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Nanofiber-based filters as novel barrier systems for nanomaterial exposure scenarios

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Abstract. In this article our latest advances in the development of efficient barrier systems against micro- and nano-particulate materials are presented. Nanofibrous polyamide 6 (PA6) mats were fabricated by electrospinning onto a nonwoven viscose substrate. The influence of electrospinning parameters including solution concentration, viscosity, and conductivity, were studied for the production of nonwovens with different fiber size distribution ranging from 74 to 261 nm in diameters. Moreover, the formation of nanowebs (30-40 nm) which are widely distributed among fibers was observed. By varying several process parameters, membranes with different thickness of the nanofiber layer and therefore air permeability and nanoparticle filtration efficiency were obtained.

1. Introduction

A large diffusion of nanotechnology and nanotechnology related products, including the production processes of nanomaterials, is predicted in the coming years. Free particles can emerge in all stages of nanomaterials life cycle (production, processing, use, recycling and disposal). Therefore, the development of new barrier materials and protective systems are needed to reduce the potential risks related to human and environmental exposure to nanomaterials [1]. Nanofiber webs produced by electrospinning, due to their very large specific area, very small pore size, and high porosity, have shown to improve the efficiency of conventional materials used for filtration while reducing the pressure drop across the membrane [2].

Electrospinning is a well-established and versatile process that has been used to produce ultrafine fibers including microfibers (>1 μm) or nanofibers (<1000 nm). In electrospinning, a high voltage is applied to a polymer solution or melt, which overcomes the surface tension to form a charged jet. The charged polymer solution is ejected, dried, and solidified onto a grounded substrate. The ejected polymer solutions repel each other during the travel to the grounded collector, which forms thin fibers after solvent evaporation. By controlling the spinning conditions, the resulting fibers can range from about 20 nm to a few μm. The main advantage of electrospinning process is the relative quick and simple way to fabricate a variety of materials into nanofibrous structure.

In this paper, the development of new nanofiber-based non-wovens is described, including the study of their efficiency as barrier systems against nanoparticles. Polyamide 6 (PA6) was selected as the material for electrospun filters due to its good properties such as its toughness, resilience, and easy processability. Moreover, PA6 is extensively used in membrane and textile technologies. The fiber diameter and size distribution was studied as a function of parameters such as solution concentration, viscosity, and conductivity. The nanoparticle penetration was evaluated as a function of the nanofiber layer thickness using a polydisperse NaCl aerosol.

2. Experimental procedure

2.1. Electrospinning

PA6 and formic acid were purchased from Sigma Aldrich. PA6 was dissolved in formic acid at 50˚C and the solution was stirred for a sufficiently long time until it became homogeneous. Polymer solutions of several different concentrations were prepared, ranging from 10 to 30 wt. %. The solution viscosity and the electric conductivity were determined by a digital viscometer (DV-E, Brookfield Co.) and an electric conductivity meter (CRISON EC-meter BASIC) at 25˚C, respectively. The PA6 solutions were electrospun onto an aluminum foil or a non-woven viscose support (28 g/m^2) by using a commercially available electrospinning setup (MECC Co. LTD., model NF-103) equipped with a rotary drum collector. Typical operating conditions were: flow rates of 0.4 mL/h, applied voltages between 20 and 30 kV, and working distance of 8-10 cm.

The nanofibrous mats were characterized using a scanning electron microscope (SEM, Hitachi H-4100FE) after coating with carbon to minimize the charging effect. Images taken by the SEM were analyzed to obtain the fiber diameter by the *ImageJ* software. At least four pictures were used to calculate the mean values of the diameter of the fibers.

2.2. Aerosol filtration

The experimental system used to determine the penetration of nanoparticles through nanofibrous PA 6 filters is shown in Figure **1**. It consists of a polydisperse aerosol generator system, a filter holder containing the fiber material and the measurement equipment. Polydisperse aerosols have been used by several authors [3] after Japuntich et al [4] demonstrated that it produces similar results to the slower method of using monodisperse aerosols. The challenge polydisperse aerosol (NaCl) is generated from a 0.3% NaCl solution using a collision atomizer (TSI 3076) and then dried by passing it through a diffusion drier (TSI 3062). The filter media is mounted and clamped in a 4 cm diameter filter holder, corresponding to a filter face velocity of 1.7 cm/s. The number concentration of particles is measured upstream and downstream the filter using first an Electrostatic Classifier (TSI series 3080) with a long DMA (TSI 3081) to classify the particles followed by a Condensation Particle Counter (TSI CPC 3775) to measure them. The penetration of particles is calculated as a ratio among the concentration downstream (c_d) and upstream (c_u) ($P\% = c_d * 100 / c_u$).

For some of the filter media the effect of particle charge state was analysed [3]. To achieve this, the penetration of charged particles (coming directly from the aerosol drier) and charge neutralized particles (equilibrium distribution) were compared. The charge neutralized aerosol was achieved by passing the dried aerosol through a Kr-85 radioactive source.

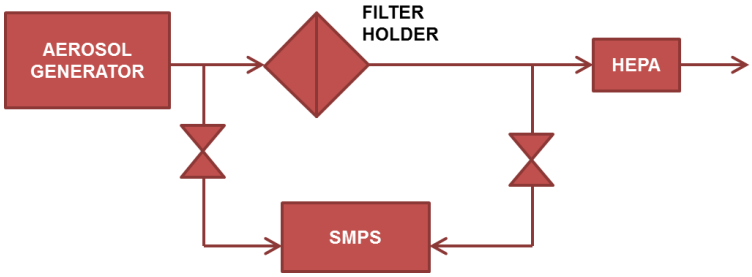

Figure 1. System used for the measurement of nanoparticle penetration through electrospun filters.

3. Results and discussion

3.1. Electrospinning

It is well known that the morphology of electrospun fibers depends on various processing parameters and environmental conditions. In order to gain control over the properties of the obtained nanofibers such as diameter, porosity, and morphology, the viscosity and the electrical conductivity were measured as function of the PA6 concentration in formic acid. Figure **2** shows that the viscosity increases steadily with polymer concentration going from 220 cP at 10 wt. % to 3840 cP at 30 wt. %. The electric conductivity of polymer solutions was between 4120 and 4880 µS/cm (Figure 2). The conductivity first increases going from 10 to 15 wt. % to then decrease with increasing polymer concentration due to the high dielectric constant (58.5 at 15˚C) and dipole moment (1.41 Debye) of formic acid [5].

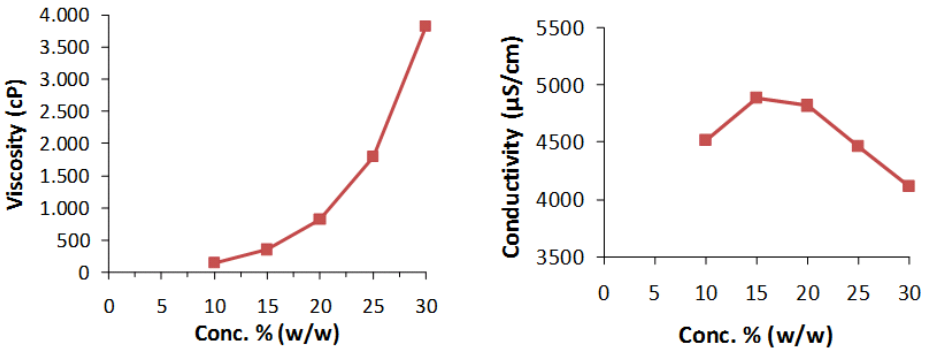

Figure 2. Solution viscosity and electrical conductivity as function of the polymer solution concentration.

The SEM images of PA6 nanofibers as function of polymer concentration are shown in Figure **3**. In general the fibers are uniform, without beads formation even at the lowest concentration of 10 wt. %. The average fiber diameter increases linearly from 74 to 261 nm going from 10 to 30 wt. % PA6 in formic acid (Figure 4). This indicates that the morphology of the nanofibers greatly depends on polymer concentration which effect viscosity. In fact, at higher polymer concentration there is more chain entanglement and less chain mobility, resulting in less extension during spinning, and therefore producing thicker fibers. Moreover, the fiber distribution is becoming gradually broader with increasing the concentration. Interestingly, the formation of a spider-net within nanofibers (nanowebs) appears at 15 wt. % concentration or above. These structures, which have a fiber diameter of 30-40 nm, although being widely present among fibers, are not homogeneously distributed over the whole

nanofiber mat. The formation of such nanowebs has been investigated by Barak at et al. [6] by the additions of ionic salts to polymer solutions. The authors concluded that nanowebs formation depends upon the concentration and the ionization of the used salt. In our case the formation of spider-net structures seems to increase with polymer concentration. Nanowebs can improve the mechanical properties of the PA6 nanofibers and may have a beneficial effect on the filtration efficiency. Therefore, more research is needed to clarify the mechanism governing the generation of nanowebs and to find a reliable process for producing homogeneously distributed structures in a controlled manner.

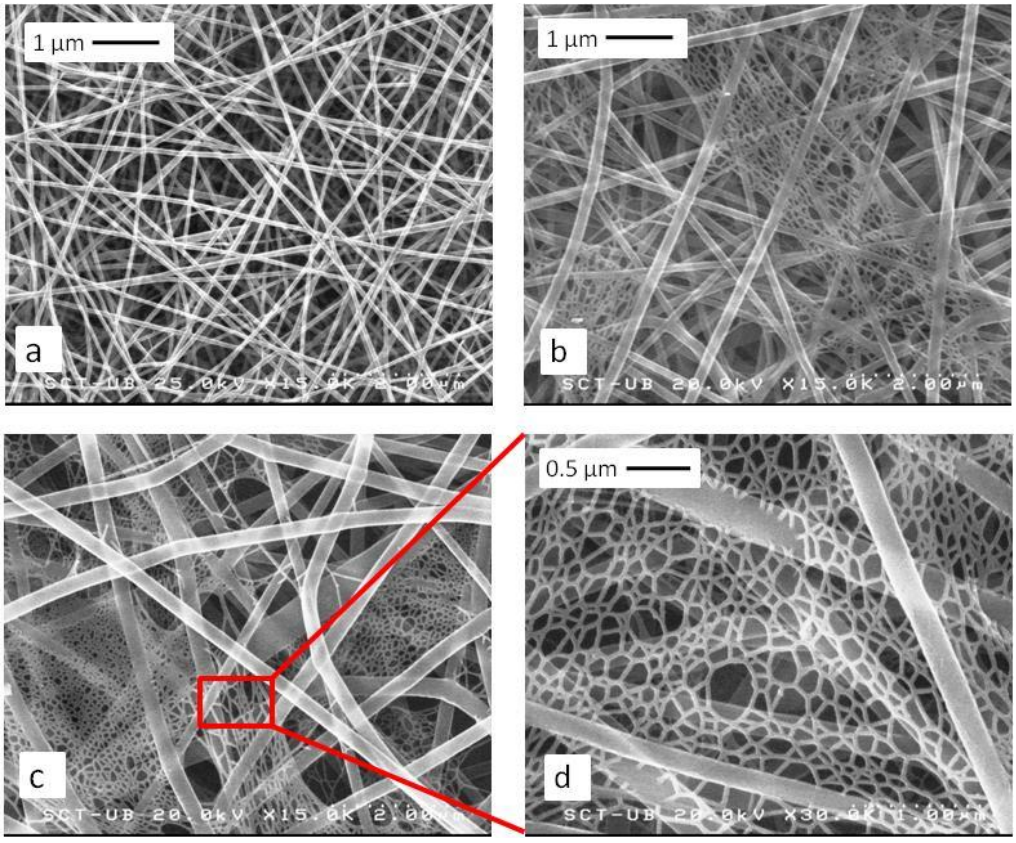

Figure 3. SEM images of electrospun PA6 nanofiber mats at different concentrations (a) 10, (b) 20, (c) 30 wt. %; and (d) PA nanowebs formation.

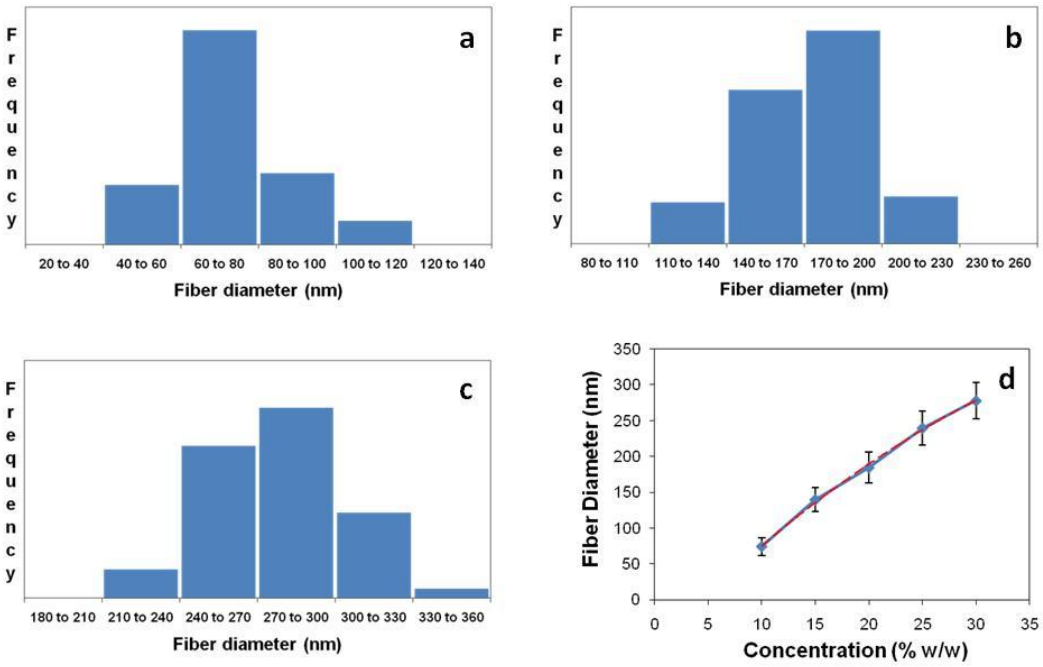

Figure 4. Fiber diameter distribution of electrospun PA6 fibers at different concentrations (a) 10, (b) 20, (c) 30 wt. %; and (d) average fiber diameter as function of polymer concentration.

3.2. Fabrication of the composite filter

For the mass production of nanofilters, the optimal conditions for steady state electrospinning have to be found. In our case a stable jet over a long period of time (several hours) was obtained using 15 wt. % of PA6 in formic acid, flow rate of 0.4 mL/h, applied voltage of 30 kV, and tip-to-collector distance of 8 cm. The viscose non-woven supports were coated with PA6 nanofibers using 5 different coating times (5, 10, 20, 30 and 60 min). By varying the nanofiber collection time allowed to generate filters with different thickness of the nanofiber layer and therefore fine tune the pore size, the air permeability, and therefore the filtration efficiency. Figure **5** shows that for shorter coating times the fibers and the structure of the viscose substrate can be clearly seen due to the small coverage and the larger pore size, while for longer coating times are almost undetectable.

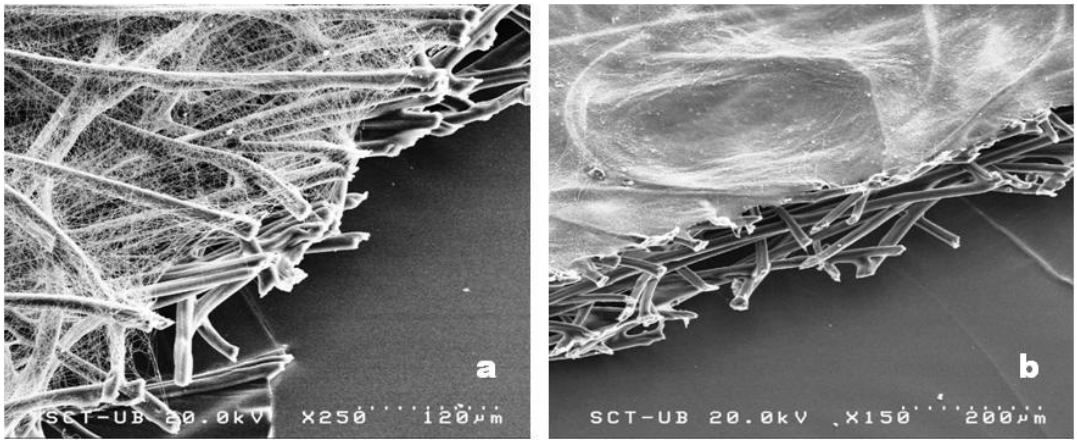

Figure 5. SEM images of the PA6 electrospun membranes with different coating times: (a) 10 min, (b) 60 min.

3.3. Nanoparticle penetration measurements

Figure **6** shows the initial results obtained for the penetration of nanoparticles (size range of 10-150 nm) through the five tested filters. The results showed that the penetration of nanoparticles through electrospun nanofibrous filters followed the classical filtration model, decreasing the penetration when decreasing the particle size, due to Brownian diffusion [7]. Figure **6** also shows that particle penetration is strongly a function of filter thickness (which is proportional to nanofiber deposition time) as predicted by other authors [8].

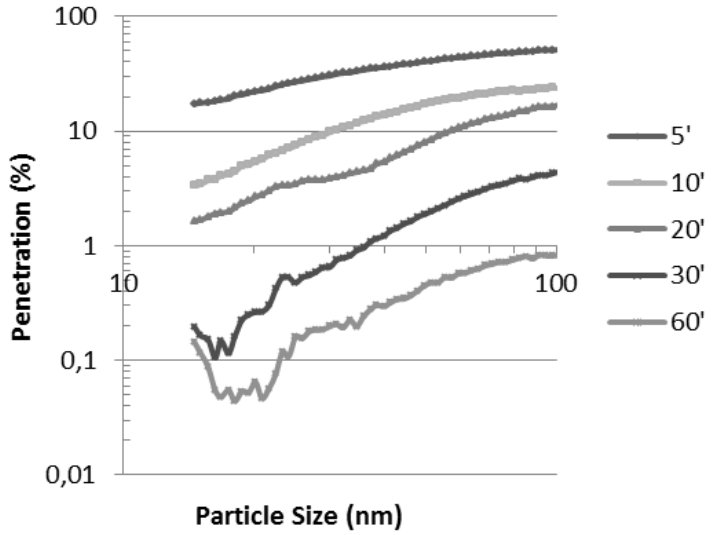

Figure 6. Penetration of nanoparticles through electrospun PA6 filters as a function of nanofiber coating time for a face velocity of 1.7 cm/s.

The study of the effect of particle charge was made comparing the penetration of charged particles versus neutralized particles (charge neutralized particles, equilibrium distribution) for some fiber samples. The results confirmed that particle penetration is independent of particle charge as predicted by other authors [4], which suggests that electrostatic interactions present between the particles and the

fibers did not lead to enhancement of particle collection. Hence, indicating that, for electrospun filters, the high collection by diffusion mechanism decreases the electrostatic collection. These results, however, have to be considered preliminary and more research is on-going using electrospun filters made from different materials and using different test conditions.

4. Conclusions

PA6 nanofibrous filters were produced by electrospinning onto a nonwoven viscose substrate. The influence of electrospinning parameters including solution concentration, viscosity, and conductivity, were studied for the production of nonwovens with different fiber size distribution ranging from 74 to 261 nm in diameters. Interestingly, spider-net structures, widely distributed among nanofibers, appear when solutions with PA6 concentration above 15 wt. % in formic acid are electrospun. The formation of such nanowebs seems to depend upon polymer concentration. By varying the nanofiber collection time, filters with different thickness of the PA6 nanofiber layer were obtained and their efficiency against nanoparticles penetration was evaluated for a face velocity of 1.7 cm/s. Particle penetration through the electrospun PA6 filters was strongly dependent on filter thickness, while the electrostatic forces did not enhance particle collection which only depends on diffusion mechanism. These results showed the possibility of applying the electrospinning technique to produce filter media and personal protective equipment against nanoparticle exposure.

Acknowledgments

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