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Filtration of fine particles in atmospheric aerosol with electrospinning nanofibers and its size distribution

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In this study, the size distribution of atmospheric aerosol in Beijing was monitored by the scanning mobility particle sizer spectrometer and the optical particle sizer. The size of particles in atmospheric aerosol was primarily distributed in the range of less than 1 μm. It showed different changes with the mass concentrations of particulate matters with an aerodynamic diameter of ⩽2.5 μm (PM2.5) for different sizes of fine particles. The amount of ultrafine particles (less than about 60 nm) decreased while the larger ones (>60 nm) increased along with the mass concentration of PM2.5 in atmospheric aerosol. This was because of the formation of the secondary atmospheric aerosol. The polylactic acid (PLA) nanofibers were prepared for filtering the aerosol by electrospinning. PLA nanofiber mats were used as the middle layer to design the composite filter membranes. Atmospheric aerosol was used as dust source in the filtration test. The results showed that the filtration efficiency of the composite filter media increased along with the thickness of nanofiber mats, which was controlled by the collection time during electrospinning. Filtration efficiency can be improved obviously by compositing with a thin layer of nanofibers.

atmospheric aerosol, filtration, electrospinning, polymer nanofibers

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1 Introduction

The pollution of particulate matters with an aerodynamic diameter of ⩽2.5 μm (PM2.5) has become more and more serious. It has attracted the attention of scientists, governments and media in recent years, especially after the serious haze pollution in December 2011 in Beijing [1,2]. PM2.5 and its extracts can induce many human diseases [3–6], visibility reduction and climate changes [7,8]. In previous studies, it has been suggested that the fine particles of Beijing were primarily composed of sulfates, nitrates, ammonium, and carbonaceous aerosol [9–11]. However, few studies were reported to study the size distribution of PM2.5 in Beijing, which is important for the analysis of aerosol formation, conversion and removal processes [12].

One of the most valid methods of removing particles from a gas stream is via fibrous filters. The smaller diameter of fibers leads to better efficiency in filtration fine particles. The electrospun nanofiber films are light weight, have a high permeability and a large surface area that make them appropriate for filtration of fine particles. The nanofibers can easily be achieved by electrospinning method. Many works have been done in the improvement of the filtration capability of media contained electrospinning nanofibers

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[13–16]. The polyactide (PLA) is a hydrophobic polymer with high biocompatibility, non-toxicity, and is quite stable under everyday conditions. PLA nonwoven fibrous mats have excellent mechanical properties and good biocompatibility in vivo [17–19]. In this study, the size distribution of fine particles in atmospheric aerosols in Beijing was monitored by the scanning mobility particle sizer spectrometer (SMPS) and the optical particle sizer (OPS). The PLA nanofibers were used for the filtration of fine particles in atmospheric aerosols, which were electrospun onto the polypropylene (PP) non-woven substrate. Part of the fine particles in atmospheric aerosol can be removed by PLA nanofibers. The filtration efficiency was increased with the increasing thickness of PLA nanofiber mats. This work put forward the use of nanofibers prepared by electrospinning in the filtration of fine particles in atmospheric aerosols (especially for PM2.5). This can be efficient in preventing the harmful effects of PM2.5.

2 Experiment platform and procedure

PLA (NatureWorks® PLA polymer 6202D) was purchased from Nature Works, INC (USA). The deionized water used in all preparations was produced by a Millipore milli-Q water purification system. N, N-dimethylformamide (DMF) and dichloromethane (DCM) supplied by Beijing Chemical Reagent Plant were used without further treatment. The PP non-woven fabrics with a thickness of about 120 μm were supplied by Handan Hengyong Protective & Clean Products Co., Ltd. Handan, China.

The real-time instruments, a scanning mobility particle sizer spectrometer (SMPS, Model 3936, TSI Inc., USA, 0.3 L/min aerosol flow rate, 3 L/min sheath flow rate, size range 14–660 nm) and an optical particle sizer (OPS, Model 3330, TSI Inc., USA, 1 L/min aerosol flow rate, 1 L/min sheath flow rate, size range 0.3–10 μm) were used to monitor the particles in atmospheric aerosol. The amount of particles in airflow before and after the air inlet being covered by the filter materials can be tested by the above instruments. And the corresponding mass concentration of aerosol can be given by the aerosol instrument manager software. Then the filtration efficiencies of the PLA nanofibers can be calculated from the mass concentration of atmospheric aerosol. The morphologies of the nanofibers were observed by the scanning electron microscope (SEM, Hitachi S-4800, Hitachi, Ltd. Tokyo, Japan). Prior to SEM measurement, the specimens were sputtered with gold to avoid charge accumulation.

SMPS and OPS were placed at the National Center for Nanoscience and Technology to monitor the size distribution of ambient aerosol under different PM2.5 concentrations, which were given in PM2.5 monitoring network. The site was approximately 250 m from the north 4th Ring Road of Beijing. Ambient air was sampled out of the 7th floor window and about 25 m above ground. The particle size distribution was monitored for at least four hours under each concentration of PM2.5.

Different concentrations of PLA solutions were prepared by dissolving PLA in DMF/DCM weight ratios (80/20) and completely dissolved by stirring. Typical parameters for the electrospinning experiments were as follows: the applied electric voltage was 20 kV, the distance between the spinneret and the grounded drum was 15 cm and the feed rate was fixed at 0.5 mL/h. The nanofibers were deposited on the PP non-woven substrate, which covered the collect roller to form the composite filter. It was dried under vacuum condition to remove the remaining solvent and used for the filtration test.

3 Results and discussion

Figure 1 shows the size distributions of fine particles under different mass concentrations of PM2.5 (10.0–195.0 $\mu g/m^3$), as given in the PM2.5 monitoring network. For the particles in the range of 14–660 nm, the peak in distribution curve was toward the right while the mass concentration of PM2.5 increasing as shown in Figure 1(a). The amount of ultrafine particles (less than about 60 nm) in atmospheric aerosol decreased with the increase of PM2.5 mass concentration. However, the amount of particles with diameter larger than about 60 nm increased along with the increase of PM2.5 mass concentration. As also shown in Figure 1(b), the amounts of particles (size range 0.3–10 μm) increased along with the PM2.5 mass concentration obviously. It was suggested that the fine particles in atmospheric aerosol were mainly distributed in the range of less than 1 μm.

Fine particles that dominated the particulate matter in Beijing were also studied before [20]. The fine particles are primarily composed of sulfates, nitrates, ammonium, and carbonaceous aerosols. Most fine particles are believed to be normally formed through secondary processes [21–23]. The SO_2 emitted from coal combustion and NO_x from vehicle exhaust and other finer particles are always less than 50–100 nm. The formation of secondary atmospheric aerosol involved gas to particle or gas to liquid conversion, the production of nanometer-size clusters, the growth of these clusters and coagulation with the pre-existing aerosol particle population. The particles need to grow further to sizes >50–100 nm in diameter until they were able to influence the climate [21]. The particles with diameters of smaller than 50–100 nm formed larger atmospheric aerosols through the above process. This is the reason for the decrease in particles of sizes less than about 60 nm but the larger ones increased with the mass concentration of PM2.5. So, some targeted filtration materials were needed to prevent atmospheric aerosols (especially for less than 1 μm) diffusing into the human body.

The electrospun PLA nanofibers with smaller diameter

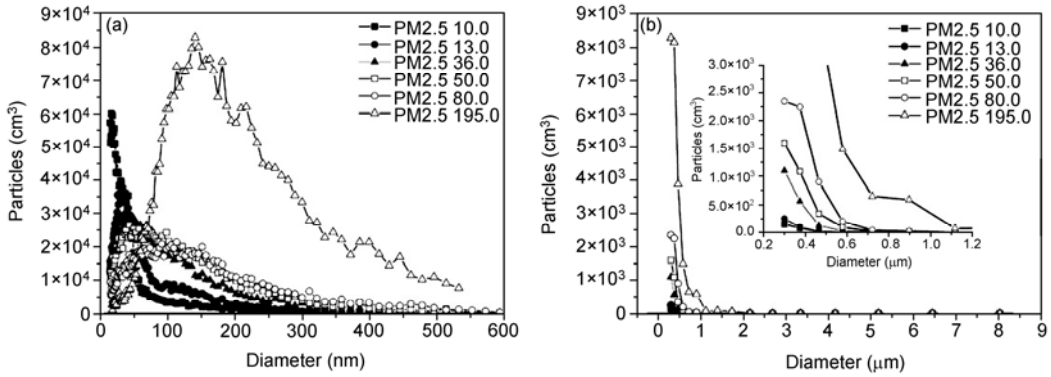

Figure 1 The size distribution of atmospheric aerosol measured by (a) SMPS and (b) OPS under different mass concentrations of PM2.5 (μg/m^3).

and larger surface area were more suitable for the filtration of fine particles in atmospheric aerosol. Figure 2 shows the SEM images of PLA nanofibers spun under different PLA concentrations. It can be seen that the morphologies and diameters of the electrospun nanofibers were obviously dependent on the polymer concentrations. The nanofibers with a large amount of beads were obtained when the concentration was 7 wt% as shown in Figure 2(a). This was caused by the little entangled polymer in lower concentration solutions, which was discussed in detail in previous studies [24,25]. However, uniform fibers were obtained when the concentration was higher than 7 wt%. The diameters of fibers were increased along with the increase of polymeric concentration. And it was about 282 ± 75 nm for 9 wt%, 486 ± 45 nm for 10 wt% and 813 ± 196 nm for 12 wt%. The thicker fibers were obtained at a higher concentration. In view of the fineness and uniformity of nanofibers, PLA (10 wt%) solution was used for the following study.

The PP non-woven substrate with a diameter larger than 20 μm was used to collect the nanofibers. The PLA nanofiber mats were used as the middle layer to design the composite filter mats as shown in Figure 3(a). The SEM image of composite mats was shown in Figure 3(b). As can be seen in Figure 3, a thin layer of nanofibers was sandwiched between two layers of PP. So, PLA nanofibers can be well fastened between the PP non-woven fabrics without slipping away.

The layers of nanofibers with thickness of about 2.2, 3.0, 4.5 and 8.8 μm controlled by electrospinning time were used to design different composite filter materials. Two layers of PP non-woven fabrics were also designed as a contrast test. The fine particles in atmospheric aerosol on a haze day (PM 2.5 was 195.0 μg/m^3) were used as dust source for filtration test. Filtration efficiency (η) can be expressed by the mass concentration of particles in airflow before and after the use of the filter materials:

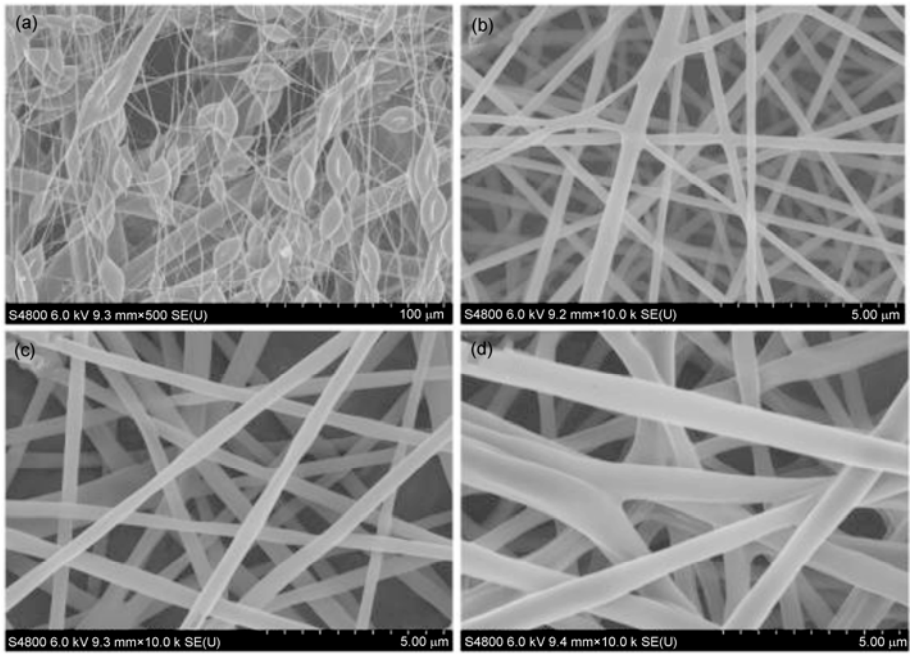

Figure 2 The SEM micrographs of PLA nanofibers spun under different PLA concentrations. (a) 7 wt%; (b) 9 wt%; (c) 10 wt%; (d) 12 wt%.

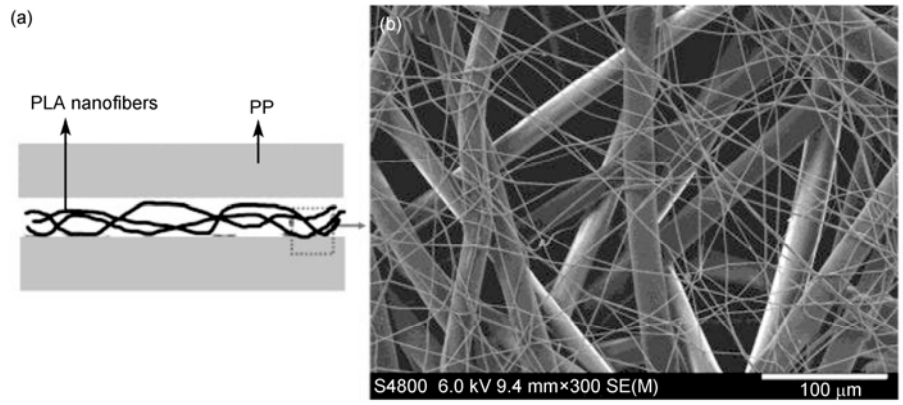

Figure 3 (a) The structural diagram; (b) the SEM image of the composite filter membranes.

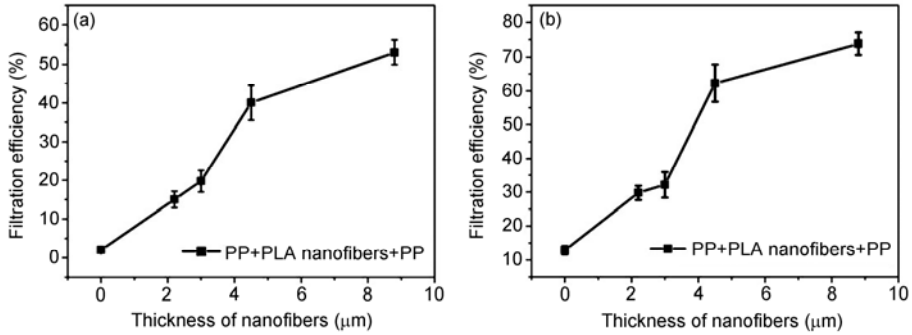

Figure 4 The filtration efficiency of the composite filter media versus the thickness of nanofibers for particles in the range of (a) 14–660 nm and (b) 0.3–10 μm. Each data point represented an average obtained from testing of five mats separately. Error bars indicated the standard deviation.

$$\eta = \frac{\rho_1 - \rho_2}{\rho_1}, \tag{1}$$

where ρ_1 and ρ_2 (μg/m^3) are the mass concentrations of particles in airflow before and after the use of the filter materials, respectively. The mass concentration of particles ranging from 14 to 660 nm could be obtained from the test of SMPS, while that of particles in the size range 0.3–10 μm were obtained by OPS. Filtration efficiency could be calculated from the eq. (1).

Figure 4 shows the filtration efficiency of the composite filter media, which changed with the thickness of nanofibers. For finer particles (ranged from 14 to 660 nm), the PP non-woven fabrics showed lower filtration efficiency at 2.0%. It can reach above 15.1% after compositing with a thin layer of nanofiber mat. The filtration efficiencies of the composite membranes versus increased thickness of nanofibers (2.2, 3.0, 4.5, 8.8 μm) were 15.1%, 19.8%, 40.1% and 53.2%, respectively (Figure 4(a)). As can be seen from Figure 4(b), the filtration efficiency on particles (ranged 0.3–10 μm) versus increased thickness of nanofibers (0, 2.2, 3.0, 4.5, 8.8 μm) were 12.9%, 29.8%, 32.2%, 62.3% and 73.9%, respectively. It showed the same change trend as the particles ranged from 14 to 660 nm. But it showed higher efficiency while using the same nanofibers. The larger particles are easier to be captured by filter madia. Filtration efficiencies can be significantly improved by compositing with a thin layer of nanofibers for fine particles.

4 Conclusion

The size distribution of fine particles in atmospheric aerosols in Beijing was measured under different PM2.5 concentrations. The particles were in a range less than 1 μm. It showed different change trend for different sizes of fine particles. The amount of finer particles (less than about 60 nm) decreased but the larger ones increased with the mass concentration of PM2.5. This was a result of the formation of the secondary atmospheric aerosol. A thin layer of PLA nanofiber film was sandwiched between two layers of PP to filter the atmospheric aerosols. Filtration efficiency increased with the thickness of PLA nanofiber mats. It was higher for particles in the range of 0.3–10 μm than for 14–660 nm particles while using the same filter media.

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