration

*Contact information: The School of Forestry and Resource Conservation, National Taiwan University. No. 1, Sec. 4, Roosevelt Rd., Taipei, 10617 Taiwan; *Corresponding author: fcchang@ntu.edu.tw*

INTRODUCTION

Lignin makes up 15% to 40% of the dry mass of wood and acts as a structural component for supporting and conducting tissues of vascular plants. Rather than existing in its simple form in nature, lignin is compounded with celluloses through hemicellulose connections in plant material cell walls. The wood pulp industry typically applies chemicals such as sulfuric acid during the pulping process to break down the lignin-cellulose bonds. This practice produces a byproduct called technical lignin, such as kraft lignin and lignosulfonates, which is usually discarded or used as a fuel source (Schubert 1965; Duarte 1994). As a result, the development of ways to properly reuse of lignin would have a beneficial environmental impact because of lignin's favorable biodegradability.

Lignin can be transformed into a fibrous state for use in various industrial applications (*e.g.*, air filtration). In lignin fiber production, two types of techniques have been used extensively: conventional fiber-producing techniques, such as wet spinning and melt spinning, and the electrospinning technique, which has recently gained increased attention.

Electrospinning is a technique for extracting fibers from polymer solutions or melts by using high-voltage electric charges. Basically during electrospinning the high-voltage charged polymer solutions will overcome its surface tension; meanwhile, the electric field will guide the solution to a certain collector. At the same time the solution will experience a whipping process, which will evaporate the solvents and form a fiber structure.

Electrospinning is a relatively easy process that can be used to produce long and continuous fibers while concurrently enabling control of the diameter of fibers, such that nanoscale fibers can be produced (Ramakrishna *et al*. 2005).

Many studies have investigated the use of electrospinning to generate fibers from natural polymers. These polymers include silk fibroin, gelatin, and chitosan (Min *et al.* 2004; Ohkawa *et al.* 2004; Zhang *et al.* 2005). These polymers allow the production of micron-scale and even submicron-scale fibers suitable for various applications (Bhardwaj and Kundu 2010). Lignin, cellulose, and hemicellulose have also been used to produce electrospun fibers (Kim *et al*. 2006; Han *et al*. 2008; Dallmeyer *et al*. 2010; Ago *et al*. 2012; Gan *et al*. 2013).

Some studies have indicated that electrospinning can be used to generate fibrous materials from synthetic polymers. These polymers include polyethylene oxide (PEO), polyvinyl acetate (PVA), and polypropylene (PP). Such fibrous materials are suitable for filtration applications because of their nanoscale dimensions (Dotti *et al*. 2007; Wang *et al*. 2007). However, only a few studies have explored the use of lignin to develop lignin-based filter products. Dallmeyer *et al*. (2010) used distinct types of technical lignin to produce lignin fibers with diameters ranging from nano- to submicron scales. Graham *et al*. (2002) revealed that nanoscale fibers could improve the filtration efficiency of filters by substantially decreasing the pressure drop through the filters. Electrospun lignin fibers therefore exhibit a great potential for filtration applications.

This study aimed to apply an electrospinning technique to develop high-performance filters based on technical lignin, which is a byproduct of pulping processes. Moreover, a preliminary study was conducted to determine an optimal collector rotating speed for producing electrospun lignin fibers. A series of tests were then conducted to evaluate the filtration efficiency and dust-holding capacity of the developed lignin-based air filters. Filter models were also developed to simulate the filtration efficiency of the proposed lignin-fiber-mat filters.

EXPERIMENTAL

Materials

A lignin solution was prepared by dissolving soluble lignosulfonates (Borregaard, Sarpsborg, Norway; M_w= 8000), a byproduct of the sulfite pulping process, in deionized water. To facilitate electrospinning, a small portion of poly(ethylene oxide) (PEO, Acros, New Jersey, USA; M_w= 600000) was dissolved in the lignin solution (Dallmeyer *et al*. 2010). The solution was then mixed and heated in an oil bath, and then vortexed until it was completely dissolved. To generate electrospun PEO fibers, a pure PEO solution was also prepared following the same procedure. The ratio of lignin solution used in this study was 20 wt% mixture, containing 97 wt% lignosulfonates and 3% PEO, on the other hand, pure PEO solution used was 6.5 wt% which gave better results on fiber formation.

Methods

Electrospinning process

In the electrospinning process, the formulated lignin solution was loaded in a syringe and then charged using a 15-kV power supply. The syringe needle and a collector were connected to the power supply’s positive terminal and the ground, respectively. The processing parameters of the electrospinning process are summarized in Table 1, and the major electrospinning devices are demonstrated in Fig. 1.

The electrospun lignin fibers must be collected on a substrate to form lignin fiber mats. To determine an appropriate substrate material, the adhesive performances of the lignin fiber to substrates made of polyethylene terephthalate (PET), thermoplastic polyurethane (TPU), or PP were assessed. The results of these assessments showed that the PET substrate outperformed both the TPU and PP substrates in adhering to lignin fibers. Therefore, the PET substrate was utilized to produce lignin fiber mats.

The basis weights of the electrospun fiber mats were determined before subsequent tests, and measurements were then conducted.

Table 1. Processing Parameters of Electrospinning

Parameters	Values
Concentration of lignin solution (%)	20
Power voltage (kV)	15
Syringe-to-collector distance (cm)	20
Needle gauge (G)	18
Flow rate of solution (mL/min)	0.03
Collector rotating speed (rpm)	240 and 720

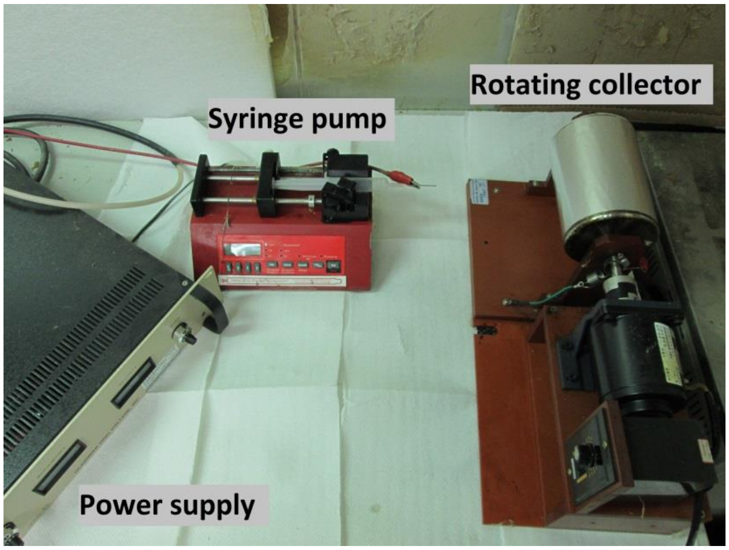


Fig. 1. Electrospinning setup

Fabrication of lignin-based composite filters

To develop lignin-based filters, typical surgical masks were used. These were purchased from Haw Ping Co. Ltd. The masks were composed of two non-woven fabric layers and a middle filter layer made with PP, and fiber mats formed in the current work using electrospun lignin fibers and PEO fibers. Lignin-based composite filters were fabricated either by laminating a lignin fiber mat layer with a surgical mask filter layer or by laminating an additional PEO fiber mat layer between the lignin fiber mat layer and the surgical mask filter layer (Fig. 2). To ensure that the fiber mats and surgical mask fibers were properly bonded, the masks' fabric layers were removed because of inadequate bonding between the lignin or PEO fiber mat layers and surgical mask fabric layers.

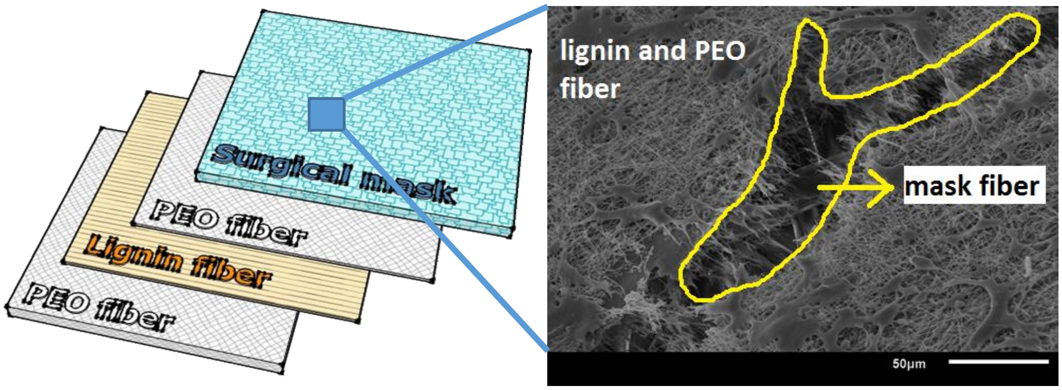


Fig. 2. Picture of mask/lignin/PEO composite filter

Air filtration tests

Air filtration tests were conducted according to the USA commercial respirator regulation (42 CFR Part 84) of the manufactured lignin-based filters. Pressure drop (ΔP) and particle penetration (p) are the major indicators of a filter's filtration efficiency, and these quantities were measured using TSI 8130 (TSI Inc., St. Paul, MN, USA). Specifically, low pressure drops and particle penetrations indicate favorable filter efficiencies. In the tests, sodium chloride (NaCl) particles with an average diameter of 0.3 μm and a flow rate of 32 L/min were employed. Subsequently, according to the measured ΔP and p, the quality factor (Q_f) representing filter quality was calculated using Eq. 1:

$$Q_f = \ln(1/p)/\Delta P \tag{1}$$

Microstructural analyses

The electrospun lignin fibers' microstructures were inspected using a scanning electron microscope (SEM, JSM-6510, JEOL, Peabody, MA, accelerate voltage 15kV, and the samples were sputter coated with gold for observation) to measure the average diameter of the fibers. Moreover, the filter surface areas and pore size distributions were determined using a BET-201A sorptometer (Porous Material, Ithaca, NY). The average diameter of fibers was measured by ImageJ, an open source image processing toolkit, for randomly selected 50 fibers. Furthermore, the statistical analysis, including group comparisons (Tukey's test) and the analysis of variance (ANOVA) (α= 5%), was conducted out using Minitab (Minitab Inc., State College, PA).

Tensile tests

Tensile test samples were prepared by tailoring the filters solely composed of an electrospun lignin fiber mat into 3 by 1 cm strips, and the basis weight of each sample was measured. Subsequently, the filter samples were mounted on a Microtest strength tester (Deben UK, Suffolk, UK) and tested under a static tensile load with a loading speed of 1.5 mm/min. The tensile strengths of each of the samples were determined according to the method used by Gandhi *et al*. (2009).

Filtration efficiency simulation

Filter models were developed using Geodict software (Math2Market GmbH, Kaiserslauter, Germany) to simulate the performance of the lignin fiber mat filters in an attempt to realize the filtration efficiency prediction of such filters. Using Newtonian fluid theory, the Navier-Stokes-Brinkman model was adopted to simulate the filtration tests conducted using NaCl penetration particles under an air medium.

RESULTS AND DISCUSSION

Preliminary Study on Collector Rotating Rates

Lignin fiber mats were prepared by an electrospinning technique. Microstructural analysis revealed the distinct fiber alignments of each of the electrospun fiber mats formed using different collector rotating rates (*i.e.*, 240 and 720 rpm) during the electrospinning process (Fig. 3). The surface area and average pore size of the fiber mats were 12.56 m^2/g and 35.39 Å for 240 rpm, and 12.83 m^2/g and 36.01 Å for 720 rpm. A statistical analysis was conducted, and the results indicated that there were no significant differences between the surface areas and average pore sizes of the two fiber mat types. This indicated that the collector rotating rate did not significantly affect the microstructure of the manufactured fiber mats. As a result, the fiber mats formed at 720 rpm were used to develop the lignin-based filters for the subsequent filtration tests.

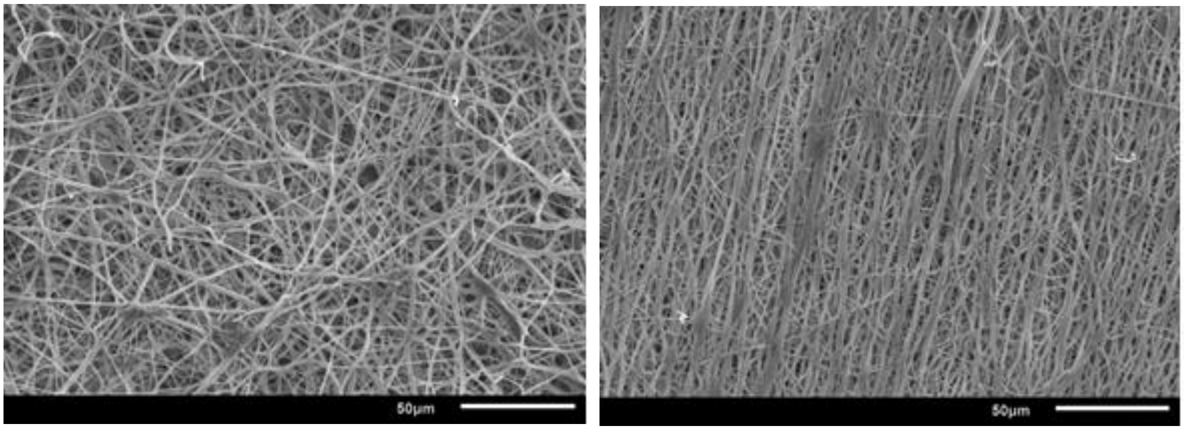
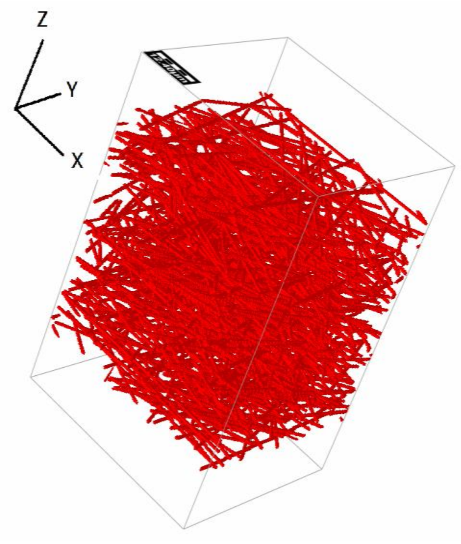


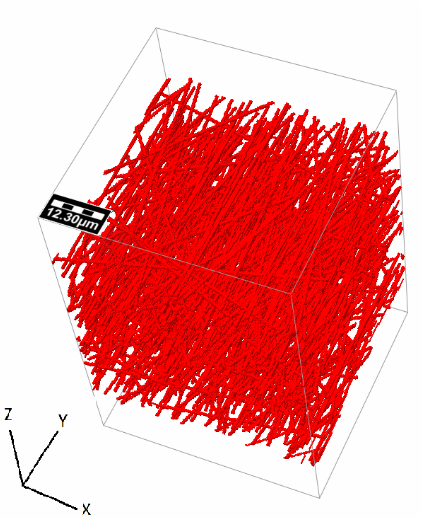
Fig. 3. Distinct lignin fiber patterns at different revolving rates (left: 240 rpm; right: 720 rpm)

To estimate the filtration efficiency of the electrospun lignin fiber mats, filter models were developed with an individual lignin fiber mat as a filter. Filter simulation models were developed taking into account the major parameters affecting the performance of the proposed lignin-based filters. The measured values of such parameters are presented in Figs. 4 and 5. To investigate the effect of the fiber alignment of the fiber mats on the filtration efficiency, the fiber alignments of the simulation models were set to be Y-aligned and XY-random to mimic the aforementioned fiber alignments that occurred at 240 and 720 rpm (simulated as Figs. 4 and 5). According to the model simulation results, the estimated pressure drop and particle penetration of the filters with an XY-random fiber alignment were 56.02 Pa and 18.1%, respectively. The estimated pressure drop and particle penetration of filters with a Y-aligned fiber orientation were 56.40 Pa and 18.7%, respectively. The difference between the estimated pressure drop and particle penetration of both filter types was insignificant, indicating that the collector rotating rate had an insignificant effect on the filtration efficiency.



Filter simulation parameters	Values/Setting
Fiber diameter (μm)	0.7
Basis weight (gsm)	4.197
Fiber density (g/cm^3)	1.54
Accuracy	0.001
Air flow rate (m/s)	0.05
Fiber orientation	XY-random Z-compressed
Simulation outputs	Values
Pressure drop (mmH$_2$O)	5.71
Penetration (%)	18.1
Note: Accuracy denotes the simulation error tolerance in Geodict software.	

Fig. 4. Simulation of the XY-homogeneous filter structure and simulation outputs



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Fiber diameter (μm)	0.7
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Fiber density (g/cm^3)	1.54
Accuracy	0.001
Air flow rate (m/s)	0.05
Fiber orientation	Y-aligned Z-compressed
Simulation outputs	Values
Pressure drop (mmH$_2$O)	5.75
Penetration (%)	18.7
Note: Accuracy denotes the simulation error tolerance in Geodict software.	

Fig. 5. Simulation of the Y-aligned filter structure and simulation outputs

Filtration Results of Lignin Fiber Mat Filters

Lignin fiber mat filters with distinct basis weights were produced by controlling the electrospinning duration, and approximately 5 gsm would require 5 to 8 h. According to the simulation results and reviewed research, the fabrication of air filters by integrating a small portion of lignin fibers can achieve favorable filtration effectiveness (Wang *et al*. 2007; Dotti *et al*. 2007). However, the results of the filtration tests indicated that the filtration efficiency of the manufactured lignin fiber mat filters was inadequate and that the quality factor may have indicated that the filters might not meet required quality specifications, due to excessively high penetration values (Table 2).

Moreover, cracks were observed on the filters during the filtration tests (Fig. 6), implying an unfavorable mechanical performance of the filters. The tensile test results showed that the average tensile strength and Young's modulus of the filters were 1.36 MPa and 0.38 GPa, respectively, which were inadequate compared to that of regular filters.

Table 2. Filtration Efficiency of the Lignin-Based Filters

The basis weight of the filter samples (gsm)	Pressure drop (mmH_2O)	Penetration (%)	Quality factor (Q_f)
0	0.2 (0.0)	92.4 (0.3)	0.40
0.172	0.2 (0.0)	87.3 (2.4)	0.68
0.315	0.2 (34.6)	86.3 (0.8)	0.74
1.877	0.4 (17.3)	86.3 (3.5)	0.37
4.197	0.5 (10.8)	86.5 (1.6)	0.30
Notes: 1. The numbers in parentheses denote the coefficients of variation; 2. A zero basis weight denotes a PET substrate.			

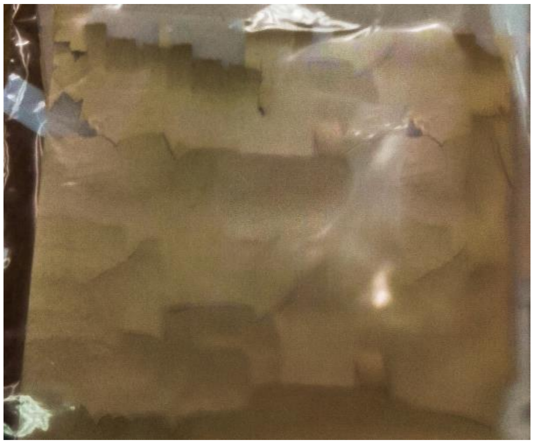

Fig. 6. Lignin filter cracking during the filtration tests

Filtration Results of Mask/Lignin/PEO Composite Filter

To overcome the inadequate strength of the lignin fiber mat filters, certain modifications were made to thicken the substrate and/or apply additional PET substrates and composite filters, according to designed lamination patterns. The effectiveness of such modifications were analyzed, and the results indicated that the multilayered composite filters fabricated by integrating the surgical mask and PEO fiber mats showed relatively satisfactory filtration performance (Fig. 2). Through electrospinning, PEO fibers with an average diameter of 400 nm were obtained. The diameter of the fibers of the surgical mask filter layer were also measured, which had an average fiber diameter of 3000 nm.

Through the determination of the optimal ratio of lignin to PEO fibers in the filter, composite filters with a particle penetration of less than 5% were developed (Fig. 7), indicating that such filters satisfy the penetration standard of N95 (*i.e.*, filter out 95% of small particles) respirators. Nevertheless, the pressure drop of the composite filters was unfavorably high, due to the presence of a considerable number of nanoscale fiber layers (Fig. 8), thereby leading to unfavorably low quality factors (Fig 9). Han (2008) indicated that the average values for Q_f of industry-grade respiratory filters and filtering facepieces are 0.55 and 0.50, respectively. As a result, further work will be needed to improve the quality of this proposed filter, which had simultaneously low penetration rates and high pressure drop values, to enhance the filter's feasibility for future filtration applications.

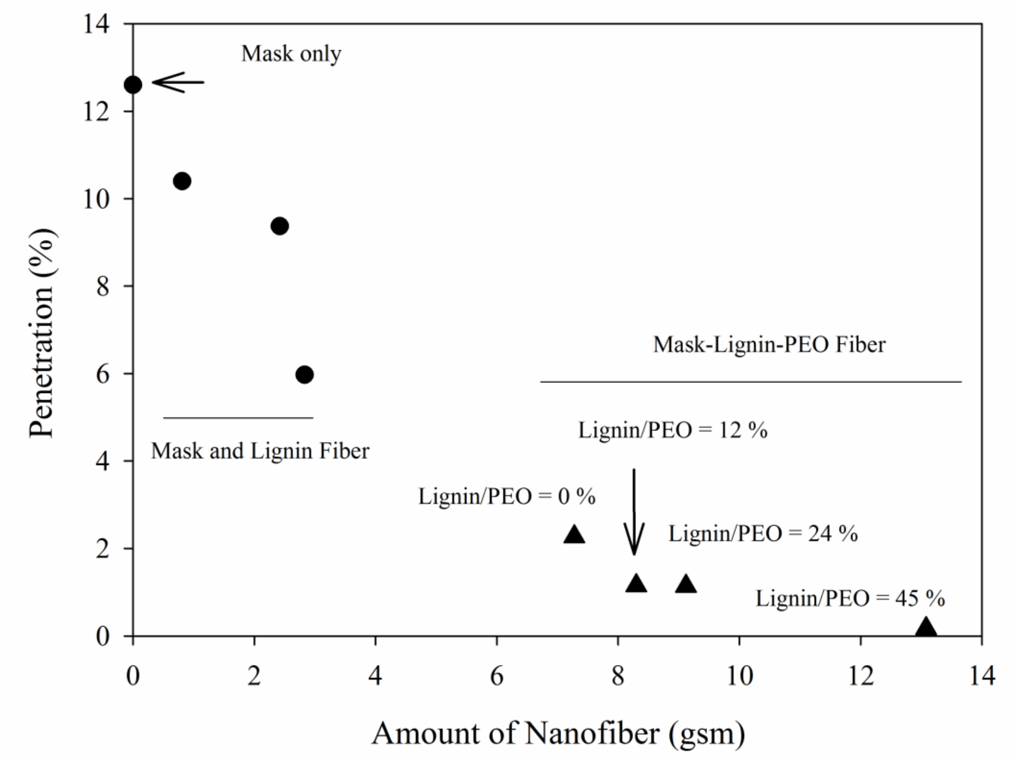

Fig. 7. Penetration of the composite filters with different basis weights

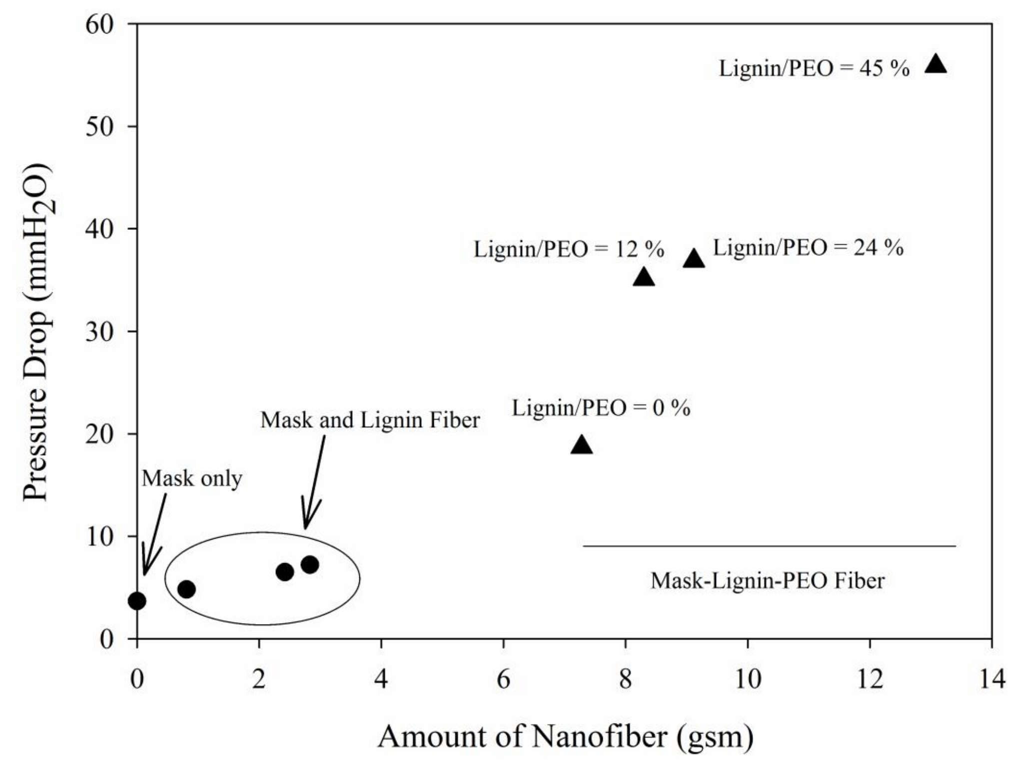

Fig. 8. Pressure drop of the composite filters with different basis weights

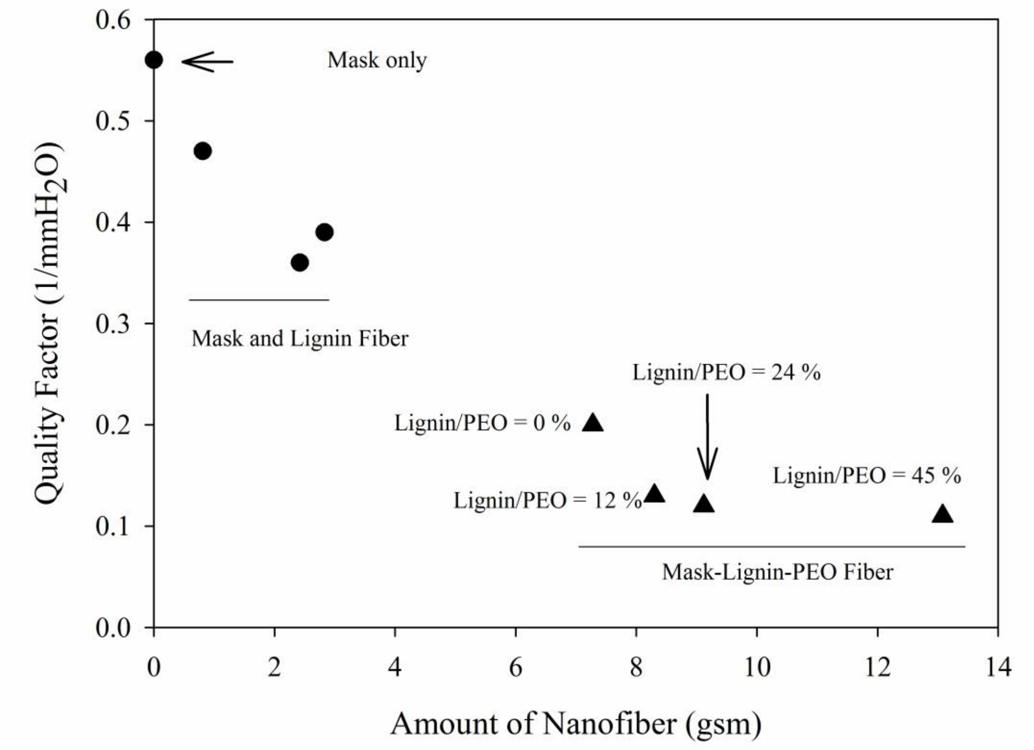

Fig. 9. Quality factor of the composite filters with different basis weights

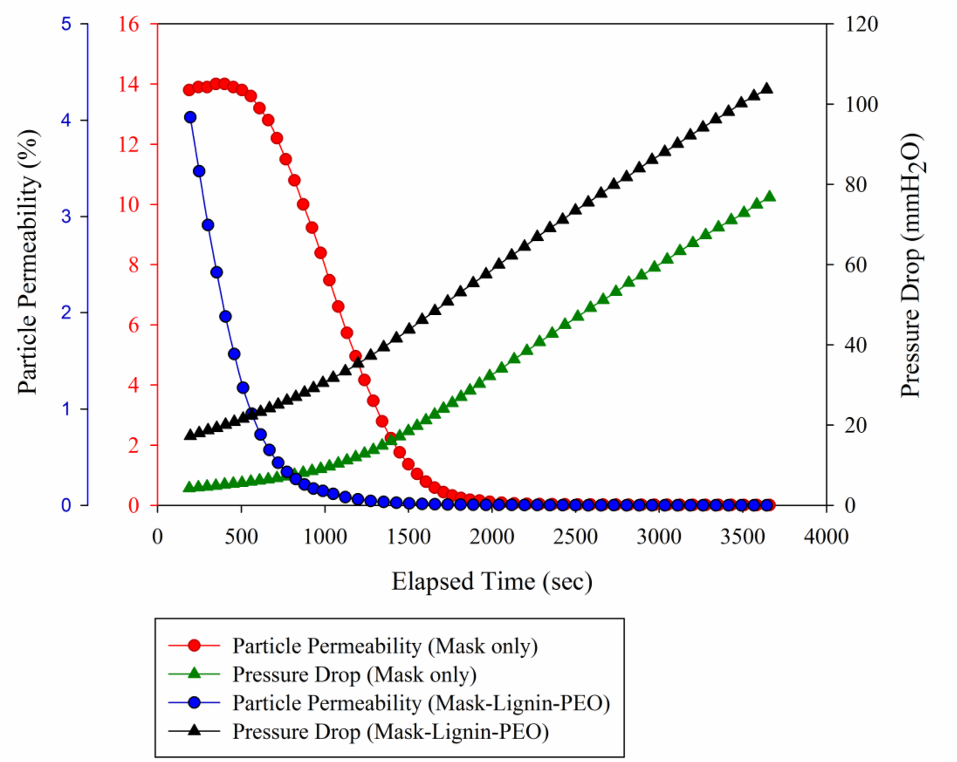

Fig. 10. Comparison between the dust-holding capacity of the composite filter and surgical mask

To evaluate the dust-holding capacity of the proposed composite filters, a dust-loading test was conducted by loading the composite filters with a large number of NaCl particles for a one-hour period. The tested composite filter samples had a basis weight of 13.64 gsm and a lignin concentration of 64 wt%. The results showed that the composite filter's particle penetration dropped to 0.1% after the first 1000-s period of the dust-loading process and that the pressure drop steadily increased over time. However, under the same dust-loading process, the particle penetration of most surgical masks was 7.5%, and the pressure drop of such masks exhibited no substantial increases in the first 1000-s period of dust loading (Fig. 10).

The substantial reduction of the particle penetration of the composite filters indicated that the lignin and PEO fiber mat layers had favorable filtration efficiencies. However, the increased pressure drop implies that the composite filters would have a decreased service life. Moreover, as shown in Fig. 11, the SEM images of the laminated layers of the composite filters showed that most of the feeding particles were captured by the surgical mask's filter layer, whereas only particles with small diameters that cannot be intercepted by the surgical mask were then captured by the lignin fiber mat layer. As such, a balance between cost and efficiency should be considered when developing lignin filters using the electrospinning technique.

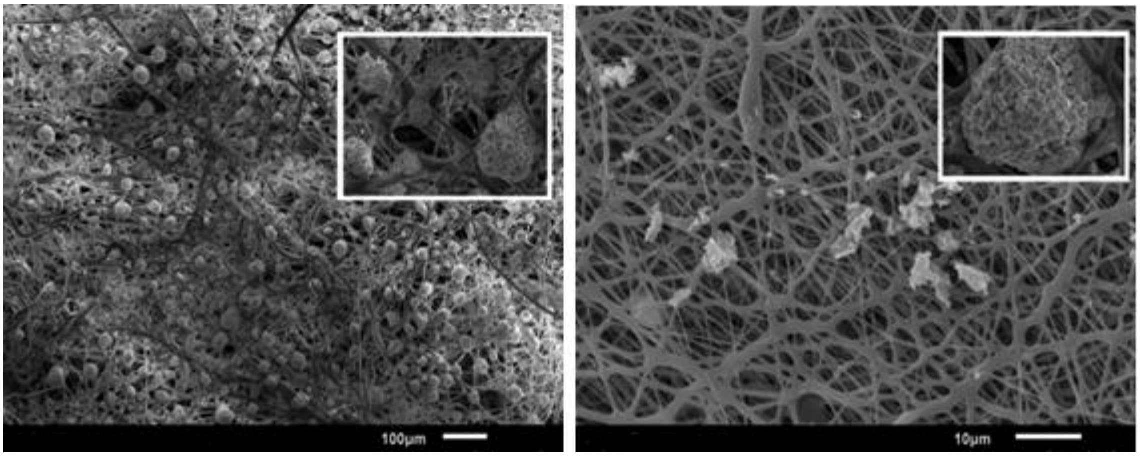

Fig. 11. SEM images of the layers of the developed filters after the dust-loading test (left: the filter ply of surgical mask; right: the lignin fiber mat)

CONCLUSIONS

This study investigated the feasibility of developing value-added, lignin-based air filters using electrospinning technology. The filtration efficiency of such filters was evaluated by conducting a series of filtration tests. The conclusions of this study are as follows:

1. Although the lignin fiber mat air filters could be produced using the electrospinning technique, the unfavorable mechanical properties (*i.e.*, the tensile strength and Young's modulus) of such filters, however, may limit their widespread use.
2. To overcome the disadvantages of the lignin fiber mat filters, mask/lignin/PEO composite filters were developed. The composite filters exhibited N95-equivalent filtration efficiency, indicating that electrospun lignin fiber mats are a promising material for developing high-performance air filters.

3. The pressure drop values of the mask/lignin/PEO composite filters were excessively high, suggesting that further modification may be required.
4. According to the filter model simulations and microstructural analysis of the lignin fiber mat filters, the fiber alignment of the fiber mats exhibited no significant effects on the filtration efficiency of the lignin fiber mat filters.

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