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Published In:
Materials letters

OPEN ACCESS

1   **Development of microporous electrospun PIM-1 fibres**

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5

6   **Abstract**

7   Microfibrous PIM-1 membranes have been produced by electrospinning process. Conditions for the
8   fabrication (concentration of polymer, voltage, feed flow rate and distance between tip and
9   collector) have been investigated, and smooth fibrous materials with an average diameter of 2 μm
10   have been obtained in these following conditions: [PIM1]=5%wt, voltage=20kV, flow rate=5 ml/h
11   and distance=16 cm . These membranes presented a high hydrophobic character but a low liquid
12   entry pressure LEP.

13

16   1. **Introduction**

17   The preparation of hydrophobic membranes has been the subject of several recent studies in
18   membrane science to meet the demand of hydrophobic membrane-based processes such as
19   membrane distillation (MD), membrane emulsification (ME) or osmotic distillation (OD), for water
20   treatment. The hydrophobicity of the membrane is crucial for these applications in order to prevent
21   the loss of efficiency.

22   Membrane distillation (MD), which uses a hydrophobic membrane to separate pure water from a
23   saline solution, is regarded as a promising technology for desalination. One of the major challenges
24   that MD faces is that the membrane has to remain dry during the whole process; otherwise the
25   saline feed can intrude the pores, pollute the permeate stream and reduce the efficiency of the
26   process. The liquid entry pressure (LEP), defined as the minimum transmembrane pressure required
27   for liquid to enter into a pore, should be as high as possible. A high LEP can be achieved by using a
28   super hydrophobic material with a relatively small pore size [1].

29   The electrospinning technique is one of the best solutions to create easily materials with high
30   porosity and pore size ranging from ten nanometres to several micrometres [2]. One of the
31   advantages is the possibility to act on several different parameters, which can be optimised to tightly
32   control the resulting membrane morphology. In the present study, electrospun fibres of PIM-1 are
33   developed. PIM-1, which belongs to the PIM family (Polymers of Intrinsic Microporosity) is a
34   microporous material with a high internal surface area (typically 300-1500 m^2/g) [3]. Thanks to its
35   hydrophobic character [3], numerous studies have looked into its application for pervaporation [4,
36   5]. However, to our knowledge, there is no report on the use of PIM-1 fibres for membrane
37   distillation.

38   Initially, the structure of the electrospun fibres is studied as a function of the electrospinning process
39   conditions (PIM-1 concentration, feed rate, voltage). In the second part, the contact angle and LEP of
40   the fibres are determined.

1

2. Experimental

2.1. Materials

PIM-1 was kindly provided in powder form by the University of Edinburgh (School of Chemistry, group of Prof N. McKeown). The purity and the detailed synthesis procedure are reported elsewhere [4].

Solvents (anhydrous tetrahydrofuran THF, *N,N*-Dimethylformamide DMF) were purchased from VWR and used without purification.

2.2. Electrospinning technology

During the electrospinning process, the extruded polymer solution forms a conical shape under the electrical field. The jet is then elongated by a whipping process caused by electrostatic repulsion initiated at small bends in the fibre, until it is finally deposited on the grounded collector. The electrospinning apparatus (IME Technologies) used in this study is shown in Figure 1.

PIM-1 nanofibers have been already obtained by electrospinning with tetrachloroethane [6, 7]. However, to avoid highly toxic solvents, a mixture of THF/DMF is used in this study. A solution of PIM-1 in THF/DMF (9:1) is prepared by stirring the mixture at room temperature for 4 hours. To carry out the electrospinning process, the obtained solution is placed in a syringe pump and ejected through a needle charged with a potential of 5-25 kV at different feed rates. A piece of aluminium foil is placed towards the tip as grounded collector at a distance varying between 5 and 20 cm.
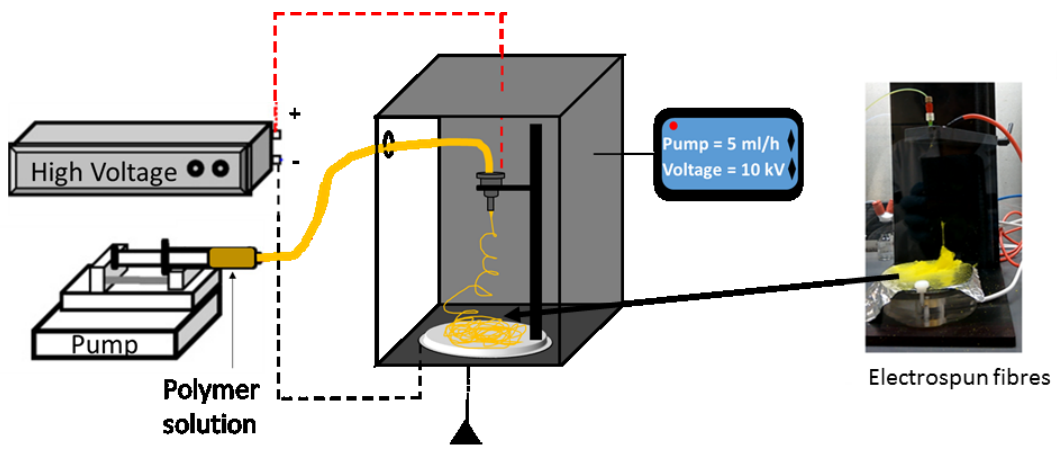

Figure 1: Electrospinning apparatus (on the left) and electrospun fibres (on the right).

2.3. Contact angle

Contact angle measurements and image analysis have been done using a FTA200 Dynamic Contact Angle Analyzer. The measurements were taken at room temperature using distilled water. The measurements were repeated (5 times) on different locations (3 locations) of the samples and averaged. The tangent method was used to calculate the contact angle. For each measurement, an approximate 10 μl droplet was dispensed onto the fibrous membrane or dense film. For the dynamic experiment, the sample was maintained in a close system.

1   2.4. <u>Sample imaging</u>

2 The membranes have been examined with a Hitachi 4700 II cold Field-emission Scanning Electron
3 Microscope operating at ~5 keV. Before SEM analysis, the samples were sputtered with a thin layer
4 of gold.

5   2.5. <u>Porosity</u>

6 The pore sizes of the membranes were measured using Quantachrome Porometer 3Gzh with the
7 wet/dry flow method. The sample was initially wetted by using a wetting liquid with low surface
8 tension (Porofil liquid). The pressure range was 0.1 bar to 1.4 bar. Three different parts of the
9 sample were analysed.

10

11 **3. Results and discussion**
12
13   3.1. <u>Effect of the process conditions</u>

14 The morphology and porosity of the fibre can be tuned by adjusting the process conditions. In this
15 study, we attempt to fabricate fibrous PIM-1 with a thin diameter and without defects, i.e. with no
16 bead-like structure. The influence of polymer concentration, flow rate, distance between the tip and
17 the collector and voltage are investigated in order to find the optimal conditions.

18 The operating conditions are listed in Table 1 and representative SEM pictures shown in Figure 2.
19
20 *Table 1: Operating conditions electrospinning process.*
21

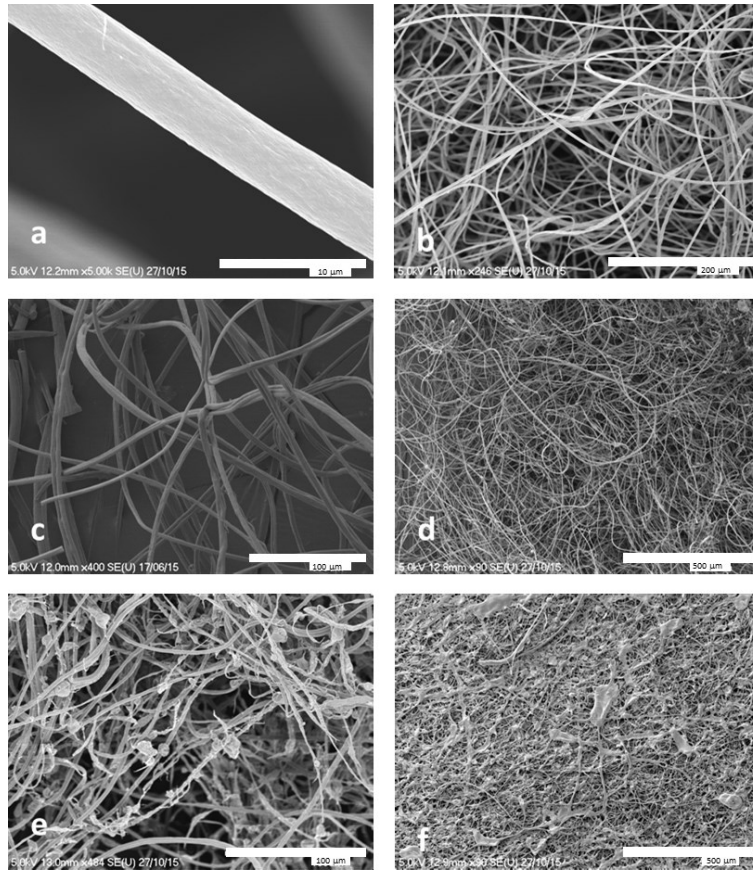| Sample number	PIM-1 concentration [%wt.]	Flow rate [ml/h]	Voltage [kV]	Gap [cm]	Results SEM analysis
1	5	5	20	16	Micro fibres – Fig.2a, 2b
2	5	10	20	16	Micro fibres – Fig. 2c, 2d
3	5	5	25	16	Micro fibres – Fig. 2e
4	5	5	15	16	No fibres
5	5	5	20	8	No fibres – Fig. 2f
6	10	5	20	16	No fibres

22

Figure 2: SEM analysis electrospun fibres of PIM-1: a,b=Sample1, c,d=Sample2, e=Sample3, f=Sample5. (See Table 1 for electrospinning conditions).

3.1.1. *Effect of concentration*

Three concentrations, 2.5%, 5% and 10% wt, of PIM-1 are studied. At low concentration (2.5%wt), non-fibrous material is obtained. At 5%wt, smooth fibrous materials are observed (Fig. 2a, 2b) with an average diameter of 2 μm. A further increase in concentration (10%wt) hinders the fibre formation. At the low concentration, there is an insufficient number of entanglements in the polymer chains that does not lead to fibre creation. By increasing the concentration of PIM-1, entanglements become prevalent conducting to fibre formation. At higher concentration, the solution is too viscous and blocks the needle.

3.1.2. *Effect of flow rate*

Two flow rates of the polymer solution inside the needle, 5 ml/h and 10 ml/h, are used. At 5 ml/h, fibres with a diameter of 2 μm are formed (Fig. 2a, 2b). At 10 ml/h, thicker fibres are collected (Fig. 2c, 2d) with a diameter of 5 μm. This is due to increased volume leading to a lower bending instability and subsequently an increase in fibre diameter. Moreover, for higher flow rate (10 ml/h), some beads appear. The electrospun fibres may not be completely dry when they reach the target, which leads to bead formation in the final membrane morphology.

3.1.3. *Effect of gap*

Several distances between tip and collector are tested. With a low distance (< 8 cm), fused fibres are obtained due to the fact that the solution did not have enough time to solidify (Fig. 2f). By increasing the distance, thinner fibres are formed due to a greater stretching distance.

1 *3.1.4.Effect of voltage*

2 With a low (10kV) and high voltage (25 kV) (Fig 2e), no fibres are obtained. If the voltage is
3 insufficient to overcome the charge of the solution, Taylor cone formation is inhibited and no fibre is
4 developed. On the contrary, with an extreme voltage, the repulsive forces from the surface charges
5 cause the droplet to disperse prior to the ejection.

6

7 ## 3.2. Characterisation

8 The best obtained fibres (sample 1) are characterized to investigate the suitability of using them as
9 materials for membrane distillation.

10 The thermal stability of the sample has been shown by a TGA analysis. The results are available on
11 the Supplementary Information.

12

13 *3.2.1.Contact angle*

14 Table 2 shows that PIM-1 processed into microfibers has higher hydrophobicity character compared
15 to unspun PIM-1. The electrospun fibre is highly hydrophobic, with a contact angle greater that
16 130°C. The same value has been found by Zhang et al. [6] for electrospun microfibrous PIM-1
17 membranes obtained with tetrachloroethane as a solvent. The contact angle is higher than for dense
18 membrane due to the rougher surface of the electrospun fibres. Our membranes present a contact
19 angle only slightly lower than PVDF or PTFE, which are membranes commonly used for membrane
20 distillation.

21

22 *Table 2: Characteristics of electrospun PIM1 fibres (Sample1) and others classical electrospun fibres used for membrane distillation*
23 *application.*

	Dense film PIM-1	Microfibrous PIM-1 Our work	Microfibrous PIM-1 [7]	PTFE [8]	PVDF [9]
Water contact angle θ [°]	75	135	135	140	137-141
Maximum pore radius r_{max} [μm]	-	1.7	0.8	0.45	0.5-0.65
Liquid entry pressure LEP [kPa]	-	59.5	-	206	63-112

24

25 Moreover, the contact angle remains stable with time (Figure 3). This result is very interesting for a
26 distillation process where the wetting of the fibres will have a negative impact on the process
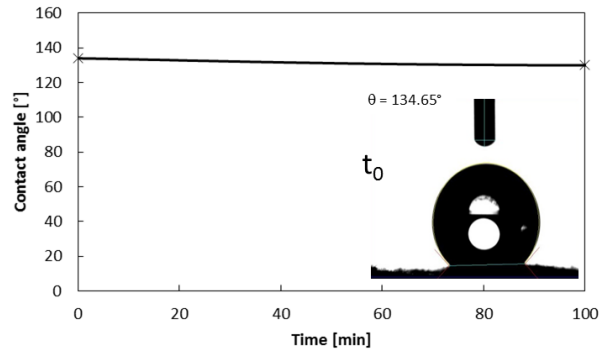27 efficiency.

Figure 3: Contact angle of PIM1 Microfibers (Sample 1) with time contact. (Liquid=Distilled water).

Additionally, a high hydrophobicity should lead to better vapour transport. Dumée et al. [10] showed that the hydrophobic forces generate a thin insulating air film on the surface, which allows reducing the temperature polarisation and the heat diffusion within the membrane material, therefore increasing the MD performance.

3.2.2. *LEP*

The wetting resistance of a membrane can be quantified by its liquid entry pressure (LEP), which defines the maximum liquid pressure a membrane can withstand without getting wet. The LEP of the PIM-1 microfibres is determined by using the Young-Laplace modified equation [11]:

$$LEP = \frac{-2\gamma B cos\theta}{r_{max}}$$ (1)

Where γ is the surface tension of the wetting liquid, θ the contact angle between the wetting liquid and the material, B the shape factor and r_{max} the maximum pore radius of the membrane. The eq. (1) shows that the contact angle is a critical parameter for the wetting resistance of the membrane. A high contact angle is required to prevent pore wetting of the membrane.

Our LEP are determined with water as wetting liquid (γ=72.8 mNm^{-1}) and for B=1, which assumes uniform cylindrical pores [12]. This assumption gives the maximum LEP of the membranes, which is higher than the real value of the wetting pressure. The LEP of the electrospun microfibrous PIM-1 in this work is lower than the materials commonly used for membrane distillation. This is due to the fact that the pore size of the microfibrous membrane is two times-bigger than in literature [7]. The fabrication process needs to be optimised further. For example, increasing the time of spinning will result in higher thickness and a smaller pore size [9].

4. Conclusion

In this study, hydrophobic microfibrous PIM-1 membranes are successfully fabricated with an electrospinning process. The effects of the electrospinning process are investigated. PIM-1 microfibre is obtained with a diameter of 2 μm and a maximum pore size of 3.4 μm. This membrane presents a high hydrophobic character with a water contact angle of 135°, which induces a LEP of 60 kPa. Despite this low value of LEP, these initial results are very encouraging and suggest the potential of PIM-1 to be used as materials for a membrane distillation application.

Acknowledgements:

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version.

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