

POLY(VINYLDENE FLUORIDE) NANOFIBER MEMBRANE WITH POLYPROPYLENE SUPPORT LAYER AS A LITHIUM-ION BATTERY MEMBRANE

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ABSTRACT

This work aims at preparation of poly(vinylidene fluoride) (PVdF) nanofiber membranes using electrospinning along with the use of polypropylene (PP) spunbonded non-woven fabric as its support for enhancing mechanical properties. Morphology and size of the membranes are studied by the scanning electron microscopy and optimum diameter of nanofibers are obtained by adjusting of electrospinning control factors. The tensile strength of the membrane increases from 39.67 to 52.75 MPa with the increase of spinning time from 1.5 to 2.0h. The studies of tensile behavior of membranes display that PP spunbonded fabric increases the tensile strength of prepared membranes. Thermal stability of the prepared membranes was determined using the TGA method and the dimensional stability was investigated by the measuring of shrinkage ratio at 105°C. Shrinkage ratio, electrolyte uptake level and electrical resistance of the prepared membrane indicate its potential for battery separators.

Keywords: lithium-ion battery; membrane; electrospinning; poly(vinylidene fluoride) fibrous separator; polypropylene spunbonded fabric support

INTRODUCTION

In today's world, battery is considered as the heart of mobile electronic tools. Nowadays, lithium-ion batteries are used in modern pieces of technologies such as cell phones and laptops. Many giant car factories had huge investments on fabricating hybrid electrical cars using electrical energy supply to reduce weather pollution. Storage of electrical energy in such hybrid cars is available using rechargeable batteries [1 - 3].

Separator in a battery is a part between the cathode and anode which transports ionic conductors and prevents the electronic contact. Electrospinning is a continuous technique which can be used in producing electro-spun nanofiber membranes [1]. The most of the separators used for lithium-ion batteries are prepared from polyethylene (PE), polypropylene (PP) and PE/PP, but low porosity, poor thermal shrinkage, and poor electrolyte uptake make such batteries susceptible to failure [1, 3 - 5]. Polyethylene terephthalate [5], poly(vinyl chloride)/poly(ethyl methacrylate) [6], polyacrylonitrile [7], [8], polyamide 6,6 [1] and many other non-woven electro-spun membranes have also been fabricated and studied. However, these membranes do not have desirable mechanical properties and enough dimensional stability when a large tension applies.

Nowadays, poly(vinylidene fluoride) (PVdF) is used as a common substrate for membranes due to good electrical properties, chemical resistance and thermal stability, however, these membranes do not have enough mechanical properties [3].

Recently, PVdF nanofiber membranes were fabricated by Hwang et al. and their mechanical and thermal stabilities were more than a commercial PE membrane [4]. Effects of PVdF solution concentration used for electrospinning on morphology and adhesion energy of membranes were studied. The results showed that when PVdF concentration increases the mean nanofiber diameter goes up and this causes in adhesion energy reduction and better fibrous morphology with no bead-like texture [9 - 10]. Furthermore, addition of TiO₂ or SiO₂ fillers to PVdF solution during electrospinning results in enhancement of ionic conduction [11 - 12]. The addition of an ion-complex of SiO₂-PAALi to PVdF causes better physical properties, higher thermal resistance, and higher ionic conductivity [13]. PVdF nanofiber membranes were also used along with other substrates such as poly(ethylene oxide) (PEO) and PE to overcome poor mechanical properties of pure membranes. Furthermore, PE layer was introduced to ethylene plasma-treated PVdF nanofiber membranes for improving strength and modulus of the membrane [14]. The addition of 12.8% phosphotungstic acid to PVdF converted α into β phase crystals and reduced porosity of the membranes [15]. In PEO/PVdF nanofiber membranes, the good electrochemical properties and excellent charge/discharge cycle stability are inherited from PEO and PVdF, respectively [2, 12]. The addition of poly (methyl methacrylate) (PMMA) to PVdF nanofiber membranes enhanced the electrolyte uptake [16] and the addition of PMMA-grafted TiO₂ improved electrochemical properties, especially the ionic conductivity [17]. Recently, a copolymer of PVdF and hexafluoropropylene (HFP) was dissolved in a solution of polyimide (PI). These solutions were simultaneously electro-spun with two spinnerets. The prepared PVdF-HFP/PI nanofiber membrane had higher porosity, higher thermal dimensional stability and better electrolyte uptake than the commercial PP membrane [18] as well as PI/PVdF/PI nanofiber membranes [19]. Also, a trilayer PVdF-HFP/PVC/PVdF-HFP membrane using electrospinning was developed with better electrochemical properties compared with commercially available PP/PE/PP trilayer membrane [20]. Applying a polydopamine coating on the electro-spun PVdF nanofiber membranes induced better critical membrane properties over the pure PVdF membrane [21].

As it is mentioned, PVdF membranes in spite of having many required lithium-ion battery properties, do not have enough mechanical strength. The aim of this study is to prepare a PVdF nanofiber membrane by electrospinning along with the use of PP spunbonded non-woven fabric as the support to enhance its mechanical properties. Morphology of the prepared membrane was investigated; afterward, optimal fiber size and optimal solvent concentration were obtained. The electrospinning was performed during two different spinning times and in what follows applied properties of the membranes were investigated.

EXPERIMENTAL

Materials

Poly(vinylidene fluoride) (PVdF), dimethylacetamide (DMAc), acetone and lithium hexafluorophosphate (LiPF₆) in ethyl carbonate (EC)/diethyl carbonate (DEC) (50/50 volumetric ratio) were purchased from Sigma-Aldrich and PP spunbonded non-woven fabric was purchased from Yazd Behpood company.

Preparation of PVdF nanofiber membranes

Electrospinning is a method for preparation of nanofibers which can be adjusted by control of its parameters to reach desirable properties and morphology. The nanofiber membranes are prepared by the electrospinning method and use of suitable solvent mixture. In this work, 25 wt % PVdF and a solvent mixture of DMAc and acetone (75/25 wt %) were used. Also, PP spunbonded non-woven fabric was used as the support of PVdF nanofibers to be put on it (Fig. 1). The suitable levels of electrospinning factors such as voltage, flow rate, and tip-to-collector distance were chosen after several trials and errors to reach a secure adhesion of the nanofibers to PP spunbonded non-woven fabric. Furthermore, PVdF nanofibers are prepared with different spinning time to investigate its effect on the morphology and properties. Electrospinning details of the prepared membranes are demonstrated in Table 1.

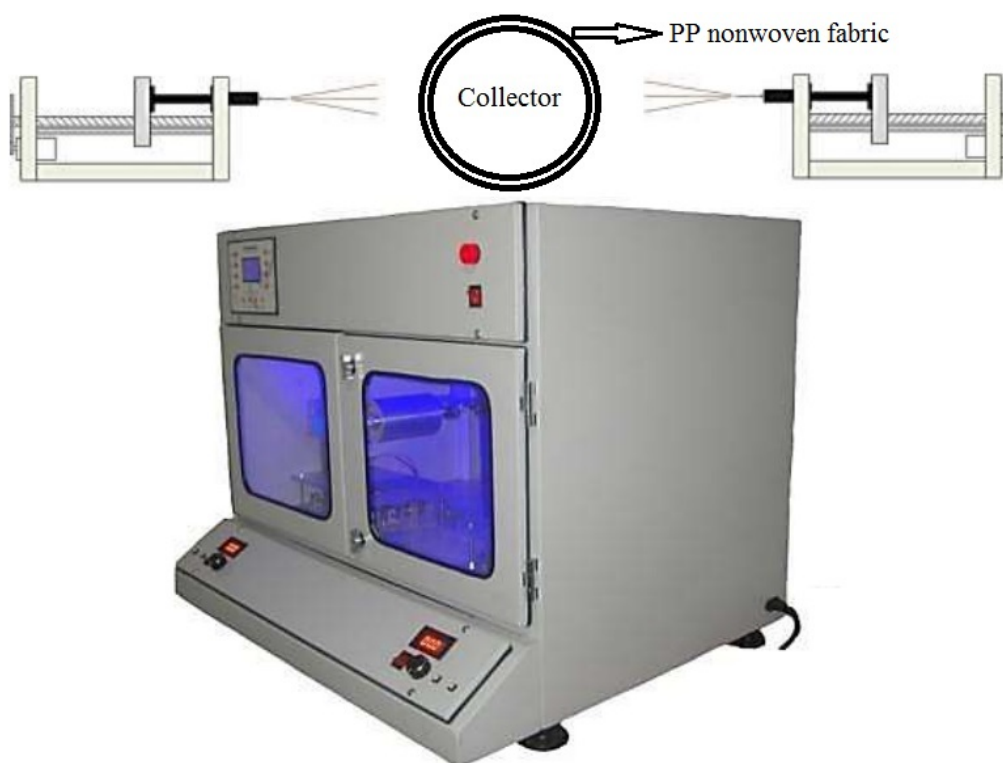


Figure 1. Schematic illustration of the electro-spun PVdF nanofibers collecting on the PP spunbonded nonwoven fabric (reprinted with permission from reference 3)

Table1. Control factors of electrospinning apparatus

| Sample | Spinning time (h) | Tip-to-collector distance (cm) | Flow rate (mL/h) | Voltage (kV) |
|--------|-------------------|--------------------------------|------------------|--------------|
| PVdF1 | 1.5 | 13 | 0.8 | 16 |
| PVdF2 | 2 | 13 | 0.8 | 16 |

Characterization of PVdF nanofiber membranes

Scanning electron microscopy

Morphology of the nanofibers was observed by AIS2100 scanning electron microscope (Seron Technology) with an accelerating voltage of 26 kV. Furthermore, scanning electron microscopy (SEM) images were used to investigate dispersity and mean diameter of PVdF nanofibers.

Mechanical properties

Tensile tests performed by a Gotech universal AI-7000-LA material testing machine according to ASTM D882. The specimens were held tightly between static and moveable clamps at room temperature. Sample dimensions were 50mm×10mm and the upper clamp was raised at the speed rate of 5 mm/min.

Thermal stability

A thermogravimetric analyzer TGA Q50 was performed for the investigation of PVdF nanofiber membrane thermal stability. The TGA was operated over the temperature range of 25-600°C with a heating rate of 20°C/min under argon atmosphere.

To study the dimensional stability, samples were weighted at room temperature (25°C), then they were heated to 105°C and stayed at this temperature for 6h in an oven. Afterwards, samples were cooled down to room temperature and were weighted to calculate the shrinkage ratio, using the Eq. (1):

$$\text{Shrinkage ratio (\%)} = \frac{M_0 - M}{M_0} \quad (1)$$

where M_0 and M are the weight of samples before and after being kept in the oven.

Wettability Test

The contact angle of deionized water was measured by dropping very small droplets (~5 μ L) at ambient temperature by using the Kruss G10 apparatus. The distance of vibrating syringe was about 5 cm and all contact angles were obtained at the initial stage (i.e., <10 s). Every contact angle was measured at three points of the sample surfaces. Since each water droplet has a right and left angle, six different contact angles were used to calculate the average one for each sample [22], [23]. The variation of every contact angle measured in this study was less than 1°.

Electrolyte uptake and electrical properties

Measurement of the electrolyte uptake level of the samples was done using LiPF_6 in ethyl carbonate/diethyl carbonate with a ratio of 50/50 vol %. Then, materials were mixed and put into an enclosed glass container for 24h to calculate the electrolyte uptake level by Eq. (2):

$$\text{Uptake (\%)} = \frac{\text{weight of wet membrane} - \text{weight of dry membrane}}{\text{weight of dry membrane}} \quad (2)$$

Therefore, after soaking of the membrane in an electrolyte, uptake level and electrical resistance were calculated and studied.

RESULTS

Morphology of the PVdF nanofibers was observed by SEM to investigate the dispersion and diameter of nanofibers which significantly affect membrane properties (Fig. 2). Diameter of the nanofibers was between 50 to 200 nm and the mean diameter is estimated ca. 100 nm.

Determination of dispersion and mean diameter of the nanofibers are important keys for estimation of membranes' final properties.

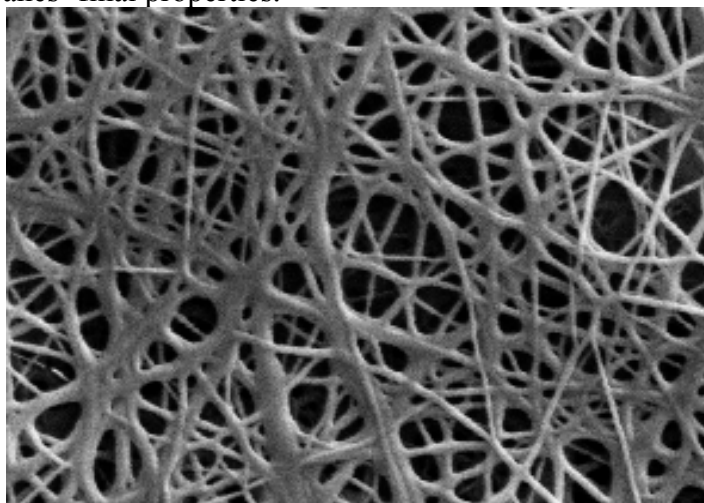


Figure 2. SEM observation of PVdF nanofiber membranes

Fig. 3 shows the tensile behavior of the PVdF nanofibers and as shown the tensile strengths are high due to the use of PP spunbonded non-woven fabric as the support. This material induces enhancement in tensile strength of the prepared membrane due to its inherent high mechanical strength. When nanofiber membranes are used in batteries, high movements can damage them, but if the PP spunbonded non-woven fabric is used as a support the membrane will be almost immune from damages in sudden movements. Fig. 3 reveals that PVdF2 has more tensile strength than PVdF1 because of increased spinning time and consequently the thickness (the first was 39.67MPa and the second was 52.75MPa). Besides, its elongation at break goes up from 16.4% to 23.6% by increasing the electrospinning time.

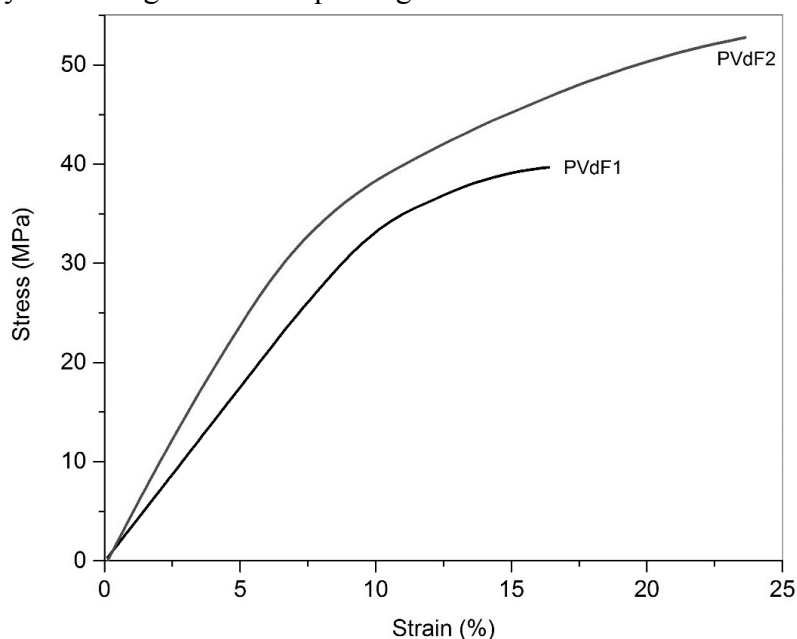


Figure 3. Tensile properties of PVdF1 and PVdF2

As is shown in Fig. 3, elongation at break of PVdF2 is also greater than that of the PVdF1 although elongation at break of them are not so high due to the inherent low elongation of PP. The effects of temperature and time on the shrinkage of the PVdF nanofibers are illustrated in Table 2. As shown, both PVdF nanofiber membranes have a shrinkage ratio of less than 1.6%, revealing the high dimensional stability.

TGA method was used to determine the thermal stability of the electro-spun PVdF membranes and the TGA curves are shown in Fig. 4. A weight loss of around 3% was observed for the PVdF1 and PVdF2 membranes at around 120°C, which is attributed to the removal of residual solvents and absorbed moisture. A clear weight loss at around 400°C was observed for both PVdF1 and PVdF2, relating to the decomposition of PP spunbonded non-woven fabric. Likewise, a steep weight loss, corresponding to the decomposition of PVdF in the range of 440 to 530°C for the prepared membranes. These results indicate the fact that the prepared membranes are thermally stable up to a temperature of 330°C in argon atmosphere. The residual amounts at the temperature of 600°C for PVdF1 and PVdF2 were 32 and 38%, respectively. PVdF2 due to the higher spinning time has a more PVdF content in the composition, which has more residual amounts compared with PP [24 - 26], therefore, PVdF2 shows more residual amounts at a temperature of 600°C. When batteries are used for a long time, the heat is built up, therefore the membrane substance should be dimensionally stable at high temperatures to prevent damages. The shrinkage results prove the high thermal stability of the PVdF nanofibers, which is very important for the selection of material for lithium-ion batteries.

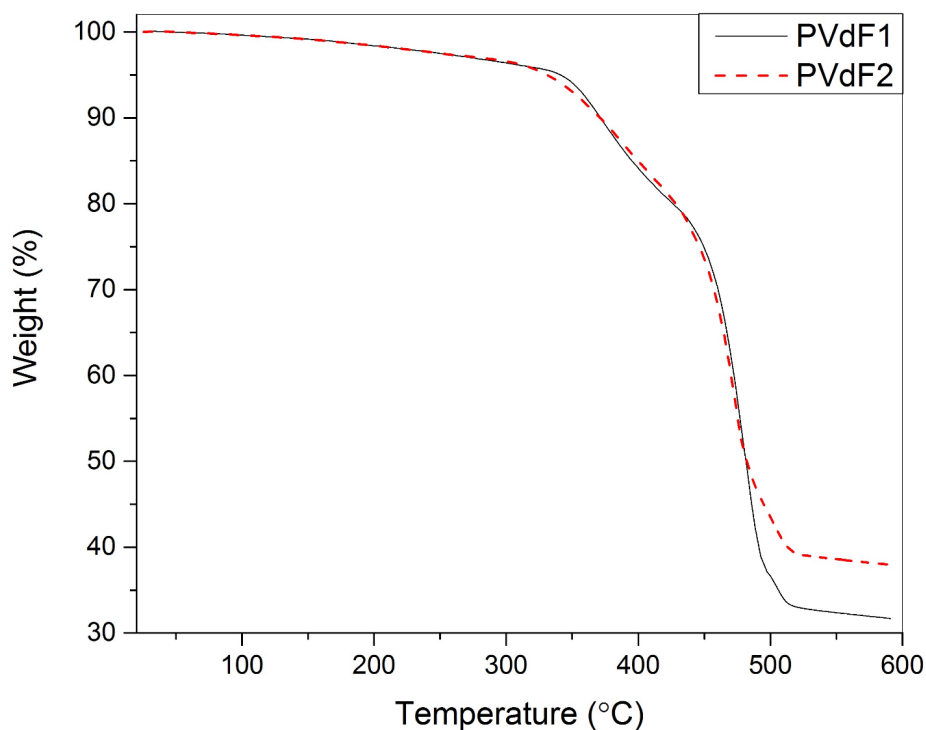


Figure 4. TGA thermograms of PVdF1 and PVdF2 membranes

Water contact angle mostly is used to predict wettability, adhesion, and surface free energy. Water contact angle of samples was $121.1 \pm 2.6^\circ$ (Fig. 5). The high contact angle of these samples reveals the hydrophobic behavior of the electro-spun PVdF nanofiber membranes.



Figure 5. Contact angle image of PVdF nanofiber membranes

Electrolyte uptake level for the two PVdF nanofibers was measured and the result is illustrated in Table 2.

| Table 2. Shrinkage ratio, electrolyte uptake level and conduction coefficient of samples | | | |
|------------------------------------------------------------------------------------------|---------------------|------------------------------|-------------------------------|
| Sample | Shrinkage ratio (%) | Electrolyte uptake level (%) | Conduction coefficient (S/cm) |
| PVdF1 | 1.5 | 483 | 1.76E-04 |
| PVdF2 | 1.6 | 547 | 1.43E-04 |

High electrolyte uptake level is due to the PVdF and PP inherent high electrolyte absorption (uptake). Electrical resistance is an important feature in PVdF nanofiber membranes for lithium-ion batteries. Electrical resistance was measured in the two PVdF samples and listed in Table 2. Conductivity of PVdF nanofibers in the two samples are logical values for lithium-ion battery membranes, which is also affected by PP spunbonded non-woven fabric.

CONCLUSION

Hydrophobic PVdF nanofiber membranes with a contact angle of $\sim 121.1^\circ$ were successfully prepared using electrospinning method and by controlling the electrospinning factors a desirable nanofiber morphology was attained. Furthermore, by adjusting electrospinning factors good dispersion of nanofibers and appropriate mean diameter of 100 nm for PVdF nanofibers are obtained. Moreover, the use of PP spunbonded non-woven fabric as the support of membrane enhanced mechanical properties of the PVdF nanofibers which increases the mechanical strength of the membrane when it is used in lithium-ion batteries. Studies of electrical and thermal properties display that prepared membranes have adequate electrical and thermal resistance. Investigations of the thermal stability of membranes reveal that both PVdF1 and PVdF2 are stable up to around 330°C . Also, it is shown that at a temperature of 600°C , the residual amounts of PVdF2 are more than that of PVdF1 because of the higher PVdF content. Dimensional stability of the prepared membranes at 105°C demonstrates enough thermal resistance for use in lithium-ion batteries. Thus, the prepared membranes show sufficient values of every necessary

parameters for use in lithium-ion batteries as a membrane, along having enhanced mechanical strength which makes it more durable.

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