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The effect of electro spinning parameters on polystyrene nano fiber morphology: oil-water separation

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ABSTRACT

This manuscript reports optimized conditions necessary to prepare electro-spun nano fibers and microfibers using two different forms of polystyrene (PS) in dimethylformamide (DMF). We conducted a systematic and methodical study on the influence of all electro spinning parameters to obtain bead-free PS fibers by dissolving the samples in DMF. Polymers with two different molecular weights are used for electro spinning, and they show significant changes on fiber morphology of PS even after maintaining similar electro spinning conditions. After optimizing the parameters, bead-free and uniform PS electro spun fiber mats were prepared and used as efficient, low-cost, and oil-water separator.

Keywords: Electro spinning; Fiber; Hydrophobic; Membrane

1. Introduction

Electro spinning is a versatile technique for the preparation of multi functional polymer fibers. In this technique, a polymer solution is extracted via metal capillary under the influence of a strong electrostatic field. This causes the solvent to evaporate; very thin fibrils in the micro and nano scale are deposited on a grounded collector in the form of a non woven mat [1]. This reduction in fiber size results in a notable increase in the physical and chemical properties of the polymer film to improve the functional properties and surface area-to-volume ratio. The appreciably larger surface area and pore size distribution improve surface fictionalization and design ability. Electro spun fibers are currently used in filtration, chemical/biological resistant protective clothing, tissue engineering, and electronics [2].

Polystyrene (PS) is one of the most widely available and cost effective polymeric materials. It is used extensively in packaging, filtration, insulation, food service disposables, and consumer electronics [3]. It is used to make melts, films, and foams. It is generally processed by injection molding, extruding, and thermoforming [4]. Electro spinning of polystyrene produces interesting changes in the structure of the polymer. Electro-spun polystyrene finds use in the form of sensors, tissue engineering scaffolds, and filters [2,5–9].

The surface morphology of the electro-spun fiber depends on several parameters. These include the solution properties such as concentration, viscosity, elasticity, surface tension, and conductivity of the polymer solution. These can be controlled by either adjusting the solvent or using additives in the solution [1,10–12]. Ambient parameters such as applied electric field, pressure, temperature, humidity, and air velocity in the electro spinning chamber can also be adjusted in the instrument [13]. Instrument operation parameters like applied voltage, flow rate, distance between the needle and the collector, internal diameter of the needle, type of collector, and the speed of rotation of the collector can also be used to prepare the ideal morphology [14–16]. Finally, molecular weight of the polymer has a very significant effect on the properties of the polymer fibers.

Here, we present a systematic study on the effect of the various parameters on electro-spun fiber morphology. Electro spinning is a simple, versatile, low-cost, one-step method for the preparation of uniform fibers of different dimensions based on end application. However, obtaining

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uniform bead free fibers using electro spinning is always a challenge because a very small change in any of the electro spin parameters may significantly affect the end output. Here we have tried to optimize four electro spinning parameters for two different molecular weights of PS to prepare super hydrophobic and superoleophilic PS nano fiber membranes. We utilize them for the separation of low-viscosity oil from water.

2. Experimental section

The following section describes the materials used, preparation methods, characterization techniques, and filtration methods adapted using an electro spun polymer fiber membrane.

2.1. Materials

Two different types of PS pellets those were white-coloured, had glass transition temperature of 100°C, refractive index of 1.5916, Mw = 280,000 kg/k mol, and 35,000 kg/k mol and density of 1.047 g/mL at 25°C were procured from Sigma Aldrich (Sigma-Aldrich Chemie GmbH). Dimethylformamide (DMF) was used as a solvent to dissolve PS, and it was also obtained from Sigma Aldrich; ACS reagent 99.8% purity, density = 0.948 g/ml, Mw = 73.09 kg/kmol. Diesel oil was obtained from Woqood, Doha, Qatar. The thermal and physical properties of the diesel oil are listed in Table 1. Double distilled deionized water was used throughout the experiment.

2.2. Electro spinning of PS fiber membrane

Two different molecular weights of PS were used for electro spinning: 35,000 (W_1) and 280,000 (W_2). Due to big differences in molecular weight of the two PS materials, we used different sets of electro spinning parameters. Concentrations for W_1 were 10%, 20%, and 30%; for W_2 they were 10%, 20%, and 25%. Both were dissolved in DMF followed by continuous stirring for 24 h prior to electro spinning process. The optimized concentration of each type of the polymer with three different flow rates of the precursor solution were utilized via a syringe pump to yield a stable Taylor cone and uniform fibers. Throughout the experiment, a needle with an inner diameter of 0.25 mm was used for electro spinning. The charging needle and the substrate were grounded by connecting them to voltage supply wires. Three different voltages were used for PS W_1 (15 kV, 20 kV and 25 kV). Four different voltages were used for PS W_2 (10 kV, 15 kV, 20 kV and 25 kV). These were applied to the needle to produce an electric field and - nano fibers. The aluminum sheets were cleaned using absolute ethanol and acetone prior to the electro spinning deposition. A constant deposition time was maintained for all systems. The needle collector distances were changed to optimize the distance between them. The flow rate of the polymer solution used a syringe pump from the electro spinning needle tip that was adjusted to prepare a uniform fiber.

The electro spinning parameters along with the values of the needle collector distances and flow rates are detailed in Table 2. The morphology of the PS fiber membrane prepared on the aluminum sheet by electro spinning at room temperature is provided in Section 3.1. A schematic of the electro spinning process is shown in Fig. 1.

Table 1
The thermal and physical properties of the diesel oil

	Density	Surface tension	Viscosity
Diesel oil	0.820	0.03	2.98

2.3. Characterization methods

The surface morphology that included micro structure and nano structure of the PS membrane was characterized by high-resolution scanning electron microscopy (a nano-SEM Nova 450 at 30 kV). The fiber diameters were determined via SEM. The wettability properties of the PS nano fiber membranes were determined by static water-contact-angle measurements in open air. We used a Data physics OCA 35 to measure the contact angle of both water and diesel oil in order to check their wetting properties on PS membrane. The average static water contact angle was obtained from measurements taken at five different positions on the same membrane. In each case, the contact angle was calculated after the drop rested on the PS nano fiber membrane for 5 s. The DI water was supplied to a stainless-steel nozzle via a syringe pump at a flow rate of 180 µL/h. All measurements and experiments were performed under ambient conditions and room temperature.

2.4. Super hydrophobic and superoleophilic experiment

Apart from the contact angle measurement, another experiment was performed to determine the super hydrophobic and superoleophilic nature of the PS membrane. The experimental design used for this purpose consisted of a Gooch filter integrated with a sintered disc with porosity grade 2 on the top and bottom of the beaker; the PS fiber membrane was placed on the sintered disc between them. The water was dyed blue using a water-based ink to distinguish it from the oil; the diesel oil was used as received. The water and diesel were put into two different pairs of Gooch filter-beaker sets. It was simply a gravity-driven experiment; the details of the experiment are elaborated on in Section 3.3.

2.5. Oil-Water separation experiment setup

In order to investigate the oil-water separation efficiency of the PS membrane, two different force-driven experiments were performed. Both the experiments were performed in room temperature; the first method used a vacuum pump-driven force and second one used a syringe pump-driven force.

In the case of vacuum pump-driven force, the experimental setup consisted of a Buchner funnel fitted with sintered glass as a feeding chamber and the collecting chamber was a conical flask with a sidearm to connect to the vacuum pump. A constant flow rate (10 mL/min) was maintained by the vacuum pump throughout the experiment. Fig. 2

Table 2
Electro spinning parameters and corresponding polymer diameter and morphology

Image name	Molecular weight	Applied voltage (kV)	Polymer concentration (MW)	Tip collector distance (cm)	Flow rate (ml/h)	Size and morphology
1(a)	35,000	15	20	10	1	280 nm, beaded
1(b)	35,000	20	20	10	1	360 nm, uniform
1(c)	35,000	25	20	10	1	300 nm, beaded
1(d)	35,000	20	20	10	0.5	230 nm, beaded
1(e)	35,000	20	20	10	0.7	280–400 nm, non- uniform
1(f)	35,000	20	20	10	1	360 nm, uniform
1(g)	35,000	20	10	10	1	230 nm, beaded
1(h)	35,000	20	20	10	1	360 nm, uniform
1(i)	35,000	20	30	10	1	360 nm, uniform, broken
1(j)	35,000	20	20	5	1	360 nm, beaded
1(k)	35,000	20	20	7	1	360 nm, beaded
1(l)	35,000	20	20	10	1	360 nm, uniform
2(a)	250,000	10	20	15	1	3200 nm, uniform
2(b)	250,000	15	20	15	1	3200 nm, uniform
2(c)	250,000	20	20	15	1	2300 nm, uniform
2(d)	250,000	25	20	15	1	4000 nm, uniform
2(e)	250,000	15	20	15	0.7	4000 nm, uniform
2(f)	250,000	15	20	15	1	3200 nm, uniform
2(g)	250,000	15	20	15	1.5	2500 nm, uniform
2(h)	250,000	15	10	15	1.5	500 nm, beaded
2(i)	250,000	15	20	15	1.5	1000 nm, uniform
2(j)	250,000	15	25	15	1.5	2000 nm, uniform
2(k)	250,000	15	20	5	1.5	4500 nm, uniform
2(l)	250,000	15	20	7	1.5	3500 nm, uniform
2(m)	250,000	15	20	10	1.5	2500 nm, uniform

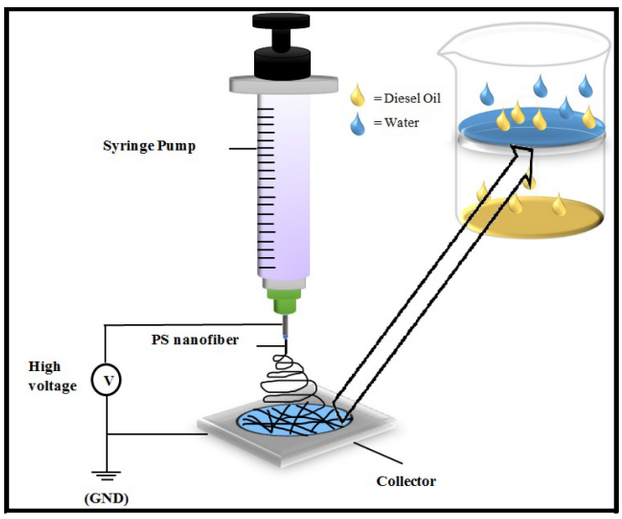

Fig. 1. The schematic diagram of the preparation of filter membrane by electro spinning process.

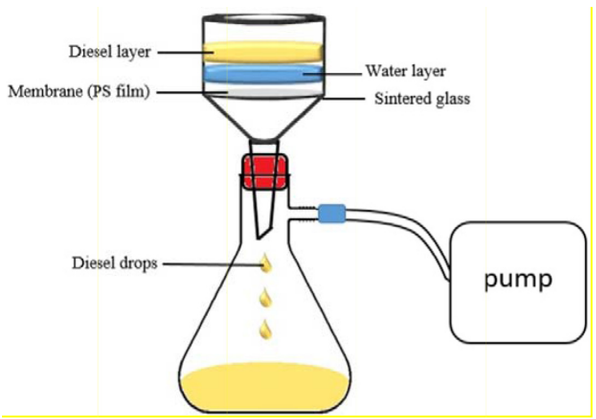

Fig. 2. Schematic diagram of oil-water separation using vacuum pump-driven force.

illustrates the schematic diagram of oil-water separation using a vacuum pump-driven force.

The syringe pump-driven force setup consisted of a horizontal setup with the syringe plunger pressed at a constant rate by the syringe pump. In this setup, the syringe pump was connected to the back of the piston of the syringe in order to give pressure. As the syringe was positioned horizontally, both oil and water were simultaneously in contact with the membrane. A constant flow rate of 2 mL/min by the vacuum pump was maintained in this experiment.

3. Results and discussion

3.1. Surface morphology studies

The effect that the electro spinning parameters had on the morphology of the fibers was studied with SEM. Figs. 3a–h and Figs. 4a–f show the SEM images of the two molecular weights, and Table 2 describes the electro spin parameters and morphology of each image. It is found that the two different molecular weights (35,000 (W_1) and 280,000 (W_2)) have distinct effects on the diameters of the fibers. The fiber diameters calculated from the SEM images are given in Table 2. This table shows that the fibers obtained using W_1 polymers have an average diameter of 250 nm to 400 nm. At the same time, fibers with the W_2 polymer have a higher diameter (2000 nm to 4000 nm). The W_1 polymers with three different voltages

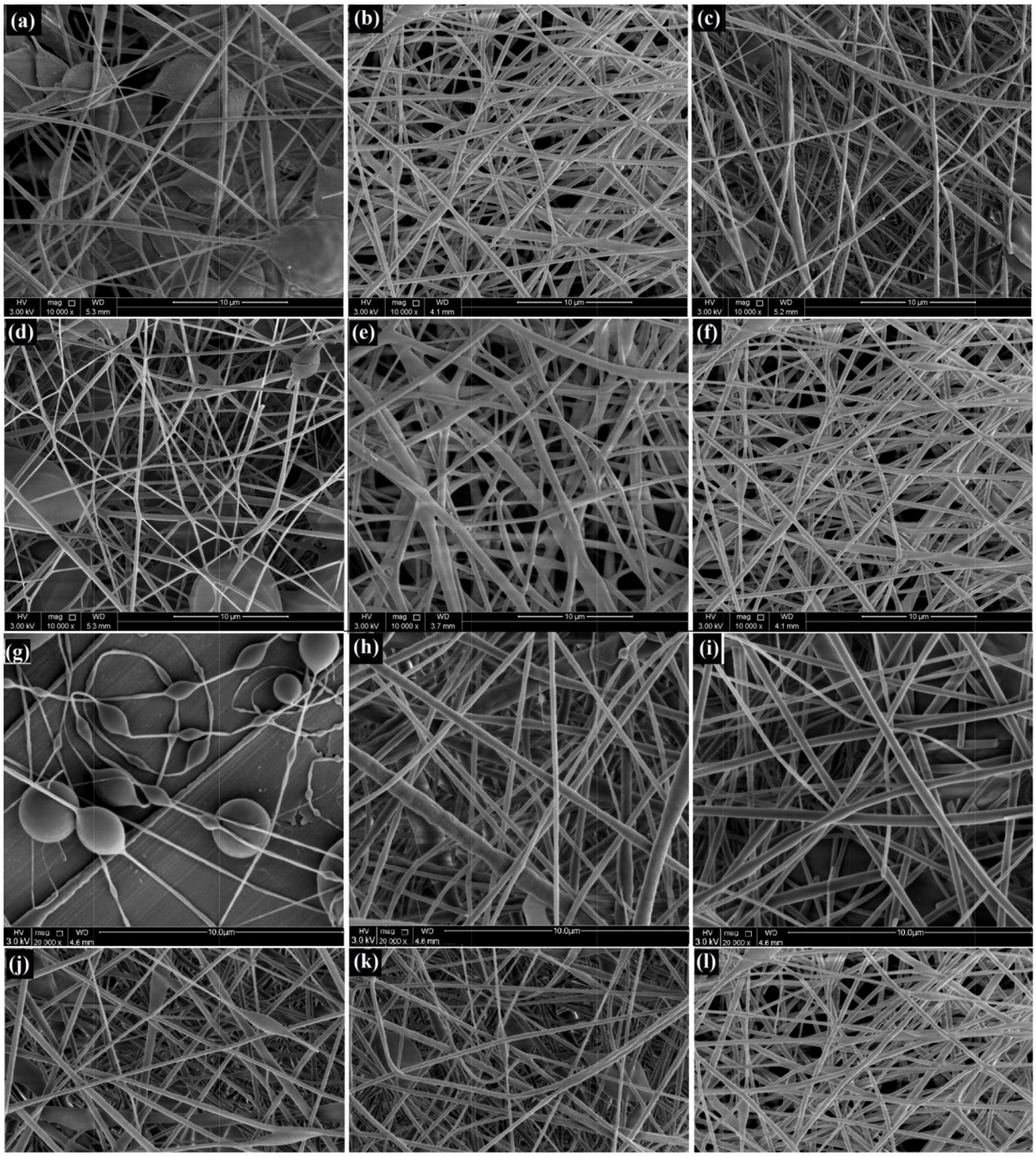

Fig. 3. SEM images of electro spinning PS fibers using PS with molecular weight 35,000. Descriptions of the electro spinning parameters for each image are given in Table 2.

(15–25 kV) and W_2 with four different voltages (10–25 kV) have also been explored.

SEM images confirm that the W_1 polymer gives the best fibers at 20 kV. The W_1 polymer gives uniform fibers with different diameters for all applied voltages. During electro spinning of the W_1 polymer, 15 kV is not sufficiently high to overcome the threshold voltage and charge the jets ejected from the Taylor Cone, and thus they become beaded [17]. The 25 kV is represented high for electro spinning and it causes bead formation [18].

Results on polymer concentrations for both molecular weights indicate that a 10% concentration does not have sufficient viscosity for electro spinning. The W_1 polymer at 20% gives the best result. At higher concentrations, it is too

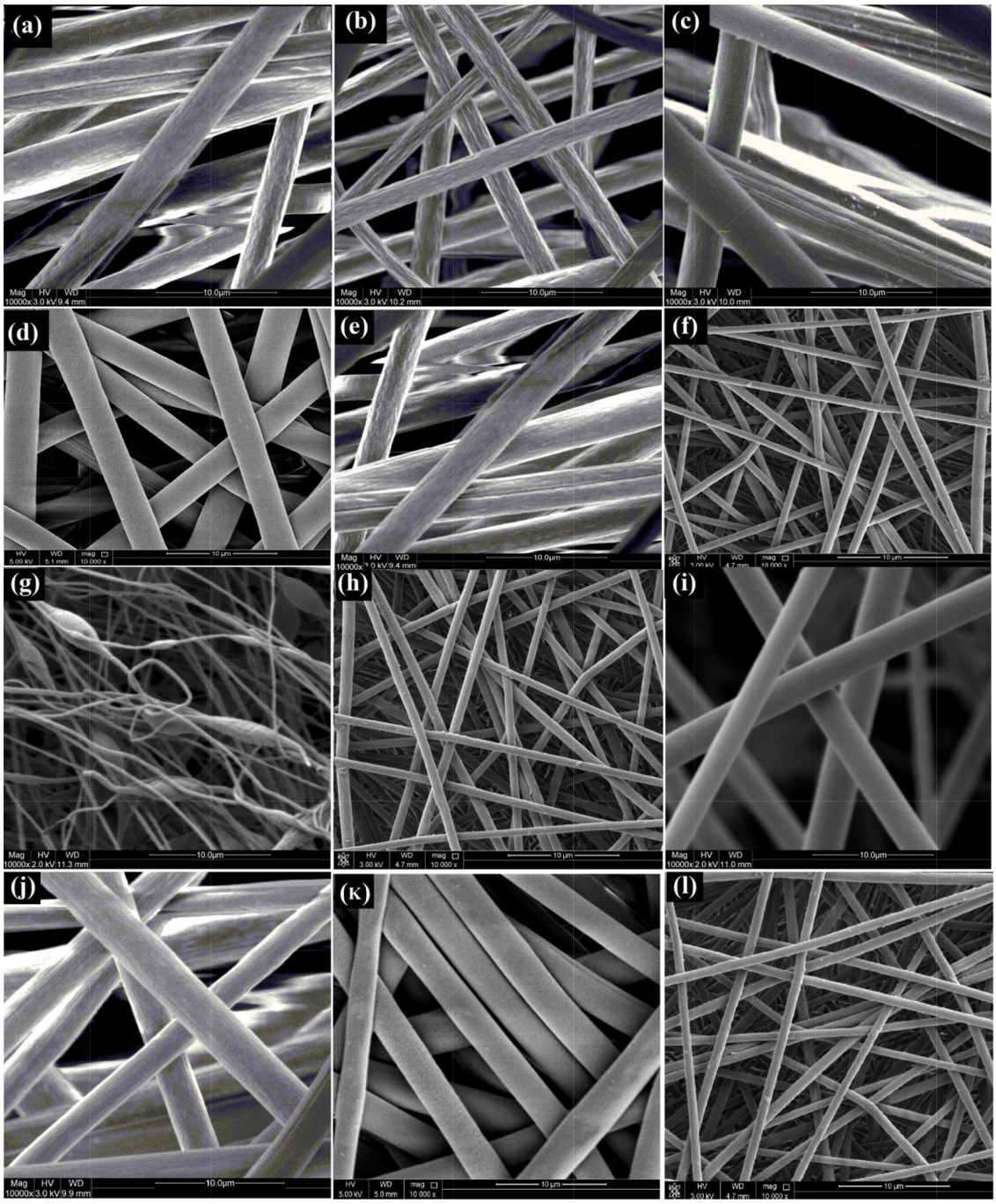

Fig. 4. SEM images of electro spinning PS fibers using PS with a molecular weight 250,000. Descriptions of the electro spinning parameters for each image are given in Table 2.

viscous for electro spinning, thus resulting in broken fibers. In contrast, W_2 polymers produce a uniform fiber at all four viscosity values, but with different diameters. The smallest diameter is seen at 20%.

The next parameter is the tip-collector distance; SEM images show that 10 cm gives the best result for the W_1 polymer; whereas 15 cm is the best for the W_2 polymer. Finally, the flow rate of the polymer solution through the needle tip has a significant effect on the fiber properties. For W_1 polymer, 0.5 and 0.7 ml/h are not suitable because they yield a beaded fiber. The 1 ml/h flow rate is found optimal, whereas he 1.5 ml/h flow rate is optimal for W_2. In summary, the W_1 polymer at 20% concentration and 20 kV of applied voltage with a tip-collector distance of 10 cm and a flow rate of 1 ml/h is the optimal and it produces uniform fibers. On the other hand for W_2, some set of conditions are 20% concentration, 15 kV applied voltage, tip-collector distance of 15 cm, and a polymer speed of 1.5 ml/h.

3.2. Contact angle studies

This section details the PS nano fiber membrane wettability. Figs. 5a–c are an optical image of diesel oil and water droplets on the PS nano fiber membrane. The contact angle of the 3 µL water droplets lying on the membrane surface is calculated to be 133 ± 2°. This suggests a highly super hydrophobic behavior (Figs. 4 b and c). The wetting property of a diesel droplet on the PS membrane is shown in Fig. 4a. The optical images suggest that the diesel droplet (~ 3.2 µL) spreads out as soon as it lands on the surface of the membrane with a contact angle of 0°. This indicates the strong superoleophilicity of the membrane towards diesel oil. These observations confirm the highly superoleophilic and superhydrophobic behavior of electrospun PS nanofiber membranes with applications in oil-water separation.

3.3. Super hydrophobicity and superleophilicity of the membrane

The study of super hydrophobicity and superleophilicity of the membrane via simple gravity-driven flow at room temperature is demonstrated in Fig. 6. This experiment only uses the membrane with a uniform fiber. There is only a slight difference in the permeation efficiency on the fiber diameter. The deposition time is fixed to 30 min for the nano fiber membrane using the electro spinning technique described in Section 2.2. As soon as the diesel is poured on the Gooch filter, it penetrates through the electro spin fiber net and is collected in the beaker lying under the Gooch filter. All 5 mL of the diesel completely permeates through the membrane within a few minutes due to the gravity driven force and the capillary flow because of the superleophilicity of the PS nano fibers.

In contrast, water remains in the Gooch filter above the membrane due to its super hydrophobic property and low water adhesion to the PS membrane. Fig. 6 shows the graph between the volume of liquid as a function of time. Figs. 6 and 7 indicate that the diesel oil starts passing through the membrane as soon as it is poured on the membrane. After 24 h, the water level remains unaltered indicating that there is no leakage through the filter membrane. This reveals the outstanding super hydrophobic features of the PS nano fiber membrane. This membrane is very stable with no visible changes after immersion in water.

3.4. Oil water separation experiment

The oil-water separation experiment was performed under two different driving forces namely vacuum pump driven and syringe pump driven forces. The following sections describe the technique; results and discussions of the experiments.

3.4.1. Vacuum pump driven flow

Fig. 8 demonstrates the performance of the membrane under more severe conditions as compared to the simple gravity-driven flow shown in the diagram. We use a vacuum pump with pressure driven flow for a liquid through the membrane. Here, the flow rate (or flux) of the vacuum pump is fixed at 10 mL/min and it does not change with time. The membrane is installed to allow the mixture of diesel and water to pass through the membrane simultaneously as shown in Fig. 8. However, the oil cannot flow from the beaker to the conical flask through the membrane because the water has higher density than oil, thus it forms a barrier layer between the oil and the membrane. So normal gravity driven force will not work in such vertical setup; needs it force to drive through the membrane. In this case the pressure using vacuum pump will drag the oil to overcome the water barrier and pass the filter. The pump is stopped when as soon as the whole oil goes

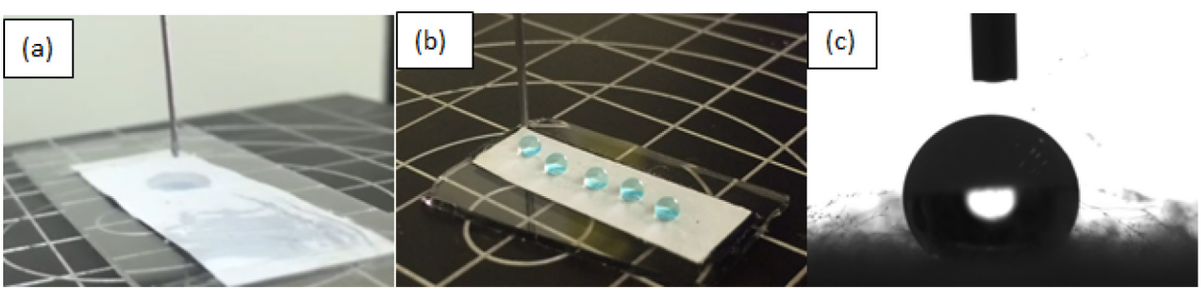

Fig. 5. (a) Optical image of diesel oil drops on a PS membrane. (b) Optical image of water drops on a PS membrane. (c) Image of water drops moving through a PS membrane.

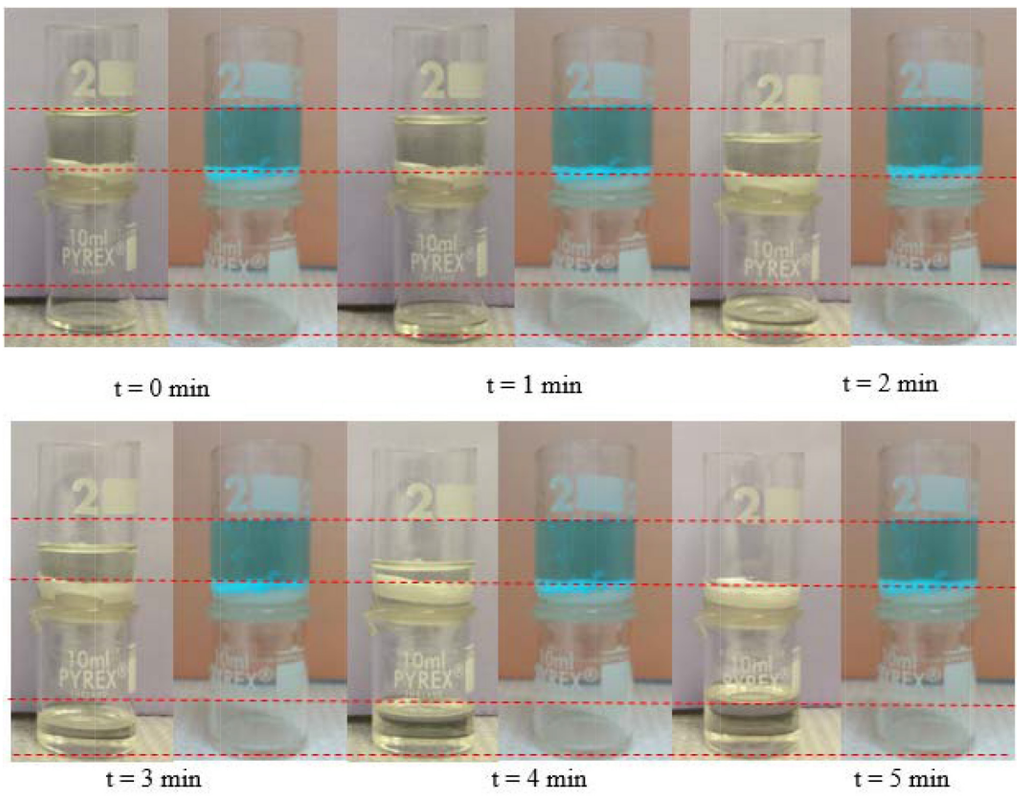

Fig. 6. Experiment showing super hydrophobic and superoleophilic properties of the PS membrane.

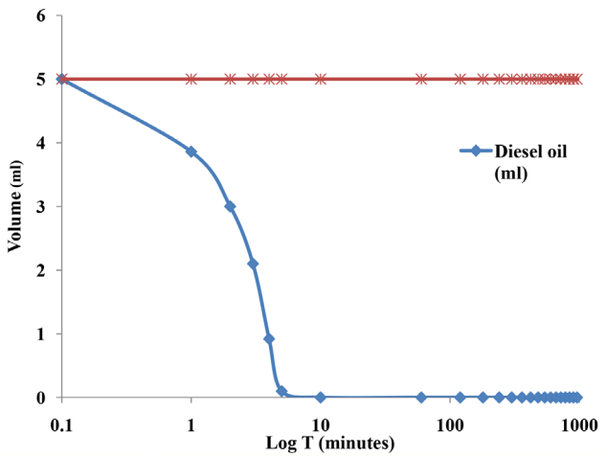

Fig. 7. Graph showing the relationship between volume of liquids permeating through the membrane as a function of time.

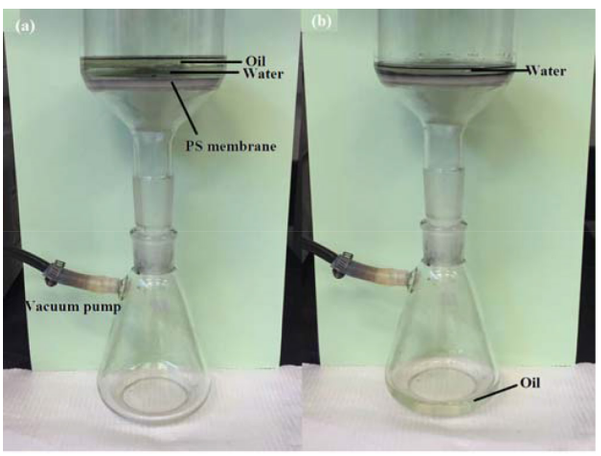

Fig. 8. Experiment demonstrating oil-water separation using vacuum pump-driven force.

through the membrane otherwise the water would start to leak. This is natural because after filtering enough oil, there remains still a large volume of water and little oil in the cylinder. Thus, the only option is to permeate water through the membrane. Despite its super hydrophobicity, the membrane will allow water to pass at sufficiently high pressure in the absence of diesel.

3.4.2. Syringe pump driven flow

An experimental setup for the syringe pump-driven oil/water separation is shown in Fig. 9. This includes a horizontally mounted syringe pump that contains diesel and water. The membrane is placed vertically inside the syringe. The syringe is installed horizontally; both diesel and water are in contact with the membrane. The cross-sectional area

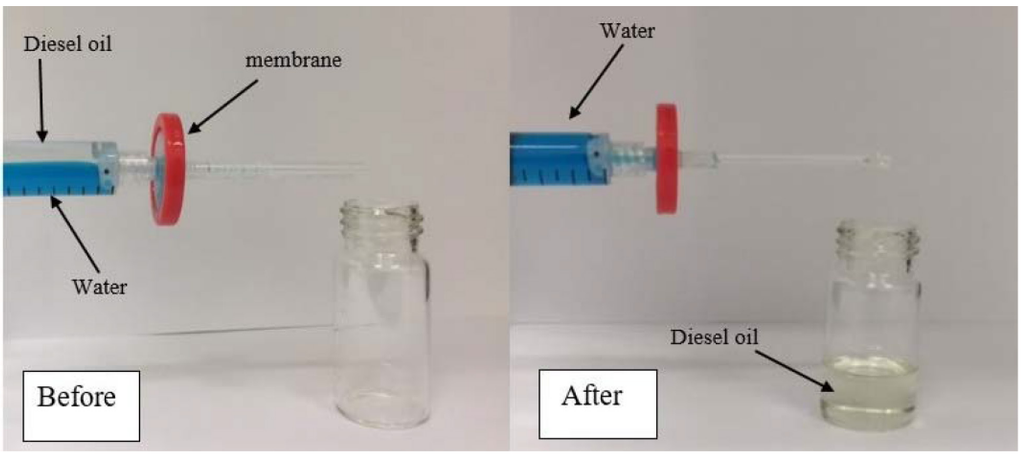

Fig. 9. Experiment showing oil-water separation process using syringe pump driven force.

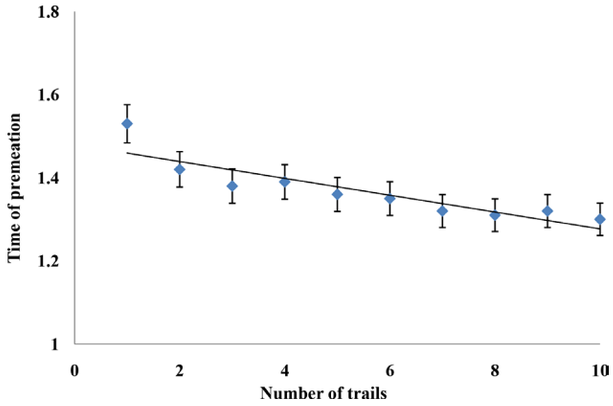

Fig. 10. Graph of the repeatability experiment.

of the syringe is 4.7 cm^2, and the flow rate of the syringe pump is 2 mL/min. Both liquids are in direct contact with the membrane, but the superoleophilicity only allows the oil to permeate and get collect (Fig. 9). The pump is stopped as soon as the oil is collected, and the superhydrophobicity of the membrane prevents water from penetrating through the membrane. Thus, the membrane can efficiently separate the water and the oil at both 2 ml/min and 10 ml/min.

3.5. Repeatability of the membrane:

Next, we characterized the ability of the electro spin membrane to be reused for oil and water separation. We repeated the vacuum pump driven oil-water separation experiment ten times using the same membrane (as described in section 3.4.1). The results show that the PS membrane can be used many times. There is only a 2% decrease in performance after ten cycles (Fig. 10).

4. Conclusion

We have presented a thorough and systematic study of the influence of different electro spin parameters on the nature of polystyrene (PS) fiber morphology using dimethylformamide (DMF) as the solvent. PS with two different molecular weights (35,000 (W1) and 280,000 (W2)) were used for the electro spinning. We optimized electro spinning parameters for both polymers including viscosity, needle-collector distance, applied voltage, and flow rate. The SEM results show that all electro spinning parameters play a pivotal role on fiber morphology. A different set of optimized parameters is needed for the two polymers in order to obtain uniform and bead-free fibers. The wettability test of this membrane via contact angle measurements with oil and water indicates the super hydrophobic-superoleophilic behavior. Therefore, we utilized a uniform electro spun fiber membrane for a diesel oil/water separation experiment. PS electro spun fibers are of low cost, and the mechanism to produce a membrane is simple. The results of the oil-water separation measurement and repeatability experiment confirm that it is an excellent tool to separate the diesel oil and water repeatedly using the same membrane. Our future work will implement these electro spun membranes to separate other organic solvents or oils from water at larger scales.

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