

Synthesis and employment of PEGDA for fabrication of superhydrophilic PVDF/PEGDA electrospun nanofibrous membranes by in-situ visible photopolymerization

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Abstract—A methodology for the synthesis of light curable poly(ethylene glycol) diacrylate (PEGDA) is described. PEGDA synthesis was confirmed using ¹H NMR, ¹³C NMR, and infrared spectroscopy. The resin was used for fabrication of the superhydrophilic PVDF/PEGDA nanofibrous membrane in a single processing step. For the in-situ photo cross-linking reaction during electrospinning process, the electrospinning apparatus was equipped with a visible light source. Degree of conversion of double bonds during electrospinning process and interaction between the two polymers were investigated by FT-IR spectrum. To determine the potential applications of the as-prepared the membranes in wastewater treatment, parameters such as morphology, hydrophilicity and water resistance were investigated by scanning electron microscopy (SEM), tensile strength, static water contact angle (WCA) and Fourier transform infrared spectroscopy (FT-IR). The results showed that PVDF/PEGDA (40/60) nanofibrous membrane is superhydrophilic and insoluble in water.

Keywords: Visible Light Cross-linking, Electrospinning, Poly(ethylene glycol) Diacrylate, Poly(vinylidene fluoride), Superhydrophilic

INTRODUCTION

Electrospinning is a simple and versatile method for fabrication of micro and nano scale fibers in different forms. Polymers such as natural polymers, synthetic and hybrid materials can be electrospun into micro and nanoscales [1,2]. Electrospinning techniques have applications in the manufacture of membranes, reinforced composites, soft tissue prosthetics, tissue engineering scaffolds, protective garments, porous electrodes for battery separators and controlled drug delivery [3].

Among the various methods, the nanotechnology-based methods for preparing membranes are more valuable and reliable [4]. Electrospun nanofibrous membranes (ENMs) are very popular, because they have unique features such as high surface to volume ratio, high porosity (up to 80%), good mechanical properties and fully interconnected pore structures [4-7]. Recently, due to good water permeability they are widely used in wastewater treatment.

Their outstanding properties, such as excellent chemical resistance, good thermal and mechanical stability, poly(vinylidene fluoride) (PVDF), have made it as one of the most attractive fibrous raw materials especially in the preparation of the water membranes [8-12]. This polymer is widely used in the wastewater treatment, but due to the hydrophobic nature PVDF has some limitations. For example, the hydrophobic membranes have very low water flux and are susceptible to hydrophobic materials, such as proteins or oils fouling during the filtration process [13]. So to increase the effi-

ciency of the hydrophobic membranes, modifications must be done on them. Two methods are commonly used to modify PVDF membranes: surface modification and blending modification. Surface modification is performed by coating or grafting a functional layer on the prepared membrane surface. This modification, unlike blending modification, due to diffusion ability of the modifying agents into the fiber pores and closing them is restricted.

The blending method is a simple and inexpensive method for modification of polymers [14]. To correct hydrophobic properties of PVDF membranes from hydrophilic polymers or pore forming additives, amphiphilic copolymers and inorganic particles are used [15]. Three main hydrophilic polymer additives with PVDF are polyvinylpyrrolidone (PVP), polyethylene glycol (PEG) and poly(methyl methacrylate) (PMMA) [15].

Polyethylene glycols (PEG_s) are the best option to reduce the absorption of proteins and enhance the mechanical properties of the hydrophobic membranes [16,17].

In this regard, Kimura et al. investigated the effect of PEG on the various properties of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) nanofiber membranes [16]. Their research results showed that the presence of PEG in PVDF-HFP nanofiber membranes structure improves properties such as discharge capacity, porosity, and bulk resistance value than existing separator [16]. Poly(methyl methacrylate) (PMMA)/poly(ethylene glycol) diacrylate (PEGDA) copolymer were also synthesized and used to enhance the performance of PVDF hollow fiber membranes by Liu and et al. [18]. In addition, in separate investigations, properties such as flux, anti-fouling and hydrophilicity of polyacrylonitrile and cellulose fiber membranes have been improved by modifying the structure of membranes using polyethylene glycol [19,20].

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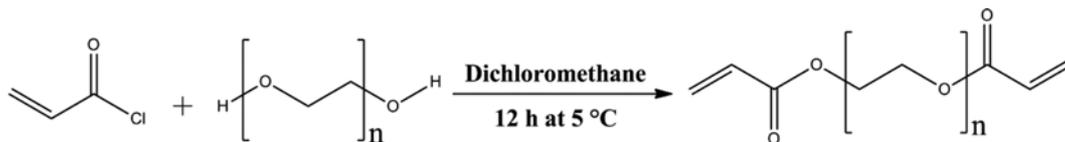


Fig. 1. Schematic illustration of synthesis of PEGDA.

Although the use of PEG has several advantages such as non-toxicity, less expensive and environmentally friendly [21], these polymers are not stable and can be easily washed away by water from the fiber structure [18], so they should be cross-linked to form a network [22].

Polyethylene glycol diacrylates are structurally similar to PEGs and can be photo-cross-linked quickly under light irradiation [23]. The light-induced polymerization is excellent because of low cost of processing, fast reaction rate and simple equipment [24].

First, we introduced a way for the synthesis of light curable poly(ethylene glycol) diacrylate (PEGDA) through an esterification reaction. ¹H NMR, ¹³C NMR and FT-IR measurements were used to characterize of PEGDA molecular structure. Second, for fabrication of the superhydrophilic membrane in a single processing step, PVDF fibers blended with PEGDA were fabricated by a visible light in-situ photo cross-linking reaction during electrospinning process. Finally, the applicability of superhydrophilic membrane in wastewater treatment was investigated by SEM, tensile strength, static water contact angle (WCA), FT-IR spectroscopy and water stability test of cross-linked the nanofibers. These hydrophilic and superhydrophilic membranes may have potential capability in wastewater treatment.

EXPERIMENTAL

1. Materials

Poly(vinylidene fluoride) (PVDF; Mw=110,000), Polyethylene glycol (PEG, Mw=10,000), Triethylamine, Dimethylformamide (DMF) and Acetone were purchased from Merck Co. Camphorquinone (CQ), acryloyl chloride (97.0% purity) and N,N-dimethylaminoethyl methacrylate (DMAEMA) were obtained from Sigma Aldrich Co.

2. Synthesis and Characterization of Poly(ethylene glycol) Diacrylate (PEGDA)

PEG (5.00 g, 0.5 mmol) and triethylamine (2.1 ml, 5 mmol) were dissolved in 60 mL of distilled dichloromethane by stirring for 30 min. Acryloyl chloride (0.11 g, 1.2 mmol) was dissolved in 5 mL of distilled dichloromethane and added slowly via an addition funnel to the reaction mixture. The reaction mixture was stirred for 12 h at 5 °C in darkness and under a nitrogen blanket to avoid exposure from ambient light and any hydrolysis. Finally, the colorless oily liquid (95%) was washed with a saturated solution of ammonium chloride and drying over MgSO₄. The reaction is shown schematically in Fig. 1.

¹H NMR, ¹³C NMR and FT-IR spectroscopy measurements were used for PEGDA analysis. ¹H NMR and ¹³C NMR spectra were recorded using a Bruker 250 MHz spectrometer at 25 °C in D₂O. Also, a Fourier transform infrared spectrophotometer (Shimadzu

IR-460) was used to study the chemical structure of PEGDA, in region of 400-4,000 cm⁻¹ with the resolution of 4 cm⁻¹.

3. Preparation of Electrospun PVDF/PEGDA Nanofibrous Membranes

The electrospinning solutions were prepared separately by dissolving of different weight ratios of PVDF and PEGDA (100/0, 80/20, 60/40, 40/60), (which are summarized in intact PVDF, M₁, M₂ and M₃ respectively), in DMF/Acetone (6/4: V/V) at a constant concentration of 8 wt% for PVDF. Then an appropriate amount (3 wt% of PEGDA) of photoinitiator system (CQ/DMAEMA: 1/2 w/w) was added to each solution.

To obtain a homogeneous solution, after adding the photoinitiator system the solutions were stirred for 12 h at 25 °C. These reaction mixtures had been stored in a glass bottle covered with aluminum foil to avoid any exposure from ambient light. The voltage between the needle and the target and the feeding rate was selected 15 kV and 1 mL/h, respectively. The distance of the needle to the target was applied 20 cm, and an aluminum foil with the dimension of 25 * 15 cm² was used as the collector.

4. In-situ Visible Light Irradiation During Electrospinning

The electrospinning apparatus with the visible light source (9 W) is shown schematically in Fig. 2. Each of the prepared solutions was poured into a plastic syringe covered with aluminum foil. The syringe containing solution was connected to the needle (0.33 mm inner diameter). The solutions were supplied by a syringe pump, and flow rate was controlled with a syringe pump. Also, the visible light was irradiated on the foil while the fibers gathered on it. Finally, all the fibers were dried in a vacuum at 50 °C for 12 h.

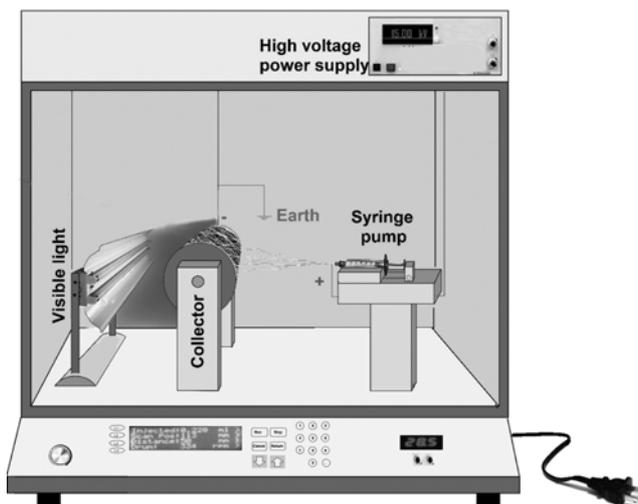


Fig. 2. Schematic of the apparatus depicting the visible light irradiation of electrospun fibers.

5. Characterization of Nanofibers

The surface morphologies of electrospun PVDF/PEGDA nanofibrous were evaluated by scanning electron microscope (SEM, JSM-5300, JEOL Ltd., Japan). Before imaging, a thin layer of gold was coated on all the samples. The fiber diameter (about 105 fibers were randomly selected) and surface pore diameter of membranes were analyzed using Image J software (NIH, USA) [25]. An outside micrometer (Series 102, Mitutoyo, USA) was used to measure the thickness of membranes. Thickness for all ENMs was controlled at 100 μm .

Fourier transformed infrared (FT-IR) spectra were recorded to study the chemical structure of the fibers. The spectra were measured in the region of 400–4,000 cm^{-1} with the resolution of 4 cm^{-1} . The hydrophilic property of the fibers was measured using an optical contact angle meter (CAM200, KSV Instruments, LTD). The five microliters distilled water was dropped on top of the fibers to measure of the contact angle [26]. All the measurements were performed in triplicate and the average value was reported as the contact angle value. The water resistance tests of the cross-linked nanofibers were performed by immersing a piece of the fibers (2 \times 2 cm) in distilled water for 24 hours. Then they were dried and changes in their morphology and structure were evaluated by SEM images and FT-IR spectroscopy [27].

For pure water flux measurement, a home-built dead-end stirred cell filtration device (with an effective filtration area 12.56 cm^2) connected to a reservoir was used and pressurized by nitrogen from the gas cylinder. The results were reported as the mean values of triplicate measurements for each membrane. To measure water flux of membranes, filtered water was collected and pure water flux J_w ($\text{L}/\text{m}^2\text{h}$) was calculated using the following equation:

$$J_{w,1} = \frac{V}{A \times \Delta t} \quad (1)$$

where V is the quantity of permeate (L), A is the membrane effective area (m^2) and Δt is the sampling time (h).

Mechanical properties of membranes were measured with a universal testing machine (GOTECH AL-7000M). Strain rate was 50 mm/min and load cell was 200 Kgf. Samples dimensions were 20 mm \times 50 mm (width and length) and also the thickness of all specimens was 50 μm .

RESULTS AND DISCUSSION

1. Characterization of PEGDA

PEGDA synthesis was confirmed using ^1H NMR, ^{13}C NMR and FT-IR analysis. Fig. 3(a) shows ^1H NMR spectrum of PEGDA. The resonances associated with the acrylate group were apparent at 5.67, 5.8 and 6.1 ppm [28]. The peaks in the range of 3–5 ppm confirmed presence of ether groups in PEGDA molecular structure [28].

In addition, the ^{13}C NMR spectrum of PEGDA, given in Fig. 3(b) exhibits three resonances associated with the acrylate group which were apparent at 127.3, 132.5, and 169.5 ppm [28]. The peaks in the range of 60–70 ppm are related to carbon atoms of PEG [28].

FT-IR spectrum as the NMR spectrum confirms the polymer synthesis (see Fig. 3(c)). The peaks at 1,615 cm^{-1} and 1,723 cm^{-1}

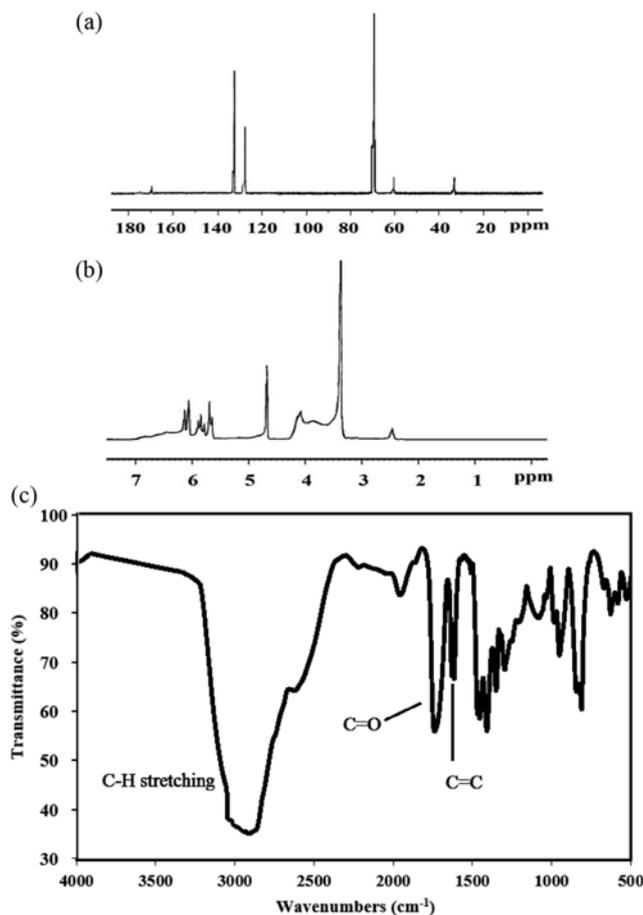


Fig. 3. ^1H NMR, ^{13}C NMR and FT-IR spectra of synthetic PEGDA.

in FT-IR spectrum are assigned to $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{O})$, respectively [28]. Both NMR spectroscopy and FT-IR spectroscopy gave a good indication that PEGDA was synthesized with high purity.

2. SEM

SEM images of PVDF/PEGDA nanofibrous membranes with composition ratio of 100/0 (Intact PVDF), 80/20 (M_1), 60/40 (M_2) and 40/60 (M_3) are presented in Fig. 4. According to Fig. 4 it is clear that ENMs are smooth, without beads and droplets with enough uniformity of fiber diameters. As Fig. 4 shows, by increasing the amount of the ether groups in the membranes structure, the fibers diameter was increased. Also, the presence of 60% ether groups in the nanofiber membranes structure increased the mean fiber diameter to 120 nm. It probably relates to the swelling properties of hydrogels.

3. FT-IR

FT-IR spectroscopy was used to study the changes in the chemical structure and molecular interaction of electrospun PVDF/PEGDA nanofibrous. The FT-IR spectra of PVDF/PEGDA nanofibers (electrospun with and without visible light irradiation) with composition ratios of 100/0, 80/20, 60/40 and 40/60 are shown in Fig. 5(a), (b), (c) and (d), respectively.

According to the sources, the peak at 1,615 cm^{-1} corresponds to the vinylene ($\text{C}=\text{C}$) stretching vibration of the acrylate group in PEGDA [29]. Because of the porous nature of fibers and thick-

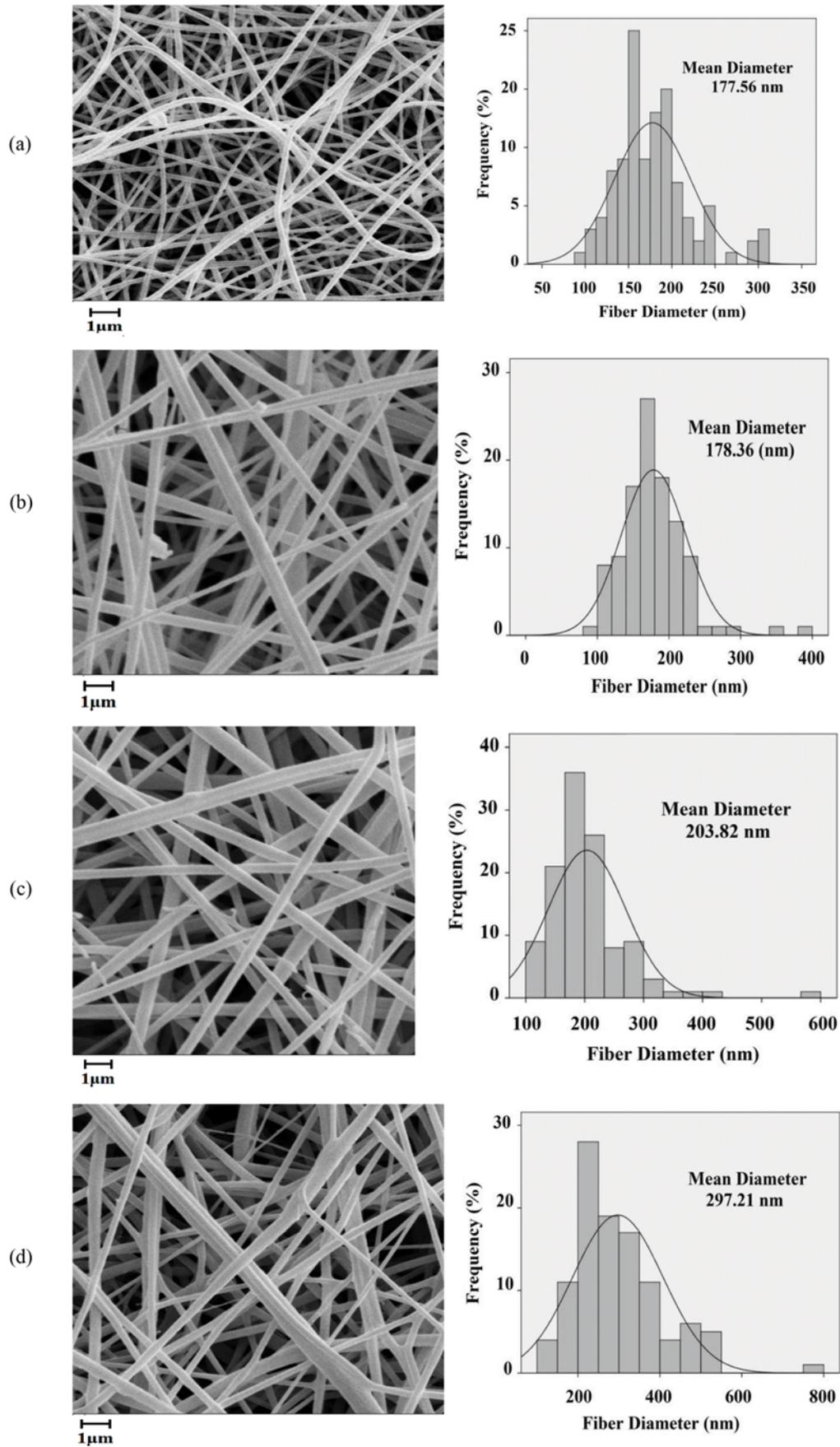


Fig. 4. SEM images of (a) intact PVDF, (b) M₁, (c), M₂ and (d) M₃ nanofibers.

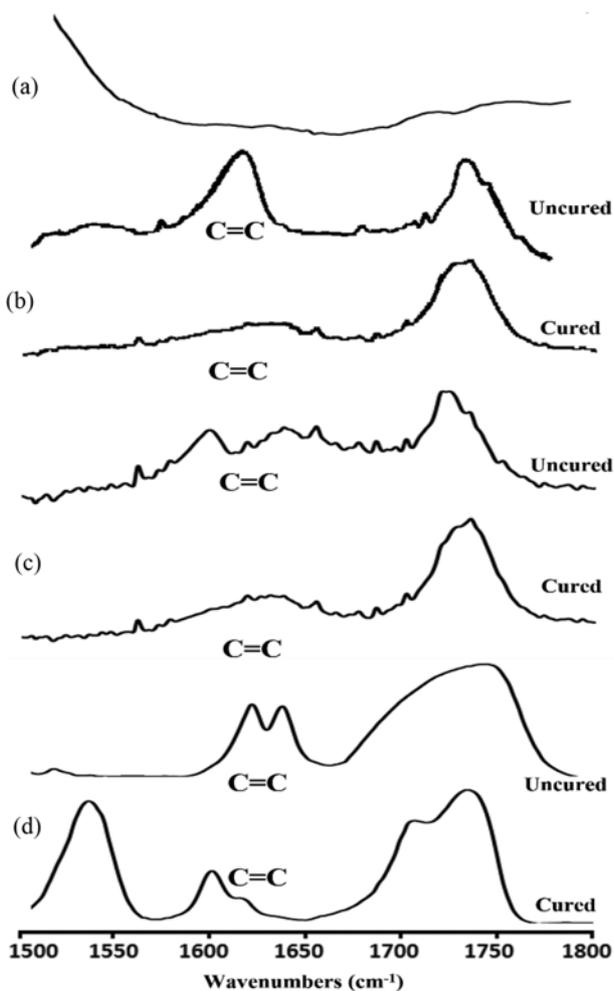


Fig. 5. FT-IR spectra of cured and uncured nanofibers: (a) Intact PVDF, (b) M_1 , (c) M_2 and (d) M_3 .

ness variations in the electrospun samples, they do not have a uniform cross-sectional composition. Therefore, it may not be a flat baseline observed for the spectra reported here [29]. To compensate for these problems, the peak intensity at 1723 cm^{-1} corresponding to the stretching vibrations of the carbonyl group (C=O) in PEGDA was considered as a reference. This group does not have

any interaction with light. As indicated in Fig. 5(b), (c) and (d) the intensities of the bands at 1615 cm^{-1} decreased with visible light irradiation in the fiber membranes. Using intensity changes, the degree of conversion (photopolymerization reaction yields (see Fig. 6) was calculated using the following equation [29]:

$$DC = \frac{[(I_{1615}/I_{1723})_{uncured} - (I_{1615}/I_{1723})_{cured}]}{(I_{1615}/I_{1723})_{uncured}} \quad (2)$$

where, $(I_{1615}/I_{1722})_{uncured}$ and $(I_{1615}/I_{1723})_{cured}$ are the double bonds peak intensity without and with visible light irradiation, respectively. DC represents the degree of conversion the double bonds.

DC values obtained for M_1 , M_2 and M_3 nanofibers were 0.85, 0.86 and 0.83, respectively. DC values obtained for both the membrane were suitable, so it can be concluded PEG completely on the nanofibers is stabilized and will not be washed by water from the superhydrophilic membrane structure. The spectrum of intact PVDF is analogous to M_1 , M_2 and M_3 (see Fig. 5(a), (b), (c) and (d)). It can be inferred that in the presence or absence of visible light irradiation, no chemical interaction occurred between PEGDA and PVDF.

4. The Water Resistance Test of Cross-linked Nanofibers

In addition to degree of conversion, the cross-linking of nanofibers was also investigated by a water resistance test. The cross-linked and non-cross-linked fibers of PVDF/PEGDA (40/60) were immersed in distilled water for 24 hours. Fig. 7 shows the results of this testing. SEM images show that photo-cured nanofibers, like before immersing, maintained their fibrous structure (see Fig. 7(a) and (b)), while the uncured nanofibers structure in comparison with the cured nanofibers were destroyed after immersing (see Fig. 7(c)) [27].

Comparing WCA of cured (Fig. 7(b)) and uncured (Fig. 7(c)) nanofibers after with before immersing, (Fig. 7(a)) shows PEGDA is washed from the uncured fibers structure. So by reducing the amount of PEGDA in the uncured fibers structure due to leaching, it has increased WCA, while it has not changed for cured fibers after immersing.

Thus, it can be concluded that during electrospinning process photopolymerization has been completed and the ether groups are resistant to leaching by water [27]. In addition to the FT-IR spectra of M_2 before (Fig. 8(a)) and after (Fig. 8(b)) washing are analogous together, especially in the range of $1600\text{-}1800\text{ (cm}^{-1}\text{)}$. These

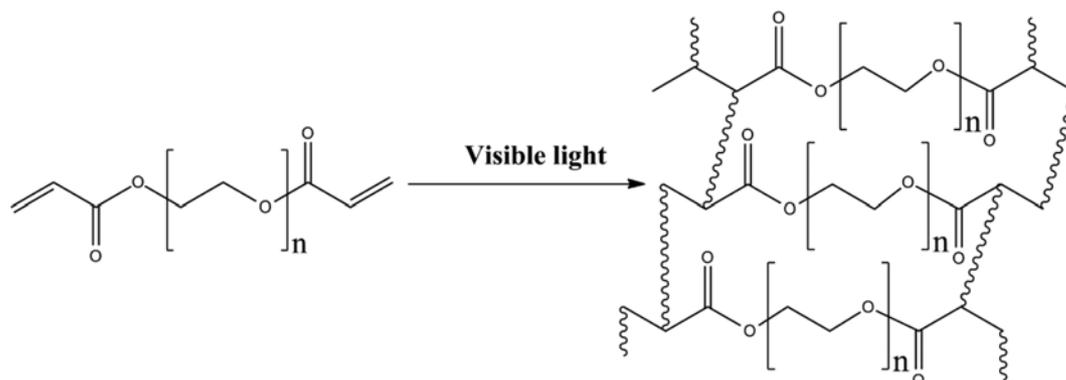


Fig. 6. Photopolymerization reaction of PEGDA during electrospinning.

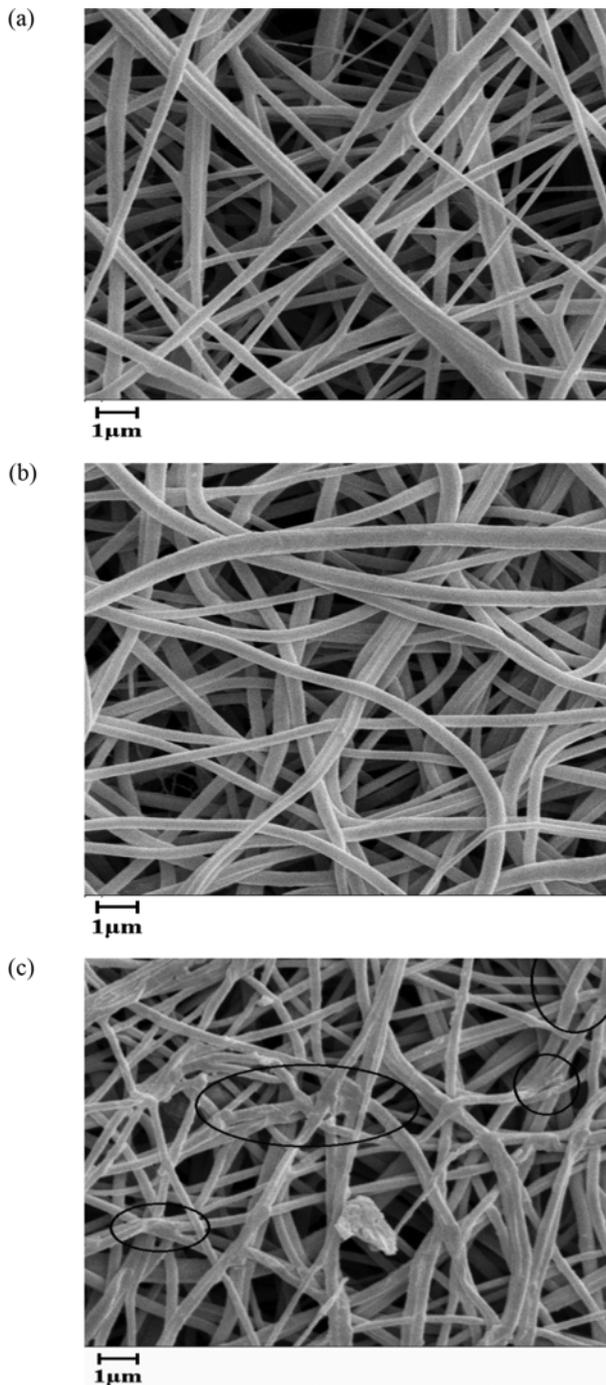


Fig. 7. SEM images of M_3 nanofibers: (a) Light cured (b) cured and soaked in water and (c) uncured and soaked in water.

results can show that a DC value of above 80% is sufficient to stabilize the PEGDA on the membrane.

5. Static Water Contact Angle, Pore Size and Pure Water Flux of Membranes

The hydrophilic properties of ENMs were measured by WCA test at room temperature. WCA was obtained for intact PVDF nanofiber membrane approximately equal to 137.1° . Also, WCA values of M_1 , M_2 and M_3 membranes were 34.28 , 22.30 and $<3^\circ$, respectively.

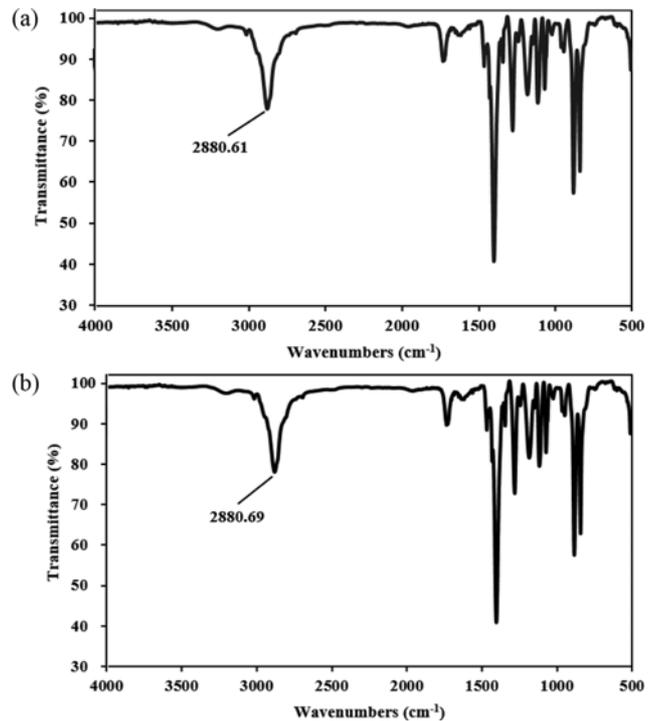


Fig. 8. FT-IR spectra of M_2 nanofiber membrane before (a) and after (b) washing.

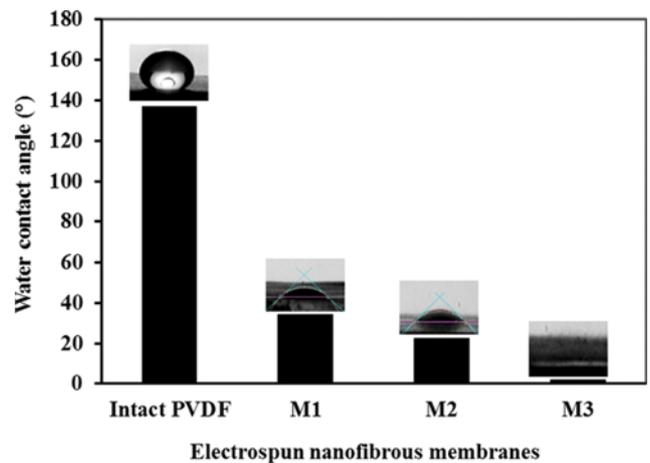


Fig. 9. Static water contact angle of (a) intact PVDF, (b) M_1 , (c) M_2 and (d) M_3 nanofibers.

Fig. 9 shows the effect of PEGDA content on the hydrophilicity of PVDF nanofiber membranes. It shows that by increasing of PEGDA the hydrophilic property has been improved. It can be related to the fact that poly (ethylene glycol) is a polymer with a hydrophilic nature [15]. So the presence of sufficient amounts of the ether groups in the membranes component can even reduce WCA to below five degrees ($<5^\circ$). According to Fig. 9, it can be concluded that M_1 and M_2 membranes are hydrophilic and M_3 membrane is superhydrophilic [15,30].

According to Fig. 10, by increasing the amount of the ether groups (polymerized PEGDA) in ENMs structure (from 0 to 60 wt%), the pore diameter increased from 298 to 453 nm.

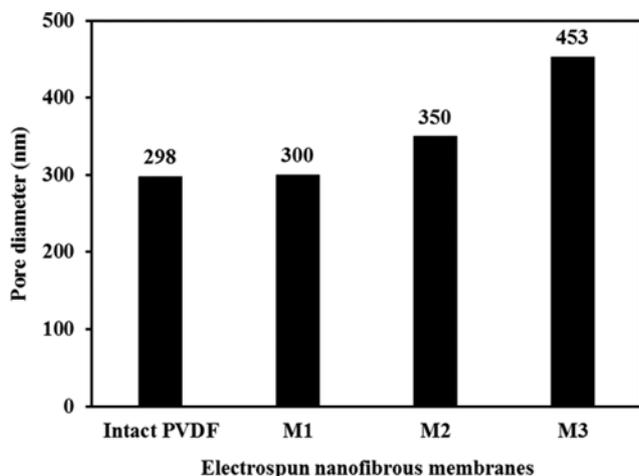


Fig. 10. Pore size measurement of the ENMs with different nanofibers.

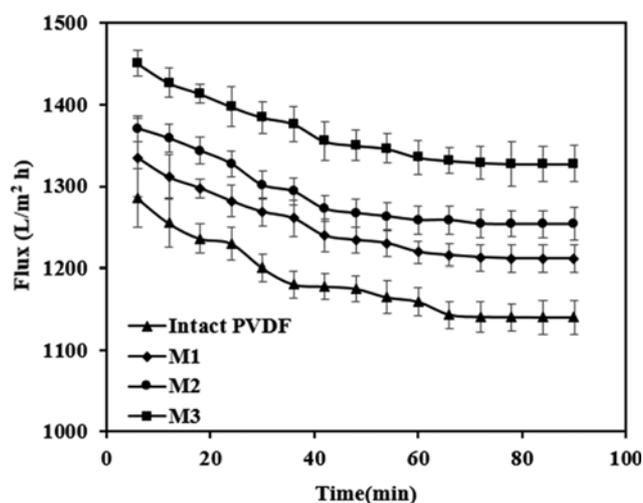


Fig. 11. Flux versus time for Intact PVDF, M₁, M₂ and M₃ ENMs at 0.2 bars.

Also, to investigate the effects of polymerized PEGDA on the performance of PVDF membranes, the membranes' pure water flux was measured. As shown in Fig. 11, by increasing the amount of the polymerized PEGDA in ENMs, the membrane flux was highly improved. This improvement was maximized in M₃ membranes. This can be due to two reasons: Increase of the pore size and hydrophobicity of ENMs. The superhydrophilic ENMs (M₃) show high flux compared to other membranes (see Fig. 11).

The tensile properties of the electrospun nanofibrous membranes were measured. Based on the analysis of the tensile properties the membranes, tensile strength, Young's modulus and elongation at break were summarized in Fig. 12, and 13. Fig. 12 shows the stress-strain curves of ENMs. For all samples, the stress increased steeply to the maximum point and then dropped rapidly. Probably the cause of the rapid stress drop of the all samples is inter-fiber bonding [31].

As shown in the Fig. 12, pure PVDF and M₂ have the highest tensile strength and elongation at break, respectively. Fig. 13 shows

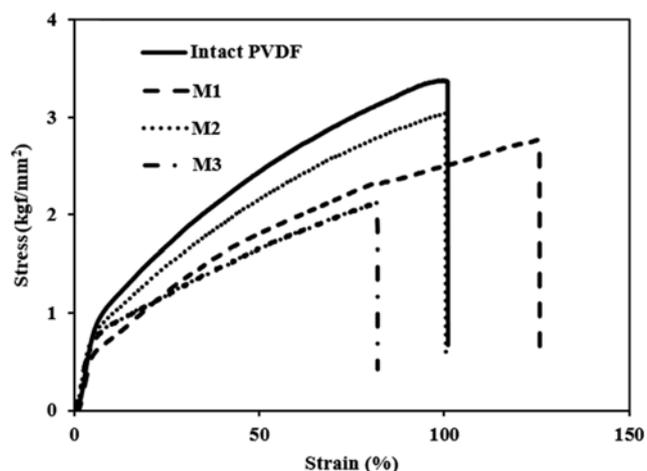


Fig. 12. Stress-strain curves of Intact PVDF, M₁, M₂ and M₃ nanofibers.

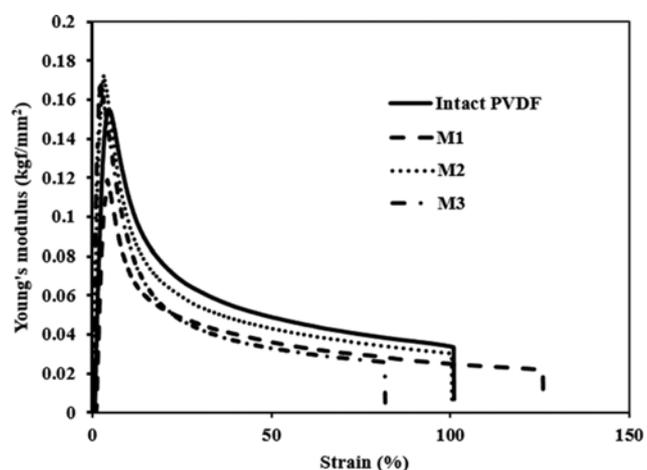


Fig. 13. Young's modulus of Intact PVDF, M₁, M₂ and M₃ electrospun nanofibrous membranes.

the stiffness changes against strain increase. It was observed that M₁ Young's modulus decreased compared to pure PVDF. This demonstrates that by adding PEG with controlled amount provides extra softness to PVDF membranes [32]. The results of the efforts to improve the flux, WCA and pore size of PVDF membranes in water treatment using PEG are summarized in Table 1.

CONCLUSIONS

Using a photopolymerization reaction the hydrophobic properties of PVDF membrane were modified. The light curable PEGDA was synthesized and utilized as a modifier. The results obtained from ¹H NMR, ¹³C NMR and FT-IR analysis showed that PEGDA was successfully synthesized. Three modified PVDF nanofibers (membranes) with different wt% of PEGDA (20 (M₁), 40 (M₂) and 60 wt% (M₃)) were made. According to the results obtained for the degree of conversion of the double bonds (the band intensity declined sharply at 1,637 cm⁻¹) and from the water resistance tests it was found that the electrospun fibers were completely cross-

Table 1. PVDF membrane modification with different materials

PVDF membranes	WCA	Pore size (nm)	Pure water flux (L/m ² h)	Ref
PVDF	85°		946 (42 kPa)	[33]
PVDF-G-PVP	32°		135 (42 kPa)	
PVDF	82°	22	578 (0.1 MPa)	[34]
PVDF-g-poly(styrene)	110°	13	23 (0.1 MPa)	
PVDF	93°			[35]
PVDF-g-PEGMA or PVDF-g-PDMAEMA	78°, 73°			
PVDF	80°		95 (1 bar)	[36]
PVDF-g-PEGMA	60°		80, 60, 4.5 (1 bar)	
PVDF	102.3°	75.56	180.4 (1 bar)	[13]
PVDF-g-PEGMA	51°	73.73	226.1 (1 bar)	
PVDF	84°	23		
PMMA casted on PVDF	64°	18	-----	[37]
PVDF	82.9°	74	~80	[38]
PVDF blended with SiO ₂	53.4°	99	301	
PVDF	124°	1610	~160 g	
PVDF blended with PVDF-g-PEGMA	34°	500	360 g	[10, 39]
Intact PVDF	137.1°	298	1140 (0.2 bar)	This research
M ₁	34.28°	300	1212 (0.2 bar)	This research
M ₂	22.30°	350	1254 (0.2 bar)	This research
M ₃	<3°	453	1328 (0.2 bar)	This research

linked with visible light radiation during electrospinning. The hydrophilic properties and water flux of PVDF nanofibrous membranes can be conveniently regulated by changing the ratio of PVDF to PEGDA. Also, the wettability of the PVDF nanofiber membranes can be readily changed from hydrophobic to superhydrophilic. Also, the modified membranes, especially M₂ and M₃, showed an acceptable strength and softness. This new one-step method utilizes a photopolymerization reaction that can be used for designing hydrophilic superhydrophilic membranes with high anti-fouling.

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