Modification of Electrospun Poly(vinylidene fluoride-*co*-hexafluoropropylene) Membranes Through the Introduction of Poly(ethylene glycol) Dimethacrylate

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ABSTRACT: For the modification of an electrospun poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF–HFP) membrane for its potential use as an electrolyte or separator in lithium batteries, poly(ethylene glycol) dimethacrylate (PEGDMA) was introduced into a polymer solution for electrospinning. A post heat treatment of the as-electrospun membrane at an elevated temperature was performed for PEGDMA polymerization, and this was verified by Fourier transform infrared spectroscopy. The results showed that no significant variations in the membrane morphology were detected when a small amount of PEGDMA (PVDF–HFP/PEGDMA mass ratio = 4/1) was incorporated. This electrospun membrane after heat treatment at 130°C for 2 h exhibited a significantly higher tensile strength (6.26 ± 0.22 MPa) than that of an electrospun PVDF–HFP membrane (3.28 ± 0.35 MPa) without PEGDMA. The porosity and liquid absorption of the electrospun PVDF–HFP/PEGDMA (4/1) membrane were 70.0 ± 1.6% and 267 ± 11%, respectively, lower than those of the electrospun PVDF–HFP membrane (76.5 ± 0.3% and 352 ± 15%) because of the introduction of PEGDMA. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 3104–3112, 2009

Key words: membranes; modification; mechanical properties

INTRODUCTION

Electrospinning nowadays has been extensively explored as a simple and versatile method for producing ultrafine fibers with diameters in the range of nanometers to submicrometers.[1–3] Jets of a polymer solution or melt are driven by high electrostatic forces, are moved toward a grounded collector, and are eventually deposited in the form of fibrous nonwoven mats. As an electrospun membrane has a very large specific surface area, a small pore size, and high porosity, it shows potential applications in tissue engineering scaffolds, drug delivery devices, biosensors, and so on.[4–7] More recent work has also paid attention to functional nanofibers by *in situ* gelation and high-temperature calcination or *in situ* surface modification.[8–11] Also, electrospinning has even been attempted from polymer solutions in room-temperature ionic liquids.[12–14]

Poly(vinylidene fluoride) (PVDF) has been widely used for making ultrafiltration and microfiltration membranes because of its excellent chemical resistance and good thermal stability. It was reported that porous PVDF matrices embedded by organic solutions of lithium salts showed a high electrical conductivity of 10^{-3} S/cm at room temperature.[15,16] Therefore, in recent years, membranes of PVDF and its copolymer poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF–HFP) have attracted much attention for the preparation of polymer electrolytes or separators in lithium batteries.[17–19] Generally, the membranes are produced by means of solution casting or phase separation.[20–22] Because of the special ultrafine fibrous structure of electrospun membranes, the electrospinning method has also been employed to fabricate PVDF and PVDF–HFP membranes.[17–19,23–25]

Until now, electrospun fiber mats have shown poor mechanical properties because of their nonwoven structure without interfiber bonding. Some methods have been attempted to strengthen them. By chemical crosslinking, the mechanical properties and water resistance of electrospun poly(vinyl alcohol) membranes can be enhanced; the tensile strength can be increased by about 10%.[26] After heat treatment at 180°C for 30 min, electrospun poly(L-lactic acid) membranes have shown interfiber bonding and exhibited a tensile strength of 4.14 MPa and elongation of 102.5%, which are higher that those of unheated membranes.[27]

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Poly(ethylene glycol) dimethacrylate (PEGDMA) is a kind of poly(ethylene glycol) oligomer containing two methacrylate end groups that can react with each other via free-radical polymerization with the help of heat or an initiator. Cheng and coworkers[28–31] prepared by a solution-casting method PVDF–HFP-based gel polymer electrolytes that were reinforced by a PEGDMA network. A higher tensile modulus and better flexibility for the porous membranes were obtained with the introduction of PEGDMA. It has been hypothesized that the addition of PEGDMA into electrospinning solutions of PVDF–HFP could possibly improve the mechanical properties of the obtained electrospun membrane after the polymerization of PEGDMA. Because PEGDMA is in a liquid state with low volatility, its introduction can influence the fibrous morphology and other related properties of electrospun membranes. Therefore, in this study, the effects of solution parameters for electrospinning, including the volume ratio of N,N-dimethylformamide (DMF) to acetone in the mixed solvent, the amount of PEGDMA (the PVDF–HFP/PEGDMA mass ratio), and the heat-treatment conditions, on the morphological changes of the electrospun membranes after the addition of PEGDMA were systematically investigated. The mechanical properties, porosity, and liquid absorption of PVDF–HFP membranes produced with or without PEGDMA are comparatively discussed.

EXPERIMENTAL

Materials

PVDF–HFP (Kynar 2801; weight-average molecular weight $= 4.77 \times 10^5$) was supplied by Elf Atochem (France). PEGDMA with a relative molar mass of 330 was purchased from Sigma–Aldrich (USA). DMF, acetone, and other chemicals were all analytical-reagent-grade.

Electrospinning

The PVDF–HFP solution for electrospinning was prepared by the dissolution of PVDF–HFP in a mixture of DMF and acetone of a given volume ratio with a magnetic stirrer at room temperature. PEGDMA in a certain mass ratio with PVDF–HFP was added, and the solution was continuously stirred for about 1 h to form a clear solution for electrospinning. The electrospinning setup used in this study was similar to that used in our previous study,[23] including a peristaltic pump, a metal capillary, a high-voltage power supply, and a collecting drum. A hypodermic stainless steel needle with an inner diameter of 0.8 mm and a length of about 3 cm was used as the capillary, the tip of which was cut into flatness. The metal capillary was connected to a high-voltage power supply (DW-P503-1AC, Dong Wen High-Voltage Power Manufactory, Tianjin, China), which could generate direct-current voltages. A peristaltic pump (DG-8, Xie Da Peristaltic Pump Manufactory, Tianjin, China) was used to control the flow rate of the solution at a certain value. Generally, the electrospun PVDF–HFP membranes containing PEGDMA were prepared from 16 g/mL PVDF–HFP solutions containing PEGDMA with a 4/1–4/4 PVDF–HFP/PEGDMA mass ratio in DMF/acetone (5/5–10/0 volume ratio) with a 15-kV voltage, a 0.47 mL/h flow rate, and a 10-cm capillary-collector distance.

Crosslinking (heat treatment)

The electrospun PVDF–HFP/PEGDMA membrane was dried in a vacuum oven at room temperature for about 12 h to remove the residual solvent. The membrane was then further heated in an air-circulation oven at an elevated temperature (125 or 130°C) for the crosslinking of PEGDMA.

Characterization

The morphology of the electrospun fibers was viewed under a scanning electron microscope (XL30, Philips, The Netherlands). All the membrane samples were sputtered with gold before observation. On the basis of the scanning electron microscopy (SEM) micrographs, the fiber diameter and its distribution in the electrospun membranes were analyzed with the help of Adobe Photoshop 6.0 software.

Fourier transform infrared (FTIR) spectroscopy (FIS3000, Bio-Rad, United States) was used to verify the thermal polymerization of PEGDMA. The crosslinked PVDF–HFP/PEGDMA fibrous membranes were cut into fine pieces and subsequently mixed with KBr. The mixture of the membrane pieces and KBr was pressed into transparent tablets to be used as the specimens for FTIR measurement.

Mechanical properties of the electrospun membranes were tested with a tensile machine (M350-20KN, Testmetric, United Kingdom) equipped with a 100-N load cell at a crosshead speed of 5 mm/min in the ambient environment. The PVDF–HFP/PEGDMA membranes were cut into a rectangular shape (10 mm $\times$ 60 mm) with a gauge length of 40 mm. All the data reported for the tensile modulus, tensile strength, and elongation represented average results of three to six tests and were analyzed statistically by the method of the Student t test.

The porosity of the obtained fibrous membrane was estimated on the basis of the difference between the density of the raw PVDF–HFP material (ρ) and the apparent membrane density (ρ_m) as follows:[20]

$$\text{Porosity } (\%) = (1 - \rho_m/\rho) \times 100\% \qquad (1)$$

ρ was estimated to be 1.76 g/mL from the density of PVDF in ref. 32, and ρ_m was calculated from the ratio of the membrane mass to the calculated membrane volume from the size measurement results.

The liquid absorption of the electrospun membranes was determined by the comparison of the mass difference of the membrane before and after incubation in diethyl carbonate for 1 h. The mass (m) of the membrane after incubation was measured after removal from the liquid and blotting with a piece of filter paper. On the basis of the following equation, the liquid absorption of the electrospun membrane was calculated:

$$\text{Liquid absorption } (\%) = (m - m_0)/m_0 \times 100\% \quad (2)$$

where m_0 is the mass of the membrane before the absorption process.

RESULTS AND DISCUSSION

In gel polymer electrolytes, PEGDMA molecules can react with one another to generate network structures through crosslinking that interpenetrates with PVDF–HFP macromolecules to form a semi-interpenetrating network.[28–31] It was hypothesized that the fibrous structure of electrospun PVDF–HFP membranes combined with the crosslinking network of PEGDMA would possibly give rise to new electrospun membranes with improved mechanical properties.

The electrospinnability of PVDF–HFP was similar to that of PVDF, which was studied in our laboratory earlier through the electrospinning of PVDF solutions in DMF/acetone.[23] However, the addition of PEGDMA, which is a low-relative-molar-mass and low-volatile substance, could strongly influence the morphology of the electrospun ultrafine fibers. Therefore, it was necessary to systematically investigate the effects of the volume ratio of DMF to acetone in the solvent mixture as well as the amount of added PEGDMA.

Morphology

Effect of the DMF/acetone volume ratio

The different volume ratios (5/5, 6/4, 7/3, 8/2, 9/1, and 10/0) of DMF to acetone were selected carefully for the mixed solvent in the electrospinning solution. In the study of the solvent mixture effect, the mass ratio of PVDF–HFP/PEGDMA was set at 4/1 (a constant value), and the process parameters are given in the Experimental section. SEM micrographs of randomly oriented as-electrospun fibers are shown in Figure 1. It was known that the number of defects in

the membranes, such as fiber bonding, beads, and droplets, would increase with higher DMF contents in the electrospinning solution. When the volume ratio of DMF to acetone was 5/5, uniform thicker electrospun PVDF–HFP/PEGDMA fibers with an average diameter of 560 ± 245 nm were obtained [Fig. 1(a)]. With a 6/4 DMF/acetone volume ratio in the solution, the electrospun PVDF–HFP/PEGDMA fiber morphology was fine, and almost no defects were found [Fig. 1(b)]. The prepared fibers were thinner, with an average fiber diameter of 347 ± 144 nm in a distribution range of 100–500 nm. On the other hand, when the volume ratio of DMF to acetone was varied to 7/3 or 8/2, fiber bonding between fibers was clearly seen [Fig. 1(c,d)], and the fiber diameter was distributed in a wider range with average fiber diameters of 484 ± 159 and 522 ± 167 nm, respectively, with respect to the results for the 6/4 DMF/acetone volume ratio. As the DMF content increased further (volume ratios of 9/1 and 10/0), there were so many beads and droplets that the integrity of the fibrous morphology was destroyed [Fig. 1(e,f)].

DMF has a higher boiling point (153.0°C at 101.3 kPa) than acetone (56.12°C at 101.3 kPa), so it is less volatile. A higher DMF content could influence the absolute volatilization when the electrospun fibers were collected, so the fiber bonding between them could be determined [Fig. 1(c,d)]. Moreover, DMF has a higher surface tension (35.2 × 10⁻³ N/m at 25°C) than acetone (23.5 × 10⁻³ N/m at 25°C), and a higher DMF content could make the electrospinning solution show higher surface tension, which would increase the possibility of bead formation [Fig. 1(e,f)]. The effects of the DMF/acetone volume ratio on the morphology and diameter of the electrospun PVDF–HFP/PEGDMA fibers in this study coincided with the results of our previous study on the electrospinning of PVDF.[23]

On the basis of these results, neither higher nor lower DMF contents in the electrospinning solution made the electrospun PVDF–HFP/PEGDMA fiber morphology acceptable; therefore, the 6/4 DMF/acetone volume ratio was chosen throughout the later investigation.

Effect of the PVDF–HFP/PEGDMA mass ratio

Because PEGDMA is a low-relative-molecular-mass oligomer, its amount could affect the solution properties and morphology of electrospun PVDF–HFP/PEGDMA fibers. Table I shows the surface tension, conductivity, and viscosity of electrospinning solutions with different PVDF–HFP/PEGDMA mass ratios (4/0, 4/0.5, 4/1, 4/2, 4/3, and 4/4). Figure 2 exhibits SEM micrographs of as-electrospun PVDF–HFP/PEGDMA fibers. As shown in Table I, with the
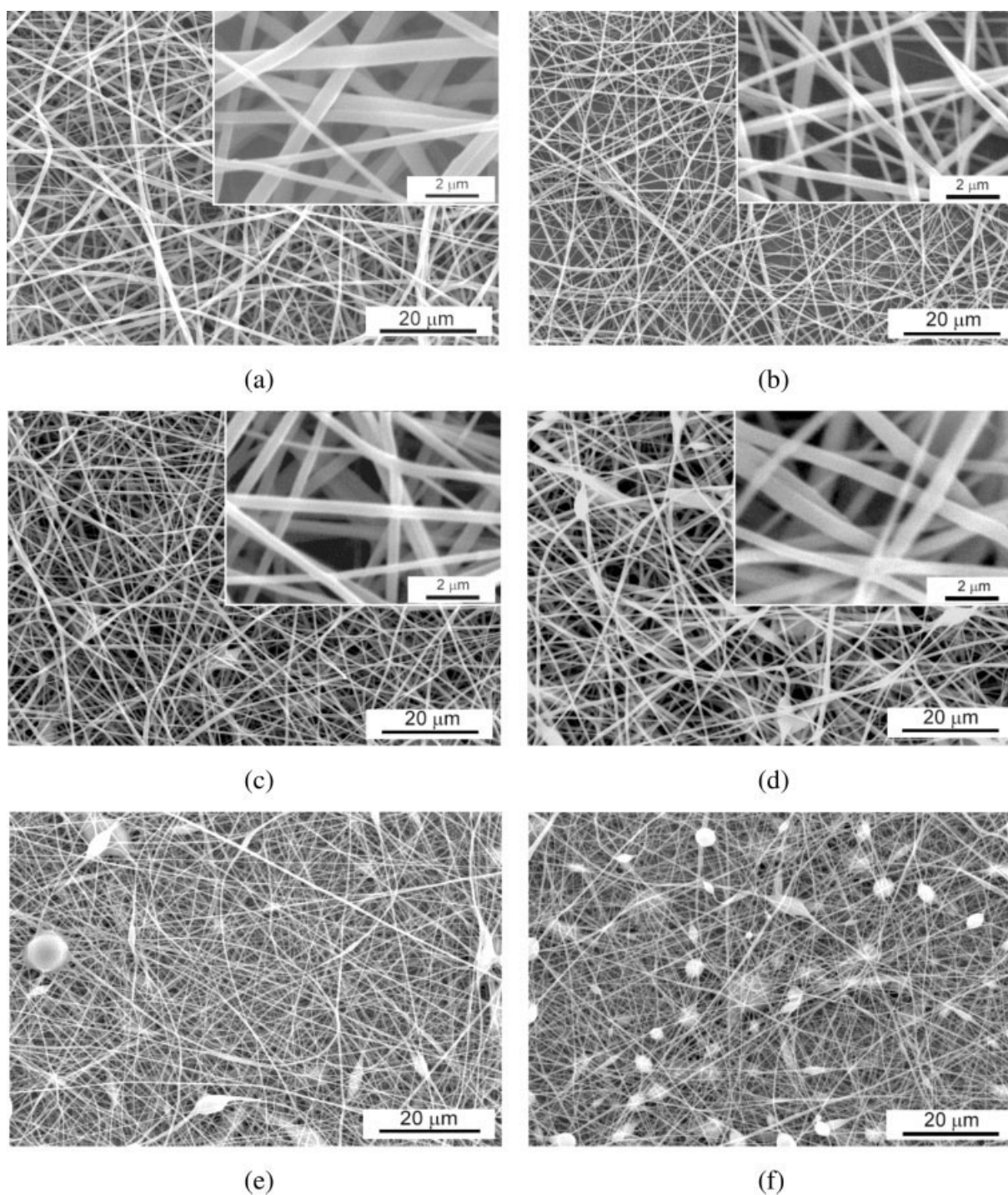
Figure 1 SEM micrographs of the electrospun PVDF–HFP membranes containing PEGDMA prepared from solutions in DMF/acetone with different volume ratios: (a) 5/5, (b) 6/4, (c) 7/3, (d) 8/2, (e) 9/1, and (f) 10/0 (PVDF–HFP concentration = 0.16 g/mL, PVDF–HFP/PEGDMA mass ratio = 4/1, voltage = 15 kV, distance = 15 cm, flow rate = 0.47 mL/h). Larger magnifications are shown in the inner boxes.

amount of PEGDMA increasing, the viscosity of the electrospinning solutions dropped obviously because of the dilution effect of PEGDMA, whereas the surface tension changed slightly. The conductivity increased with the amount of PEGDMA and reached the maximum, 2.82 μS/cm, at a 4/1 PVDF–HFP/PEGDMA mass ratio, and then declined gradually; this might have been caused by interactions between PVDF–HFP and PEGDMA. The viscosity and conductivity changes transformed the electrospun fiber morphology from fine fibers to bonded fibers, as shown in the SEM micrographs (Fig. 2). Moreover, the average fiber diameter of the electrospun fibers and the distribution range exhibited slight deviations

TABLE I
Solution Properties of the PVDF–HFP/PEGDMA
Solutions in a 6/4 DMF/Acetone Mixed Solvent
for Electrospinning

PVDF–HFP/ PEGDMA (w/w)	Surface tension (mN/m)	Conductivity (µS/cm)	Viscosity (Pa s)
4/0	32.55	1.28	33.0
4/0.5	32.62	2.72	28.5
4/1	32.64	2.82	24.0
4/2	32.76	2.72	23.7
4/3	32.70	1.99	22.5
4/4	32.63	1.46	20.0

caused by the addition of PEGDMA. The results in Table II suggest that when the PVDF–HFP/ PEGDMA ratio was varied from 4/1 to 4/4, the average fiber diameter was changed from 347 ± 144 to 393 ± 93 nm. Because PEGDMA was in the liquid state in the electrospinning solution and did not take part in PVDF–HFP fiber formation, it was thought that PEGDMA was ejected along with the polymer and adhered onto/into the polymer fibers. Therefore, the introduction of PEGDMA could have effects

only on the morphology of the electrospun fibers and not on the fiber diameter.

Morphology changes after heat treatment

Figure 3 shows SEM micrographs of electrospun PVDF–HFP/PEGDMA fibers prepared from solutions with different PVDF–HFP/PEGDMA mass ratios (4/1, 4/2, 4/3, and 4/4) after heat treatment at 130°C for 2 h for PEGDMA crosslinking. When the PVDF–HFP/PEGDMA mass ratio was 4/1 [Fig. 3(a)], nearly no differences in the fiber morphology were found between the electrospun fibers before and after heat treatment [Figs. 2(a) and 3(a)]. The average fiber diameter (334 ± 124 nm) and its distribution (100–500 nm) after heat treatment were almost the same as those of the fibers before crosslinking (347 ± 144 and 100–500 nm, respectively), as shown in Table II. By the addition of a smaller amount of PEGDMA, the fine morphology of the electrospun fiber could be perfectly preserved, despite PEGDMA polymerization. As the PVDF–HFP/PEGDMA mass ratio changed to 4/2, a little fiber bonding was seen after thermal polymerization [Fig. 3(b)]. However,
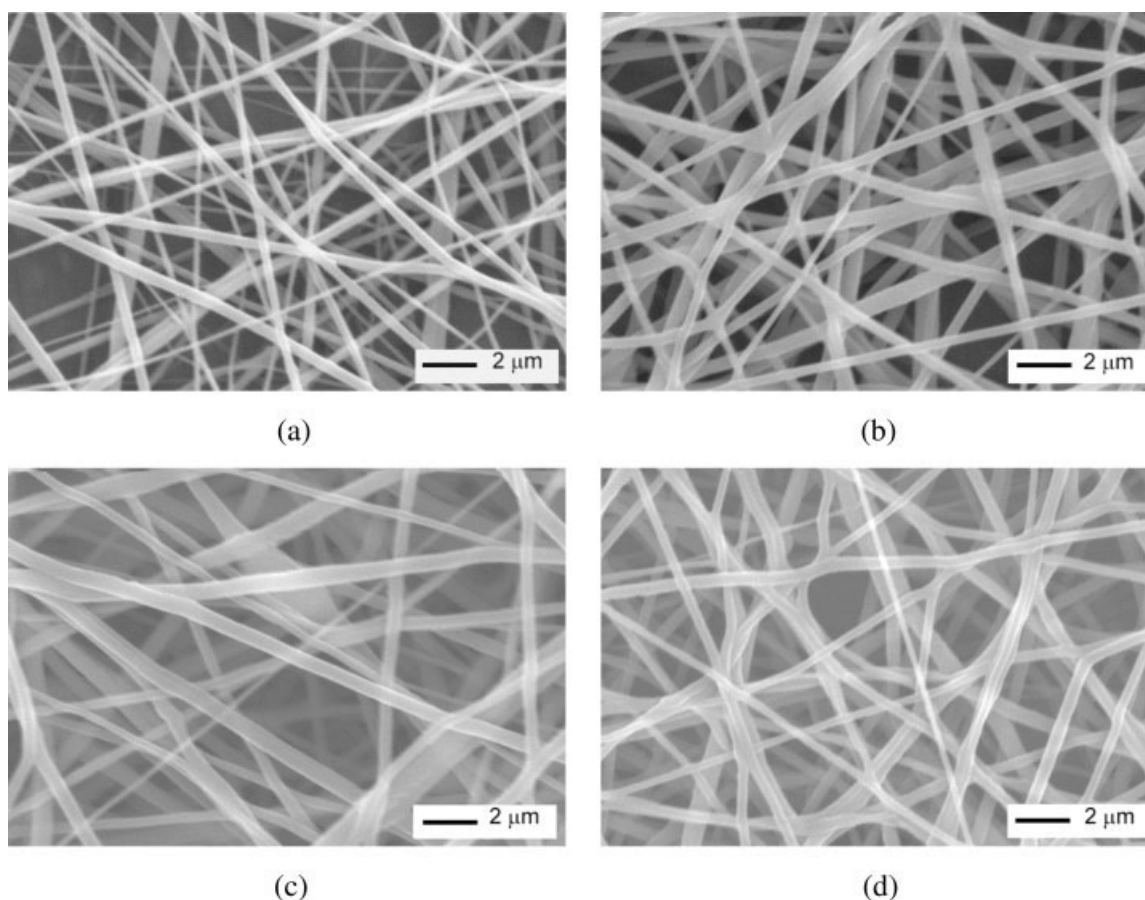

Figure 2 SEM micrographs of the as-electrospun PVDF–HFP/PEGDMA fibers prepared from solutions with different mass ratios: (a) 4/1, (b) 4/2, (c) 4/3, and (d) 4/4 (PVDF–HFP concentration = 0.16 g/mL, voltage = 15 kV, distance = 15 cm, flow rate = 0.47 mL/h, DMF/acetone = 6/4 v/v).

TABLE II
Average Fiber Diameters and Diameter Distribution Ranges with Different PVDF–HFP/PEGDMA Mass Ratios Before and After Heat Treatment at 130°C for 2 h

PVDF–HFP/PEGDMA mass ratio	Before heat treatment		After heat treatment	
	Average fiber diameter (nm)	Diameter distribution range (nm)	Average fiber diameter (nm)	Diameter distribution range (nm)
4/0	330 ± 79	200–600	370 ± 217	200–700
4/1	347 ± 144	100–500	334 ± 124	100–500
4/2	383 ± 88	100–500	356 ± 111	100–500
4/3	363 ± 86	100–300	437 ± 142	100–500
4/4	393 ± 93	200–400	407 ± 130	100–600

when the PVDF–HFP/PEGDMA mass ratio was changed to 4/3, the electrospun fibers after crosslinking became thicker, with an average fiber diameter of 437 ± 142 nm (Table II), exhibiting a weblike fiber morphology [Fig. 3(c)]. When the PVDF–HFP/PEGDMA mass ratio was 4/4 [Fig. 3(d)], there were also some distortions and more fiber bonds [Fig. 3(d)]. A large number of droplets also appeared visibly on the electrospun fibrous membrane, and the average fiber diameter was 407 ± 130 nm (Table II).

During electrospinning, most of the solvent in the fibers was volatilized, but PEGDMA remained in or on the surface of the electrospun fibers. When the amount of PEGDMA was small, thermal polymerization happened inside or on the surface of the electrospun fibers when they were heated. The addition of more PEGDMA laid the redundant oligomer in the electrospun fibers. Before crosslinking, the oligomer tended to leach out from the polymer fibers because of the thermal effect. Thus, distortion and more fiber bonds formed with the addition of a large amount of PEGDMA. As a result, the electrospun fibers became thicker, and the membrane morphology was not so fine anymore. When the mass of PEGDMA
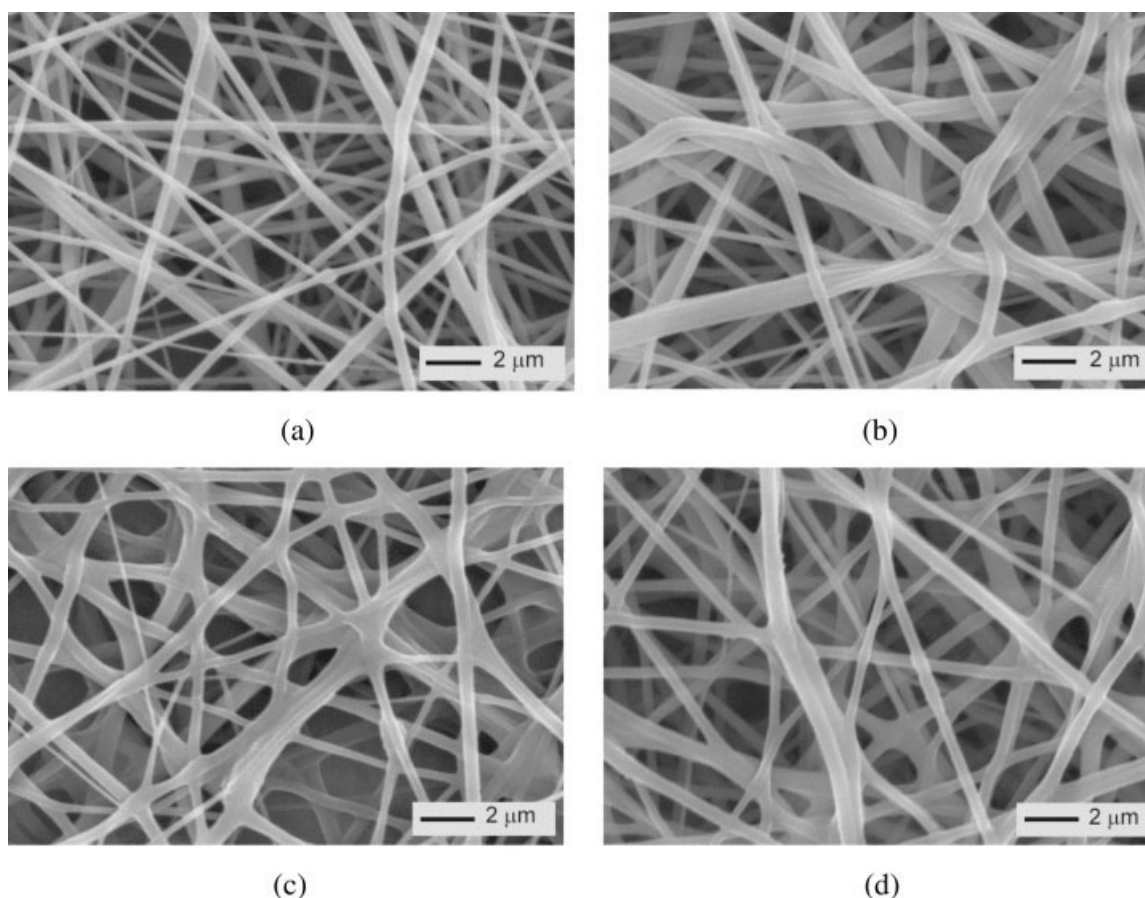

Figure 3 SEM micrographs of the electrospun PVDF–HFP/PEGDMA fibers prepared from solutions with different PVDF–HFP/PEGDMA mass ratios after heat treatment at 130°C for 2 h: (a) 4/1, (b) 4/2, (c) 4/3, and (d) 4/4 (PVDF–HFP concentration = 0.16 g/mL, voltage = 15 kV, distance = 15 cm, flow rate = 0.47 mL/h, DMF/acetone = 6/4 v/v).

was equal to the PVDF–HFP polymer (4/4), there were so many oligomers leaching out that they aggregated to form droplets, which destroyed the macroscopic morphology of the electrospun fibrous membrane. It was concluded that the 4/1 mass ratio of PVDF–HFP to PEGDMA was the optimal one, and it was employed further in our later research.

FTIR characterization

As the melting point of PVDF–HFP is 142°C, a thermal polymerization temperature was selected in the range of 120–140°C,[28] at which the fibrous structure of the electrospun PVDF–HFP membranes would not be destroyed. Furthermore, to complete the thermal polymerization of PEGDMA, a certain reaction time should be guaranteed. In our experiments, crosslinking of PEGDMA was performed at 125 or 130°C for 0.5 or 1 h, respectively, to examine proper crosslinking conditions. Figure 4 shows the FTIR spectra of electrospun PVDF–HFP/PEGDMA (4/1) membranes prepared from solutions in 6/4 DMF/ acetone (solvent) after heat treatment. When the polymerization was carried out at 125°C for 0.5 h, absorption peaks at 1730 and 1650 cm^{-1} associated with C=O and C=C of PEGDMA were both detected in the FTIR spectrum [Fig. 4(a)]. That is, a half-hour was not long enough for the completed polymerization of PEGDMA at 125°C. When the reaction time was prolonged to 1 h, the absorption related to C=C disappeared [Fig. 4(b)], and this suggested there were not unsaturated double bonds
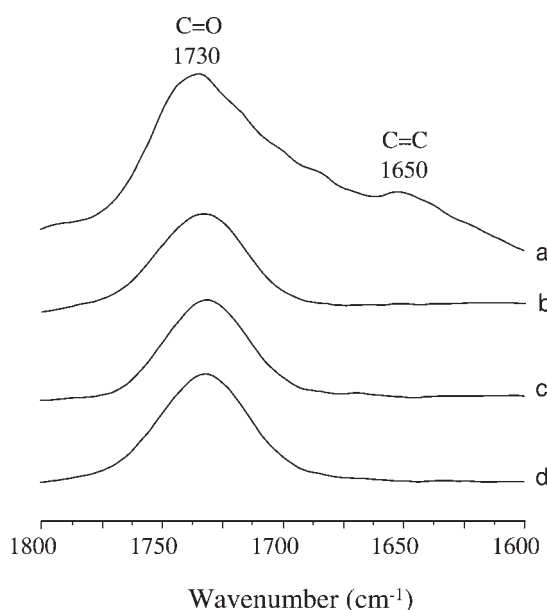
Figure 4 FTIR spectra of the electrospun PVDF–HFP/ PEGDMA (4/1) membranes after heat treatment at (a) 125°C for 0.5 h, (b) 125°C for 1 h, (c) 130°C for 0.5 h, and (d) 130°C for 1 h.
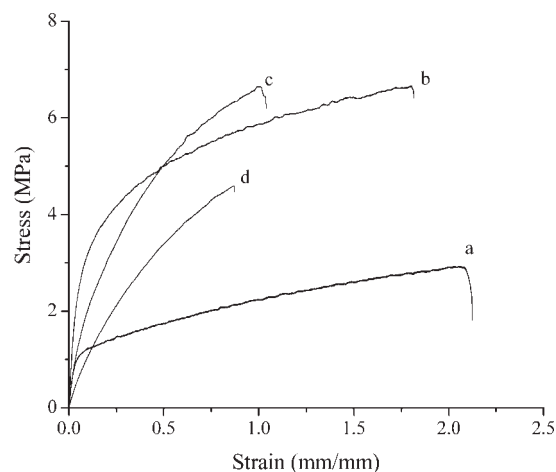
Figure 5 Typical stress–strain tensile curves of the electrospun PVDF–HFP/PEGDMA membranes with different mass ratios after heat treatment at 130°C for 2 h: (a) 4/0, (b) 4/1, (c) 4/2, and (d) 4/3.

anymore in the sample. In the case of 130°C, absorption peaks located at 1730 cm^{-1} (C=O) could be seen in the spectra of 0.5 and 1 h, whereas those peaks at 1650 cm^{-1} belonging to C=C disappeared [Fig. 4(c,d)]. It was obvious that the polymerization of PEGDMA could be finished when the electrospun membrane was heated at 130°C for at least 0.5 h. Because a further extension of the reaction time could improve the mechanical properties of the prepared membranes by annealing, heat treatment at 130°C for 2 h was employed in the later study.

Mechanical properties

Typical stress–strain tensile curves of the electrospun PVDF–HFP/PEGDMA fibrous membranes with different mass ratios after heat treatment at 130°C for 2 h are shown in Figure 5. The results of the tensile modulus, tensile strength, and elongation are summarized in Table III. Without PEGDMA, the electrospun PVDF–HFP membrane had a tensile modulus of 44.43 ± 6.12 MPa, a tensile strength of 3.28 ± 0.35 MPa, and an elongation of 236.7 ± 32.6%. When the PVDF–HFP/PEGDMA mass ratio was 4/1, the tensile curve of the electrospun PVDF–HFP/PEGDMA

TABLE III
Mechanical Properties of Electrospun PVDF–HFP/ PEGDMA Fibrous Membranes After Heat Treatment at 130°C for 2 h

PVDF–HFP/ PEGDMA mass ratio	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation (%)
4/0	44.43 ± 6.12	3.28 ± 0.35	236.7 ± 32.6
4/1	68.73 ± 2.77	6.26 ± 0.22	154.2 ± 12.7
4/2	31.51 ± 3.99	5.76 ± 0.53	89.8 ± 13.9
4/3	14.12 ± 1.12	4.58 ± 0.32	89.6 ± 4.7

membrane [Fig. 5(b)] had a shape similar to the one without PEGDMA [Fig. 5(a)], but both the tensile modulus (68.73 ± 2.77 MPa) and the tensile strength (6.26 ± 0.22 MPa) were significantly higher than those of the electrospun PVDF–HFP membrane without PEGDMA, whereas the elongation decreased significantly to 154.2 ± 12.7%. As for the 4/2 or 4/3 PVDF–HFP/PEGDMA mass ratio, samples broke with the absence of the yield stage. The tensile strength was still higher than that of the plain PVDF–HFP membrane but lower than that of the 4/1 PVDF–HFP/PEGDMA membrane. Both the modulus and the elongation showed a decreasing tendency in comparison with the values of the PVDF–HFP or 4/1 PVDF–HFP/PEGDMA membrane. Hence, it was obvious that the thermal polymerization of PEGDMA oligomers enhanced the tensile strength of the electrospun PVDF–HFP membrane significantly. This result could be attributed to the covalent bonds between PEGDMA inside fibers and chemical bonding between the fiber junctions. The formation of point-bonded structures favored the structural integrity of electrospun fibers, and this resulted in the improvement of the mechanical properties. The result coincided with a mechanical behavior study of electrospun fiber mats of poly(vinyl chloride)/polyurethane in ref. 33. However, the distortion due to the excessive addition of PEGDMA could damage the integrity of the electrospun membrane to some extent. Then, with the amount of PEGDMA further increasing to a mass ratio of 4/2 or 4/3, the tensile strength decreased a little in comparison with that with a 4/1 mass ratio. In the mean time, crosslinking could prevent the fibers from extending and also hinder slippage between fibers. Therefore, the elongation values of all electrospun membranes containing PEGDMA were lower than the elongation of the plain PVDF–HFP one. It could be seen that after heat treatment at 130°C for 2 h, the electrospun PVDF–HFP/PEGDMA membrane with a 4/1 mass ratio possessed preferable mechanical properties.

Porosity and liquid absorption

The porosity and liquid absorption of the electrospun PVDF–HFP/PEGDMA membrane with a 4/1 mass ratio were measured in comparison with the electrospun PVDF–HFP membrane without PEGDMA. The porosity of the PVDF–HFP/PEGDMA membrane after PEGDMA polymerization at 130°C for 2 h was 70.0 ± 1.6%, slightly lower than 76.60 ± 0.39%, the value of the electrospun PVDF–HFP membrane. Also, the liquid absorption dropped from 352 ± 15 to 267 ± 11%. The introduction of PEGDMA into the electrospun PVDF–HFP membranes was responsible for the results.

CONCLUSIONS

An electrospun PVDF–HFP membrane was formed by the introduction of PEGDMA. When the mass ratio of PVDF–HFP to PEGDMA was 4/1, the fiber average diameter changed slightly, and the fine morphology was preserved without beads or droplets. Mechanical testing showed that the tensile modulus and tensile strength of the PVDF–HFP/PEGDMA membranes increased whereas the elongation dropped in comparison with the PVDF–HFP electrospun membrane. The porosity and liquid absorption of the PVDF–HFP/PEGDMA membrane also showed a small reduction. A small amount of PEGDMA could improve the mechanical properties of the electrospun mats effectively, whereas the morphology and diameter of the fibers and other physical properties were grossly preserved. The produced PVDF–HFP/PEGDMA membrane could be a promising membrane for use as an electrolyte or separator in lithium batteries.

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