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Mechanically enhanced electrospun nanofibers for wastewater treatment

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Abstract. A novel high-performance polyamide 6, polyacrylonitrile and polyvinylidene fluoride nanofibers were fabricated using industrial production Nanospider equipment for liquid filtration as microfilters. The application of nanofibers has been hindered by their poor mechanical strength. This work developed a feasible approach to preparing mechanically strong nanofiber webs. The mechanical strength of the nanofibers was enhanced using special lamination technique on a supporting layer. Experimental results show that the mechanical strength of the nanofibers enhanced more than 5 times while high porosity and liquid permeability retain. The separation results indicate that nanofibers have a potential to be used in liquid filters.

1 Introduction

Membrane-based technologies for wastewater filtration are constantly being designed due to the increase in water pollution, insufficient water resources and imbalance between water supply and consumption. Membrane separation technology has been important over the last few decades due to high separation performance, ease of operation and low cost. There are various techniques to fabricate membranes such as melt extrusion, expanded film, solution casting, track etching, phase inversion, template leaching and thermally induced phase separation. Electrospinning could be considered to use in membrane fabrication. Unlike the melt extrusion, electrospinning is a technique uses solution or melt to produce webs by applying high electrical field. This technique is a simple and inexpensive method to produce functionalized membranes.

Due to unique properties of high porosity, small pore size, large specific surface area, and high selectivity, nanofibers are excellent candidate for application of many areas, such as air filtration, ion-battery separation, biomedical, liquid filtration, so on [1–4]. The mechanical strength of the nanofibers restricts their application in real life. Herein, a special lamination technique was used to improve mechanical properties of the nanofibers. Polyamide 6 (PA6), polyacrylonitrile (PAN) and polyvinylidene fluoride (PVDF) were chosen as nanofiber layer. PVDF is one of the most used polymers in membrane technology due to its outstanding chemical, thermal and oxidation resistance properties [5, 6]. PAN has good characteristics including thermal stability, tolerance to most solvents,

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and commercial availability. PA6 is good in mechanical properties, water insoluble and easy to process.

The purpose of this article is to improve mechanical properties of the nanofibers and represent the results of research investigations on the application of polymeric microfiltration membranes of various nanofibrous membrane structures for the removal of impurities from industrial wastewater using the cross-flow system. The novelty of this paper is, that nanofiber layers were produced by using the Nanospider industrial equipment and that the layers strongly adhered on the supporting layer without any damage using a special lamination technology to improve application in wastewater remediation.

2 Materials and methods

2.1 Preparation of the nanofibers

8 g of PA6 (BASF B27, Germany) was dissolved in 30 g formic acid and 62 g acetic acid. 14 g of PVDF (Solef, Solvay, Germany) and 8 g of PAN (150 kDa, Elmarco, Czech Republic) were dissolved in 84 g dimethylacetamide and 92 g dimethyl formamide, respectively. To make a viscous mixture, all the solutions were stirred under constant stirring over the night.

Nanofiber layers were prepared from the polymer solutions using Nanospider NS-Lab 1WS500U device (Elmarco, Czech Republic). The experimental conditions are given in Table 1. The fibers were collected on a silicon paper.

Table 1. Experimental conditions of electrospinning.

Samples	Effective applied voltage (kV/cm)	Temperature (C)/ Relative humidity (%)	Width of sample (mm)	Substrate speed (mm/min)
PA6	4.25	22/38	500	25
PAN	4.33	20/22	500	15
PVDF	4.33	20/22	500	15

2.2 Characterization of membranes

The surface of nanofibers was characterized using a scanning electron microscope (SEM, Tescan Vega 3, Czech Republic). Image-j program was used to determine fiber diameter, diameter distribution, and surface porosity. The water contact angle was measured at different places of the samples using a Kruss Drop Shape Analyzer DS4. Thickness of the membranes was measured using a micrometer.

Tensile tests of the nanofibers and composite membranes were performed using a universal testing machine (Labor-Tech s.r.o., CR) with the extension rate of 10 mm/min, 100 mm length and 25 mm width at room temperature with a between the two clamps was 50 mm. Both machine (MD) and cross (CD) directions were tested. The composite membranes were kept under wet conditions for 4 days before testing, and the nanofiber layers were measured under dry condition due to their low mechanical properties after wetting.

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2.3 Lamination of the membranes

The nanofibers were laminated on a supporting layer 20 g/m^2 polypropylene/polyethylene bi-component (Pegas, Czech Republic) using a Meyer RPS-L Mini fusing machine under heat (125°C) and pressure (15 N/cm) at a specific contact time (1.7 m/min) as shown in Figure 1. This process was carried out gently to avoid damaging the structure of the nanofibers such as the fiber diameter and pore size.

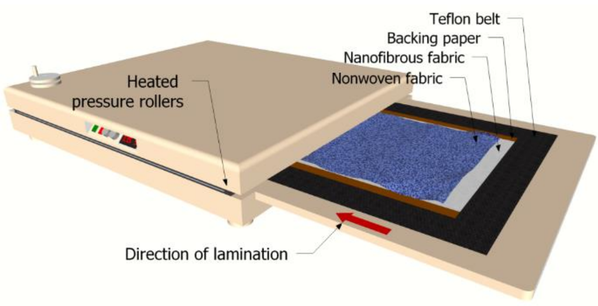

Fig.1. Lamination equipment [7].

2.4 Liquid filtration test

A custom-made cross-flow laboratory module equipped with pressure control and a constant water flow velocity through the cell (70 L/min) was used to filtrate the wastewater using the nanofibrous membranes [8]. The membranes were tested for 15 hours, and the flux was occasionally measured. All of the tests were performed at room temperature. Industrial sludge was used for the filtration test.

The permeate flux (F) and the permeability (k) of the membrane were calculated (Eq. (1) and (2)):

$$F = 1/A\ (dV/dt) \tag{1}$$

$$k = F/P \tag{2}$$

where A is the effective membrane area (m^2), V is the total volume of permeate, P is transmembrane pressure (bar), and t is the filtration time (h) [8].

3 Results and discussion

PA6, PVDF, and PAN nanofibrous composite membranes were prepared by using a special lamination technique. The lamination process carried out gently to avoid the damages of the fiber. As shown in the SEM images, Figure 2, uniform nanofibrous composite membranes were formed. Fiber diameter slightly changed after lamination process without any damage on the surface. PVDF nanofiber has a fiber diameter almost 2 times higher compared to

PAN and PA6. Fiber diameter has importance on the pore size of the material. Lower diameter means smaller pore size.

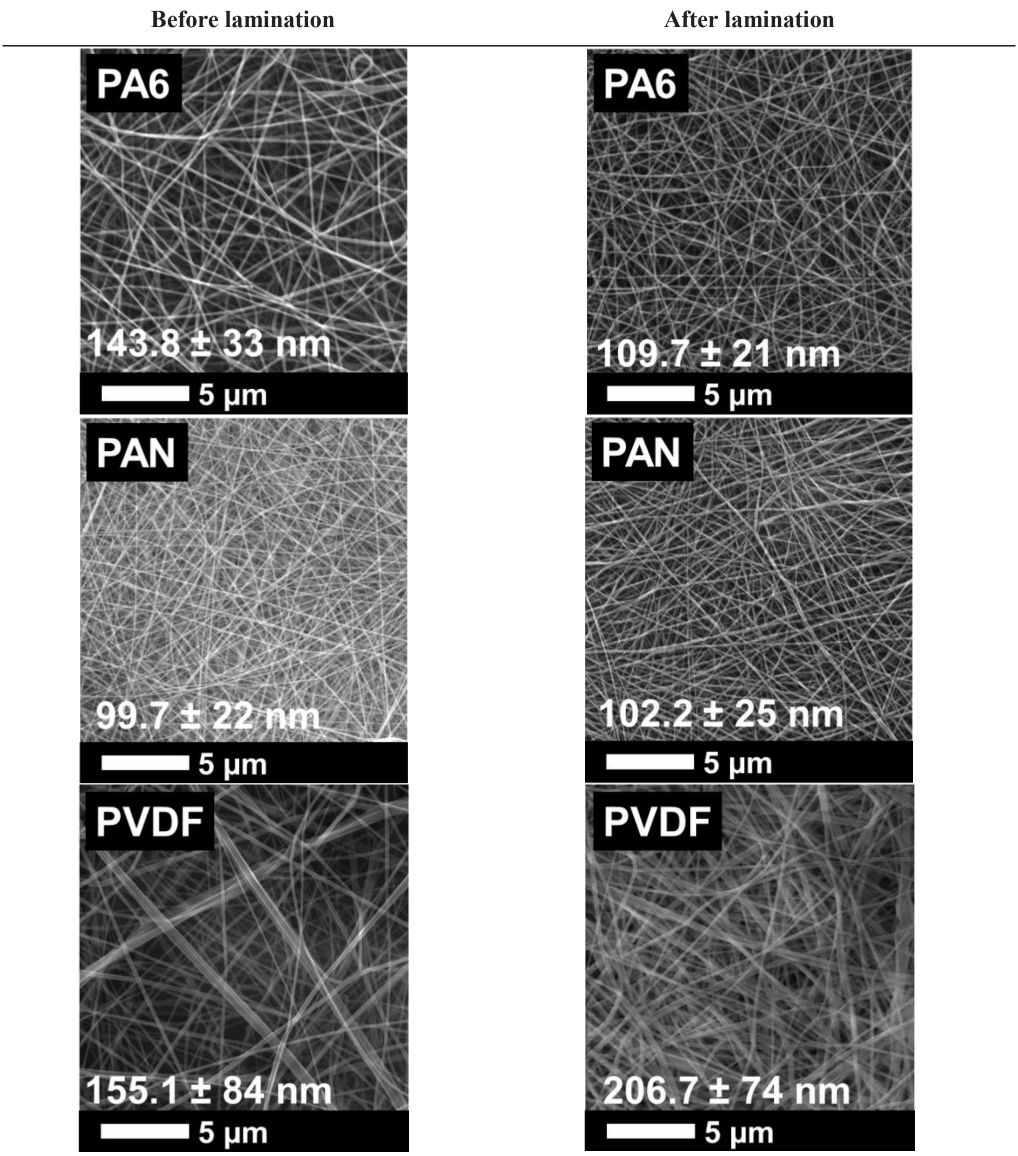

Fig. 2. SEM images of nanofibers before and after the lamination process.

The water contact angle and the porosity of the materials are shown in Table 2. The thickness of the membranes mainly depends on the thickness of the supporting layer.

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Table 2. Water contact angle, surface porosity and the thickness of the membranes.

Sample	Water contact angle (°)	Surface porosity (%)	Thickness of the membranes (μm)
PA6	125.8	88.56	259
PAN	79.45	85.13	296
PVDF	133.8	85.37	275

Membrane surface morphology has a significant effect on the permeability of the membranes. It was found that to have an idealized membrane should have a highly porous structure over than 70% of the pore size of the order of 2 μm for membrane distillation [9]. The small surface pore size could eliminate the internal fouling of the membranes. The surface porosity plays an important role to determine liquid flow across the membrane in microfiltration. All the membranes have very high surface porosity over than 85% which is advantages compared to commercial micro filters.

Hydrophobic membranes are resistant to wetting. Kim et al. found that [10] membrane fouling potential lowered by a hydrophilic membrane. On the other side, Yalcinkaya et al. [8] found that super hydrophilic membranes tend to foul easily compared to hydrophobic membranes. Among all membranes, only PAN membranes show the hydrophilic property. Figure 3 demonstrates the permeability of the membranes for the separation of industrial wastewater during 15 h separation. The permeability decline in time due to fouling of the membranes in first 3 h. The hydrophilic PAN membrane shows the lowest permeability compared to hydrophobic PVDF and PA6. The reason could be due to the high affinity of the PAN membrane for solid particles. The permeability results of PA6 and PVDF showed that nanofiber membranes could be a good candidate for wastewater separation.

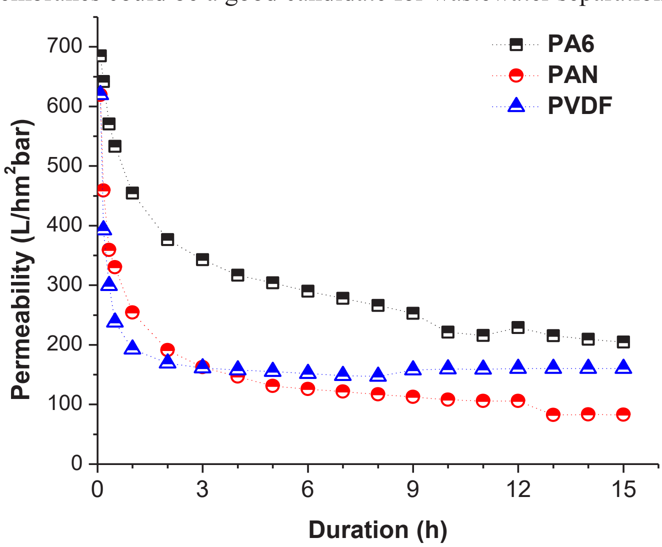

Fig. 3. Membrane permeability as a function of time.

The mechanical properties are one of the key parameters for microfiltration membranes. To determine the mechanical strength of the prepared nanofibrous composite membranes,

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tensile testing was conducted for wet membranes, and presented in Figure 4. Single nanofiber layers were examined under dry condition due to their poor wet strength.

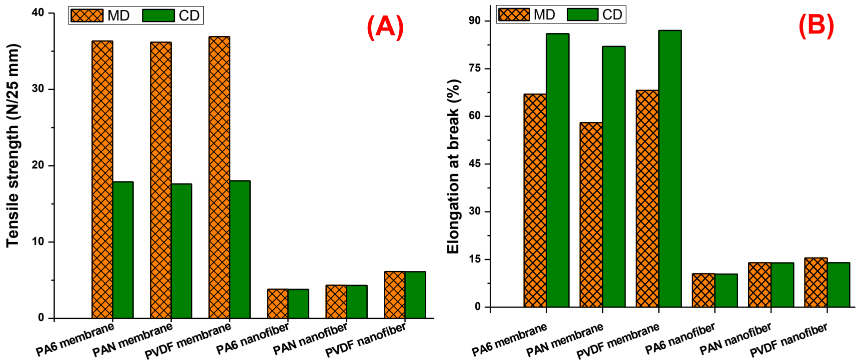

Fig. 4. Mechanical properties of the nanofibers and composite membranes (A) tensile strength, (B) elongation at break.

The tensile test showed that the mechanical strength of the nanofibers had been enhanced more than 5 times. The tensile strength of the membranes mainly depends on the property of the supporting material. The nanofibers have a slight effect on the strength of the composite membrane. It can be concluded that in wet condition of the membrane, it is stronger in the machine direction. When we compared the single-layer nanofibers, PVDF nanofibers are stronger than compared to PAN and PA6. In dry condition, nanofibers have the same strength in both MD and CD due to their anisotropic structure.

4 Conclusion

Novel high flux nanofibrous composite membranes were produced by using electrospinning system. Special lamination technique was applied to improve mechanical properties of the nanofiber web for microfiltration process. The results showed that laminated samples could strength the membrane without any damage on the nanofiber. It could be observed that for the single-layer nanofiber, the tensile strength and the elongation at break increase dramatically after lamination with a supporting material. The filtration of industrial wastewater indicates that the nanofibrous membranes can be suitable for the wastewater treatment with high permeability and good mechanical strength.

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