



# Poly(vinyl alcohol)–perfluorinated sulfonic acid nanofiber mats prepared via electrospinning as catalyst

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## ABSTRACT

Well-formed poly (vinyl alcohol) (PVA)–perfluorinated sulfonic acid (PFSA) nanofiber mats were fabricated via electrospinning process. Homogenous PFSA–PVA solutions were prepared by mixing PFSA-N, N-dimethylacetamide (DMAC) solution with PVA aqueous solution at different weight ratio. Increasing the weight ratio of PFSA in solution greatly increased the viscosity of the solution and slightly decreased the conductivity, which increased the diameter of the resulting PVA–PFSA nanofiber. The operating parameters such as tip to collector distance (TCD) and flow rate have a limited effect on the morphology of nanofibers, but high flow rate can improve the productivity. Ethyl acetate synthesis catalyzed by PVA–PFSA nanofiber mats was investigated, the results showed that all nanofibers have significantly catalytic activity, but the catalytic efficiency is related to the specific surface of PVA–PFSA nanofibers.

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## 1. Introduction

Perfluorinated sulfonic acid (PFSA) has excellent heat resistance and high mechanical strength. It is a good acid catalyst extensively used for alkylation, esterification, nitration reaction etc. [1,2]. To increase the catalytic efficiency of PFSA is very important since it is very expensive. For a catalyst, a porous structure with a large surface area can improve its catalytic performance. Electrospinning [3–5] is a well recognized and effective technique to produce nanofiber with diameter from micrometer to nanometer at present, which can significantly increase the surface area of the original material. However electrospinning a solution of neat PFSA is difficult [6], because of an insufficient number of polymer chain entanglements in its solution. PFSA does not molecularly dissolve in typical solvents, but rather forms a micellar structure. Most studies focused on the electrospinning process of PFSA blends. Chen et al. [7] investigated the electrospinning process of PFSA blended with poly (acrylic acid) (PAA). Choi et al. [8,9] fabricated several PFSA nanofiber composite membranes for fuel cell application.

In the present study, electrospun PVA–PFSA nanofiber mats were fabricated and used as esterization catalyst. Poly (vinyl alcohol) (PVA) is chosen as matrix because of its good chemical resistance and abundant resource. Moreover PVA nanofibers have been electrospun at different operating conditions, or co-spun with different additives [10–15]. Here the effects of electrospinning process parameters on the

morphology and catalytic property of PVA–PFSA nanofibers were investigated as well.

## 2. Experimental

PVA 1788 (degree of polymerization: 1700, degree of hydrolysis: 88%) was purchased from Yoshida Chemical Co. Ltd (Shenzhen, China). Reagent grade N, N-dimethylacetamide (DMAC) was purchased from Xiangyang Chemical Reagent Company (Shanghai, China). Perfluorinated sulfonic acid resin was prepared in our laboratory [16]. Briefly, PFSA was recovered from the deteriorated ion-exchange membrane F-8020 (the product of ASAHI Glass Company, Japan) used in chlor-alkali industry. F-8020 membrane is a PFSA/PFCA (perfluorocarboxylic acid) composite flat membrane reinforced by PTFE fibers.

PVA–PFSA solution was prepared by mixing 9% PVA aqueous solution and 8.3% PFSA DMAC solution (1:12 g/g) at certain ratio and heated to 100 °C with vigorous stirring, then the homogeneous solution was transferred into a 20 ml syringe with a capillary tip of 0.7 mm diameter. The high voltage power supply (16 kV) was employed to generate the electric field, which connected to the metal syringe tip. The fresh PFSA–PVA nanofibers were obtained by using a flat metal plate as collector. The nanofibers were crosslinked as follows: PVA–PFSA nanofibers were immersed into glutaraldehyde(GA)/acetone/water solution (GA content = 5 wt.%, acetone/water = 1:1 g/g) at 25 °C for 30 min with a few drop of sulphuric acid as catalyst, afterwards the samples were dried at 60 °C under vacuum for 24 h.

The viscosity of the solution was measured with a DV-II+PRO Digital Viscometer (Brookfield, USA) at 298 K. The conductivity of the solution was measured by Conductivity Meter (Ray Magnetic, China). The nanofibers were sputter-coated with gold and examined using a

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**Table 1**

The list of the PVA–PFSA nanofiber mats and the viscosity and conductivity data of the corresponding solutions.

Sample	Weight ratio of PVA to PFSA	Viscosity (Pas, 25 °C)	Conductivity ( $\mu\text{s}/\text{cm}$ , 25 °C)	Spinning condition TCD, FR
A	9/1	0.96	355	15 cm, 0.3 ml/h
B	9/2	1.30	342	
C	9/3	1.45	324	
D	9/4	1.70	282	
E	9/3	1.45	324	20 cm, 0.3 ml/h
F				15 cm, 0.5 ml/h

scanning electron microscope (SEM, JEOL, JSM-5600LV) at an operating voltage of 15 kV. The mean fiber diameters were obtained by measuring 30 single fibers randomly selected from their SEM photographs and then averaged.

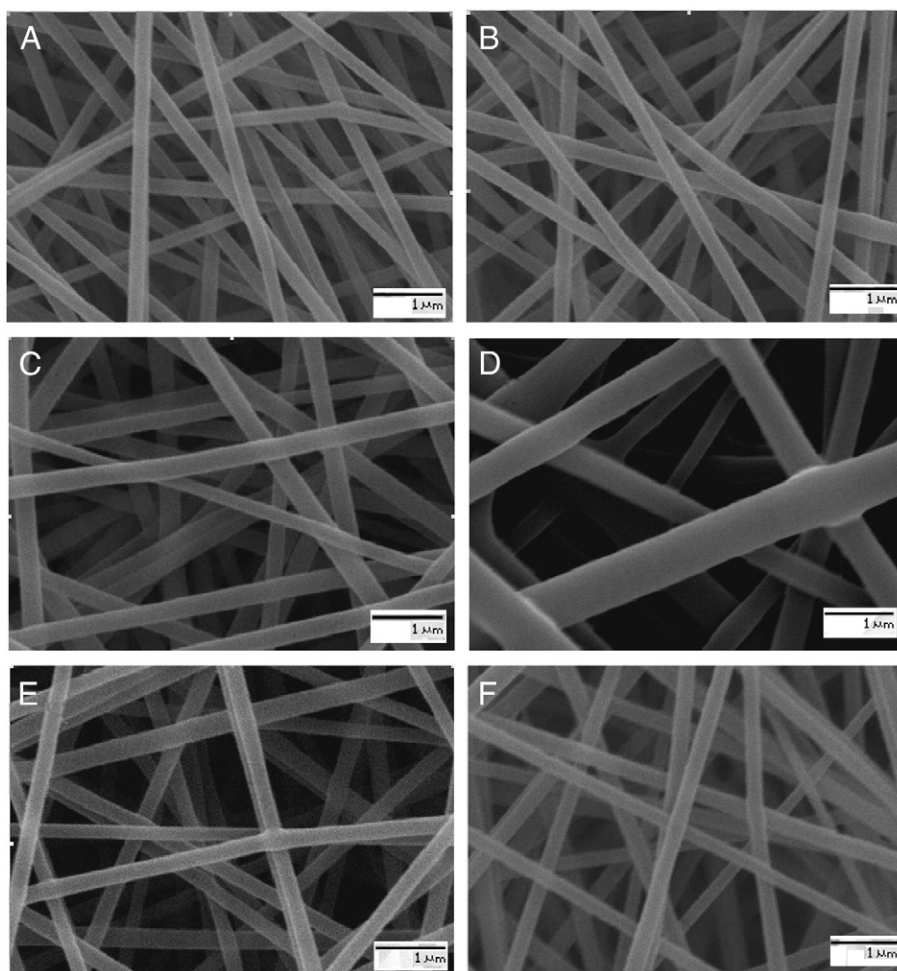
The catalytic activity of nanofibers was evaluated in an esterification reaction: 50 g Acetic acid and ethanol (Molar ratio 1:1) mixtures were weighted and added into a flask, then 0.45 g crosslinked PVA–PFSA samples were added, the reaction was carried out at 50 °C for 10 h. The content of ethyl acetate was analyzed by Gas Chromatogram (Techcomp, GC7890, China) equipped with a thermal conductivity detector (TCD) and a GDX-102 packed column, with ethanol as an internal standard, area normalization method.

### 3. Results and discussion

During the electrospinning process the properties of the solution can affect the morphology of the resulting nanofiber [17]. Here the mixture solvent was used in PFSA–PVA solution since PFSA is not soluble in water, the properties of the solution were shown in Table 1.

In Table 1, the viscosity increased quickly with increasing PFSA weight ratio in the solution. PFSA solution has a high viscosity with the existence of a large amount of water. Because its chains tend to reorganize into the complex structure [18]. Or in other words, water is the nonsolvent of PFSA, which tends to make PFSA solution to form a gel. However the reason for the decreasing conductivity of the solution is unclear. The conductivity is related to the dissociation degree of sulfonic acid groups of PFSA, which should be affected by the interaction among PVA, PFSA and mixture solvent.

The morphology of nanofibers is important for catalyst application. Fig. 1 showed the SEM photographs of PVA/PFSA nanofibers prepared from the solutions of different PFSA/PVA weight ratio, well-formed nanofibers were observed. The average diameter of PVA/PFSA nanofiber increased with increasing PFSA concentration. The variety in fiber size results from changes in the solution properties, the increasing viscosity requires more energy to split polymer solution into filaments, so the fiber size becomes larger when spun from the solution of high PFSA concentration. The average diameters of PVA/PFSA nanofibers were shown in Fig. 2.



**Fig. 1.** SEM photographs of PVA–PFSA nanofibers electrospun from the solutions of different PVA/PFSA weight ratio (A: 9/1, B: 9/2, C: 9/3, and D: 9/4.) and at different conditions. (C: 15 cm, 0.3 ml/h, E: 20 cm, 0.3 ml/h, and F: 15 cm, 0.5 ml/h).

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