Quality factors of PVA nanofibrous filters for airborne particles in the size range of 10–125 nm

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HIGHLIGHTS

- An automatic nanofiber characterization method.
- The effects of electrospinning parameters on the fiber size distribution.
- The effects of electrospinning parameters on the filter quality factors.
- The filter quality factor increased with multilayer filters.

ABSTRACT

PVA nanofibrous filter samples were fabricated in a laboratory under eight different electrospinning conditions; they were first characterized in terms of fiber size distributions by automatic SEM analysis. The quality factors of these nanofibrous filters were then evaluated using sodium chloride nanoparticles in the size range of 10–125 nm. Results showed that, as expected, single layer filters with smaller fiber diameters and greater solidity were efficient. However, these characteristics led to lower quality factors due to their greater pressure drops. Single layer filters made with higher applied voltage, longer tip to collector distance and shorter deposition time corresponded to greater filter quality factors. The quality factor of single layer filter was inversely related to filter thicknesses. Multilayer filters made by stacking thin nanofibrous filters greatly increased the filter quality factors.

1. Introduction

Coal combustion is a large form of energy production in many countries, including the USA and China [1]. It is also a major source of air emissions such as volatile organic carbon (VOC), particulate matter (PM), nitrogen oxide and sulphur dioxide [1–4]. The formation of PM from coal combustion has been well investigated [5,6]. Earlier research has shown that it contains a large amount of nanoparticles smaller than 150 nm, with the mode diameter of 100 nm [7,8]. Coal-derived nanoparticles have a large surface area to volume ratio with a complicated chemical composition, and may cause severe health problems including chronic lung disease, fibrosis and cancer [9].

Air filtration is the most effective approach for separating nanoparticles from gases, and filters with fiber diameters in the order of micrometers are widely used for nanoparticle filtration [10]. Nanofibrous filters are promising alternatives for the removal of airborne nanoparticles with higher efficiencies and low pressure drops. As the fiber diameter decreases, the filtration efficiency increases due to the slip flow. Slip flow conditions greatly benefit the filtration of nanoparticles: more particles approach the fiber surfaces, increasing the capture of nanoparticles by Brownian diffusion and interception [11,12]. Slip flow also lowers air flow resistance, due to decreased drag force on nanoparticles [13,14], results in the higher quality factor. Nanofibrous filters appear to be a cost-effective option for nanoparticle filtration owing to their long lifetime, high loading capacity, low air resistance, low basis weight and great permeability [10,15,16].

Electrospinning is widely used for the production of nanofibrous filters for air filtration [17,18]. In typical electrospinning, a polymer solution is injected through a capillary needle into an electrical field. Nanofibers produced by this method have diameters ranging from a few to several hundred nanometers. These
fibrous nanomaterials are believed to be less likely airborne and thus more environmentally friendly [14].

Researchers have characterized polyvinyl alcohol (PVA) nanofibers and their use as filter media. Through the analysis of scanning electron microscopy (SEM) images, Wang et al. [18] reported that nanofibrous PVA filters were not uniform, and beads were observed along fibers. They also showed that PVA nanofibers deposited on a conventional cotton scaffold had higher filtration efficiencies and a lower pressure drop for particles in the range of 0.3–5 μm than conventional fibrous filters [20]. Although PVA nanofibers can be employed for air filtration, only limited information is available on their characterization and performance in capturing nanoparticles, which prevail in flue gases. Furthermore, the effects of the electrospinning parameters on the filter characteristics and the performance of nanoparticle removal are not clear.

The objectives of this paper are (1) to characterize PVA nanofibrous filters produced by electrospinning with an automated image analysis method, and (2) to determine the relationship between electrospinning parameters and the filter quality factor for nanoaerosol filtration. PVA nanofibers were made with different applied voltages, tip to collector distances and deposition times. The morphologies of these electrospun filters were then characterized by SEM images coupled with an automated image analysis method. Using NaCl airborne nanoparticles in the size range of 10–125 nm, the single-layer and multilayer filters were also evaluated in terms of filter quality factor. The effects of the electrospinning parameters on filter quality factor were determined to identify the important factors affecting filtration performance of PVA nanofibrous filters.

2. Materials and methods

A custom-made electrospinning setup was used in this study for filter sample preparation. The relative humidity and temperature of the air inside the housing were 39 ± 4% and 23 ± 3 °C, respectively. A 5-ml syringe was loaded with a solution of PVA polymer, which has a molecular weight of 89,000–98,000 g mol⁻¹ (Sigma Aldrich Canada). The desired solution concentration of 10% w/w was prepared by diluting the PVA in distilled water at 90 °C and stirring overnight. A 22 gauge stainless steel capillary needle with an inside diameter of 0.413 mm was attached to the syringe. The syringe was mounted on a syringe pump (Kd Scientific), which was used to control the flow rate to 0.3 ml h⁻¹. A lab jack was used to adjust the vertical distance between the capillary needle and the grounded collector. A high-voltage power supply (Gamma High Voltage, ESSOP5-W) was employed to apply the high voltage between the capillary needle and an aluminum collector.

Stainless-steel wire screens with a diameter of 140 μm and an opening size of 368 μm were used to support the nanofibrous filters. Filter samples were then left in lab environment overnight, allowing charges to dissipate from the collector and enabling the nanofibers to dry. Table 1 summarizes the eight conditions for the electrospun sample filters.

The sample thickness was measured using a digital micrometer (Tresna IP65, series M18) with a resolution of 1 μm. Thickness was measured at the filter center, which may be greater than that at the edges due to the random deposition pattern of fibers in an electric field [21]. These sample filters were then characterized using field emission scanning electron microscopy (FE-SEM) analysis. Samples were coated with gold particles for 139s prior to imaging. The SEM images were then quantitatively analyzed using an automated method developed by us to determine the distribution of nanofiber diameters (More information is available in Supplementary Information).

Meanwhile, samples made at identical conditions were tested for the filtration performance and pressure drop. The experimental setup for air filtration test was similar to that reported in our previous publication [22]; only a brief description is provided as follows. Polydisperse sodium chloride particles in the range of 10–125 nm were generated by a constant output atomizer (TSI Model 3076). These aerosol particles were then passed through a diffusion dryer (TSI Model 3062) to reduce air humidity followed by neutralization using a radioactive neutralizer (Staticmaster Model P-2031). These polydispersed aerosol particles then pass through the test filter at an air flow rate of 2 lpm, which corresponds to a face velocity of 6.7 cm/s.

The pressure drop across the test filter was measured using a differential pressure gauge (Omegadyne, Model DPG409). A scanning mobility particle sizer with a Faraday cup electrometer (SMPS-E, GRIMM model 5.705) was used to determine the concentrations of the nanoaerosol particles downstream of the 25-mm filter holder, with and without tested filter, to determine the filtration efficiency (η).

\[
\eta = 1 - \frac{C_{\text{down}}}{C_{\text{up}}}
\]  

With this method, the error due to particle loss is minimized by the same sampling line. The corresponding filter quality factor (Qp), is calculated from the measured pressure drop (ΔP) and particle filtration efficiency (η) [23].

\[
Q_p = -\frac{\ln(1 - \eta)}{\Delta P}
\]  

Based on the measured pressure drop and filter thickness, the solidity of nanofibrous filters is determined using the Davies equation [24]:

\[
\Delta P = 64\mu ULd^2(1 + 56\pi^2/\alpha^2)
\]

where \(\mu\) is the air viscosity, \(U\) is the face velocity, \(L\) is the filter thickness, \(\alpha\) is the solidity of filter, and \(d\) is the mean diameter of the fibers. With the density of the filter (\(\rho_f\)), the basis weight of the filter (w) is determined by

\[
w = \alpha Ld \rho_f
\]

3. Results and discussion

Fig. 1 shows the SEM images, size distributions, mean diameters and standard deviations, thicknesses, solidities and basis weights of the nanofibrous filters fabricated under eight electrospinning conditions (Table 1). SEM images were taken at two magnifications of 20.00 KX and 5.00 KX for each sample.

3.1. Effect of tip-to-collector distance on nanofiber size distribution and morphology

NF1, NF2, and NF3 were fabricated at 15 kV, deposition time of 15 min and different tip-to-collector distances of 10, 12.5 and
15 cm, respectively. Numerical values in Fig. 2 show that the mean fiber diameter decreased with the tip-to-collector distance. The mean diameters are 184 nm, 164 nm and 145 nm with respective standard deviations of 72 nm, 66 nm and 63 nm when the distances were 10, 12.5 and 15 cm, respectively. Both the mean fiber diameter and standard deviation decreased with the distance.
resulting in more uniform fibers. These values and the SEM images indicate that relatively uniform fibers were produced without beaded fiber formation.

Comparison of NF1, NF2 and NF3 shows that the tip-to-collector distance directly affects filter solidity. With higher solidity and lower thickness, the basis weight of the filter decreased with the increasing tip-to-collector distance. The increase in the distance reduced the electric field intensity and increased the jet flight time. It also affects the deposition time, the evaporation rate, and the jet instability. Longer distance allows more time for the fluid jet to stretch thinner and for the solvent to evaporate more completely before its deposition on the collector, resulting in thinner nanofiber and thinner sample filters. The same trend has been reported in previous studies [25–27].

3.2. Effect of applied voltage on nanofiber size distribution and morphology

NF4, NF1 and NF5 were fabricated at same tip-to-collector distance of 10 cm, same deposition time of 15 min, and different applied voltages of 12.5, 15, and 17.5 kV, respectively. As seen in Fig. 1, the initial average fiber diameter increased from 162 nm to 183 nm when the applied voltage changed from 12.5 to 15 kV, and then it decreases to 163 nm when the applied voltage further increased to 17.5 kV. Actually, the effect of applied voltage on the diameter of nanofibers has not been conclusive. Some researchers reported that the applied voltage had a negligible effect on the nanofiber diameter [28,29]; others reported its direct effect [26,30] or its inverse effect on the mean fiber diameter [31,32]. Some researchers believe that increasing the voltage would increase the electrostatic repulsive force on the jet, leading to thinner nanofibers [33], while others believed that voltage increase could increase the volume of the solution ejected from the Taylor cone, resulting in larger nanofibers [34]. These contradictory results indicate that other parameters such as the solution properties also affect the nanofiber size [35]. Our high-speed video camera recorded stable jets for all of the applied voltages. The SEM images in Fig. 1 also show that none of these filter samples had beads along the nanofibers. The fabrication of filters with stable jets may have prevented bead formation, due to the balance between the electrospinning and feeding rates.

The results in Fig. 1 above also show that the voltage affected the solidity and thickness of nanofibrous filters. As the applied voltage increases, both solidity and thickness of the filter samples increase linearly (Fig. 3). At a higher voltage, the electrostatic force at the needle tip is greater due to a higher electric field intensity and greater cumbic forces in the jet, increasing the jet flow rate (the jet flow rate is independent of the feeding flow rate) [35]. Consequently, it increased the solidity and basis weight of the filter.

3.3. Effect of deposition time on nanofiber size distribution and morphology

NF6, NF1, NF7 and NF8 were fabricated at \( d = 10 \text{ cm}, V = 15 \text{ kV} \) and deposition times of 5, 15, 30 and 60 min, respectively (Table 1). Results in Fig. 1 show that the deposition time also affects the average diameter, the solidity and the basis weight of the nanofibers. The mean fiber diameter was 152 nm, 183 nm, 122 nm and 147 nm when the deposition time increased from 5 min to 15 min, 30 min and 60 min, respectively. First of all, this finding is quite different from the assumptions made by other researchers that the nanofiber size distributions of electrospun nanofibers remain constant over time [21,36]. Actually, at the beginning of the electrospinning process, the jet enters into a homogenous electric field and deposits on the collector with such a good contact that it allows efficient charge dissipation. After a certain time, heterogeneous charges accumulating on the deposited area cannot dissipate quickly due to the low conductivity of the PVA polymer. Thus, the jet behaves differently due to the heterogeneous electric field [37,38]. The incidence of charge buildup prevents the effective deposition of incoming fibers, leading to different fiber deposition pattern and a decreasing production rate [39,40]. In this study, up to the deposition time of 60 min, no obvious reduction in nanofiber production rate was observed as indicated by the increased thickness and basis weight of the filter samples. However, deposition time did affect the filter quality and fiber size distribution.

When the deposition time increased to 15 min, so did the mean fiber diameter, likely because the buildup of residual charges on the deposited fibers reduced the spiral motion of the incoming jet and decreased the elongation rate. As a result, the process produced thicker nanofibers [21]. However, when the deposition time was 30 min, the mean fiber diameter decreased unexpectedly to 122 nm. We believe that the changes in the buildup charges on deposited fibers may be one of the reasons for this result. The number of contacts between the deposited fibers affects the charge dissipation [39]. It seemed that for a 30 min deposition time, the number of contacts between fibers was great enough to enable timely charge dissipation, leading to thinner fibers. Newer deposited fibers are likely to have smaller diameters than previously deposited ones. For the deposition time of 60 min, the mean fiber diameter again increased due to the buildup residual charges. Another reason for this nonlinear behavior might be the uncertainty in image analysis. One of the issues in this study is employing SEM images, which show only the top layers of deposited fibers in 2D structure. This factor deserves further investigation in the future.

As shown in Fig. 4, the deposition time affects both the thickness and solidity of a filter. The longer the deposition time, the more fibers are compressed on the substrate, leading to greater filter solidity. As the deposition time increases, so do the thickness and solidity of filters, leading to a greater basis weight too. This finding agrees with those reported in literature [36].
3.4. Performance of nanofibrous filters for the filtration of nanoaerosol

Fig. 5 shows the particle filtration efficiencies and quality factors of the nanofibrous filters tested at a consistent air flow rate of 2 lpm. The fiber diameters of the tested filters were mostly less than 500 nm (Fig. 1), which should enable gas slip effect in nanoparticle filtration [36,41]. Results in Fig. 5 show that samples NF8, NF7 and NF5 have the highest filtration efficiencies (>95% for tested particle size). However, they do not have high quality factors due to their great pressure drops. Both NF8 and NF7 were fabricated at the long deposition time and are thick. NF7 has the lowest quality factor due to its great thickness (17 µm) and smaller mean fiber diameter (122 nm). NF8 is the thickest (29 µm) with the greatest solidity (0.0388); however, due to its larger fiber size, NF8 has a greater quality factor than NF7. Despite the fact that thickness does not affect the quality factor of conventional filters [42,43], it could be one of the important parameters for electrospun nanofibrous filters.

NF4 has the lowest filtration efficiency for the size range of tested particles, followed by NF6, NF1 and NF2. Comparison between the characteristics of these filters show that the filtration efficiency decreases with solidity of a filter. NF4 has the lowest filtration efficiency among all samples, which led to the lowest quality filters. Although NF6 does not have high filtration efficiencies, it has the greatest quality factors for the tested particle sizes.

3.4.1. Effect of tip-to-collector distance on filtration performance

Fig. 6 presents the effect of tip-to-collector distance on the corresponding total filtration efficiencies and quality factors of NF1, NF2 and NF3. The total filtration efficiency of a filter is calculated based on the ratio of total nanoparticles downstream of the filter to those upstream of the filter. There is a positive correlation between the tip-to-collector distance and either filtration efficiency or quality factor. Tip-to-collector distance directly affects the solidity of the filter; however, it has an adverse effect on filter thickness and mean fiber diameter. Increasing the filter solidity and decreasing the mean fiber diameter have positive effects on the filtration efficiency. On the other hand, decreases in the thickness of the filter have an adverse effect on filtration efficiency but a positive effect on the pressure drop across the filter, which increases the filter quality factor.

3.4.2. Effect of applied voltage on nanoaerosol filtration performance

Fig. 7 shows the total filtration efficiencies and quality factors of samples NF4, NF1 and NF5. The applied voltage has a positive effect on both filtration efficiency and quality factor of an electrospun filter. As the voltage increases, so do both thickness and solidity, and consequently, both the filtration efficiency and pressure drop across the filter increase; however, the increasing rate of filtration efficiency is greater than that of the pressure drop, which ultimately increases the quality factor.

3.4.3. Effect of deposition time on filtration performance

Fig. 8 presents the total filtration efficiencies and quality factors of samples NF6, NF1, NF7 and NF8, which are different in terms of deposition time. The total filtration efficiency positively correlates to the electrospinning deposition time; however, the increasing rate decreases as the deposition time increases. As shown in Fig. 4, the deposition time directly affects the thickness and solidity of the filters, resulting in increased total filtration efficiency. On the other hand, deposition time has a negative effect on the total quality factor because the filter thickness increases with deposition time and it affects pressure drop more than filtration efficiency. As a result, the quality factor of filters decreases greatly as the deposition time increases from 5 min to 15 min. The gap between total filtration efficiency and pressure drop grows with deposition time, and it may be due to the fabrication of non-uniform filters with elongated deposition time [21].

This means that a shorter deposition time may result in more uniform and thinner filters of higher quality factor. Our finding herein is different from other researchers who reported that “the quality factor of filters is independent of filter thickness [42,43]”. Again, deposition time may affect the deposition pattern over time, consequently reducing the filter quality factor [21].

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**Fig. 4.** Effect of deposition time on filter’s thickness and solidity.

**Fig. 5.** Filtration efficiency and quality factor of nanofibrous filters.

**Fig. 6.** Filtration efficiency and quality factor of filters versus tip-to-collector distance.

**Fig. 7.** Total filtration efficiencies and quality factors of samples NF6, NF1, NF7 and NF8, which are different in terms of deposition time. The total filtration efficiency positively correlates to the electrospinning deposition time; however, the increasing rate decreases as the deposition time increases. As shown in Fig. 4, the deposition time directly affects the thickness and solidity of the filters, resulting in increased total filtration efficiency. On the other hand, deposition time has a negative effect on the total quality factor because the filter thickness increases with deposition time and it affects pressure drop more than filtration efficiency. As a result, the quality factor of filters decreases greatly as the deposition time increases from 5 min to 15 min. The gap between total filtration efficiency and pressure drop grows with deposition time, and it may be due to the fabrication of non-uniform filters with elongated deposition time [21]. This means that a shorter deposition time may result in more uniform and thinner filters of higher quality factor. Our finding herein is different from other researchers who reported that “the quality factor of filters is independent of filter thickness [42,43]”. Again, deposition time may affect the deposition pattern over time, consequently reducing the filter quality factor [21].
Theoretically, increases in the layers of filters will lead to the increase in filtration efficiency according to Eq. (5) [44]; however, it shall not affect the quality factor calculated using Eq. (2) because the term \( L \) (filter thickness) is canceled out.

In reality, electrospun nanofibers may not be uniform due to the random deposition of fibers. Thus, the fabrication of multilayer filters using single layer filters may result in different fiber orientations, which overcomes the non-uniform nature of final filter and increases total filter quality factor. Similar results were also reported for PAN nanofibrous filters [21]. However, in another study, which employed PEO nanofibrous filters, the quality factor of a single layer filter was the same as those of 2-layer and 3-layer filters [43]. The PEO nanofibrous filters might be more uniform than PVA and PAN nanofibrous filters.

One would expect the identical filtration performances for all filters fabricated using with same electrospinning parameters; however, results in Fig. 9 show otherwise. For example, NF6-A, NF6-B and NF6-C were fabricated under the same operating conditions but their filtration efficiencies and quality factors are not exactly the same, although they are close to each other. Both filtration efficiencies and quality factors of filters created in the shorter time deposition time of 5 min deviate less from one another than those made with longer deposition times (15 and 30 min). Due to the random nature of electrospinning, the characteristics of filters may differ even under the same electrospinning parameters.

Fig. 10 shows the comparison of the filtration efficiencies and quality factors of multilayer filters and associated single layer filters with the same total electrospinning deposition time. In any one of these three figures, the same amount of energy, time and materials were used to fabricate these single layers and the corresponding multilayer filters. However, results show that both filtration efficiencies and quality factors of the multilayer filters of 3 * NF6 and 2 * NF1 are higher than those of the corresponding single layer filters being NF1 and NF7, respectively. This comparatively higher quality factor of the multilayer filters is likely due to the higher quality of electrospun filters at shorter deposition times, which lead to more uniform spatial distribution of the fibers and better performances.

However, the differences between the filtration efficiencies and quality factors 2 * NF7 and NF8 is negligible, indicating that at such a long deposition time of 30 min, the improvement of filter is no longer obvious, and it is likely due to the lower quality of
nanofibers as explain above. Comparing the thickness of single layer and multilayer filters revealed the differences between the thicknesses of multilayer filters and corresponding single layer filters at longer deposition times. The thickness of $3 \times NF6$ (equivalent 15 min deposition time) is $3 \times 4 \mu m$, which is the same as that for NF1 (12 $\mu m$ for 15 min deposition time); however, the thickness of $2 \times NF1$ (equivalent 30 min deposition time) is $2 \times 12 \mu m$, which is greater than that of NF7 (17 $\mu m$ for 20 min deposition time). The thickness of $2 \times NF7$ (2 $\times 17 \mu m$) is also greater than that of NF8 (29 $\mu m$) filter. At a longer deposition time, the difference between the thickness of multilayer and single layer filters increased; it is non-linear. The higher thickness lead to the lower quality factor for both multilayer and single layer filters.

In summary, electrospinning parameters affect the filter characteristics and consequent filtration performance. The filtration performance depends on filter thickness, mean fiber diameter, and solidity. Although increasing the thickness of the filter elevates the filtration efficiency, it reduces the filter quality factor even more. Increase in the solidity and decrease in the fiber diameter lead to higher filtration efficiency. In this study, among filters fabricated at the same electrospinning deposition time, filters NF3 and NF5 had the highest filter quality factors. NF3 was fabricated at the applied voltage of 15 kV and tip-to-collector distance of 15 cm and had the smallest mean fiber diameter of 145 nm. NF5 was fabricated at the applied voltage of 17.5 kV and tip-to-collector distance of 10 cm, and it had the largest filter solidity of 0.0362. The results herein show that the high applied voltage and long tip-to-collector distance seemed to lead to great filter quality factor. Overall, PVA filters with the excellent performance can be fabricated by stacking thin nanofibrous filters with small mean fiber diameter and large solidities.

4. Conclusions

Results of this study show that the applied voltage, tip-to-collector distance, and deposition time of electrospinning process affected the fiber size, solidity and thickness of the produced nanofibers, as well as the quality factors of the nanofibrous filters. Employing multiple layer thin nanofibrous filters with different fiber diameters and solidities greatly increased the filter quality factors of the PVA nanofibrous filters.

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Appendix A. Supplementary material

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References
