

# Structure and Properties of Electrospun Poly(vinylidene fluoride)/Polycarbonate Membranes After Hot-Press

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**ABSTRACT:** Poly(vinylidene fluoride) (PVDF)/polycarbonate (PC) dispersed solutions were electrospun into ultrafine core/shell fibers and modified by hot-press. Morphology, tensile properties, porosity, and liquid absorption of the electrospun membranes as well as the crystallinity of PVDF were examined before and after hot-press. Results showed that the tensile strength and tensile modulus of the electrospun membranes increased after hot-press, especially when poly(methyl methacrylate) (PMMA) or benzyl triethylammonium chloride (BTEAC) was introduced for the formation of distinct core/shell fiber structure. The elongation of the hot-pressed electrospun PVDF/PC membrane with addition of BTEAC was also significantly enhanced by

reason of the clearest core/shell structure. The crystallinity of PVDF did not change too much before and after hot-press, however the porosity and liquid absorption of the hot-pressed electrospun membranes decreased to about 58% and around 75–90%, respectively, with no significant differences between PVDF/PC, PVDF/PC/PMMA, and PVDF/PC with BTEAC membranes. This study could be an example of electrospun membranes in multi-polymer components and it could be extended to other systems of electrospinning for applications in filtration and so on. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 774–781, 2011

**Key words:** fiber; membranes; mechanical properties

## INTRODUCTION

In recent years, electrospinning was becoming an important way to produce ultrafine fibrous membranes from polymer solutions under a high electric voltage.<sup>1,2</sup> Due to the tiny diameter in several hundreds of nanometers and the high porosity, electrospun membranes showed potential applications in extensive areas such as filtration systems, biomedical tissue templates, drug delivery membranes, and so on.<sup>3,4</sup>

Nowadays, with the development of electrospinning, core/shell structured ultrafine fibers had attracted extensive attention.<sup>5–8</sup> Wei et al. processed binary polymers such as polybutadiene/polycarbonate (PC), poly(methyl methacrylate) (PMMA)/PC, polyaniline/PC into core/shell structured fibers by electrospinning to obtain functional ultrafine fibers.<sup>9,10</sup> Babel et al. prepared core/shell structured fibers from poly[2-methoxy-5-(2-ethylhexoxy)-1,4-phenylene-vinylene]/poly(9,9-dioctylfluorene) binary blend for applications in field-effect transistors.<sup>11</sup>

Functionalization and bioactivities of the electrospun fibrous membranes composed of particular

structured fibers had been widely studied.<sup>12,13</sup> The mechanical properties of electrospun fibers is important for their successful applications in tissue engineering, drug delivery, nano-composite, filtration and so on. Using a combined atomic force microscopy/optical microscopy technique, the mechanical properties of a single electrospun fiber of collagen type I could be determined.<sup>14</sup> However, due to the weaker interaction between the ultrafine fibers in the electrospun membranes, it was difficult to directly evaluate the influence of the microstructure of electrospun fiber on the tensile properties of the electrospun membranes. Little researches were approached to the difference between the properties of the fibrous membranes in different microstructures.

By crosslinking or heat treatment, the electrospun poly(vinyl alcohol) and poly(L-lactic acid) membranes exhibited better mechanical properties.<sup>15,16</sup> Continuous hot-press was also a simple method to improve the mechanical properties as well as the tidiness of the fiber aggregates and decrease the porosity of the electrospun membranes.<sup>17</sup> When continuous hot-press was used in treating electrospun membranes under a suitable temperature, the morphology and crystallinity of electrospun fibers changed slightly, but the tensile strength and tensile modulus increased obviously, whereas the elongation, porosity, and liquid absorption decreased.<sup>17</sup>

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In this study, continuous hot-press was utilized to enhance the interaction between ultrafine fibers in electrospun membranes, so that the detailed difference between the tensile properties of the multi-component electrospun membranes in different microstructured fibers could be easily distinguished.

Core/shell structured poly(vinylidene fluoride) (PVDF)/PC fibers were ever systemically discussed after addition of a proper amount of PMMA or benzyl triethylammonium chloride (BTEAC) in our previous study.<sup>18</sup> In this article, the microstructure and tensile properties of the electrospun PVDF/PC membranes with introduction of PMMA or BTEAC were characterized before and after hot-press to study the impact of the core/shell fiber structure to the electrospun PVDF/PC membranes. The changes of the porosity and liquid absorption of the electrospun membranes were also discussed.

## EXPERIMENTAL

### Materials

PVDF with weight-average relative molecular mass of  $3.1\text{--}3.5 \times 10^5$ , was purchased from Kureha Chemical Industry (Japan). PC was supplied from General Electric (USA) with a weight-average relative molecular mass of  $3.1 \times 10^4$  determined by Gel Permeation Chromatography. PMMA with relative molecular mass of  $3.5 \times 10^4$  and BTEAC were collected from Aldrich. *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were solvents in chemical grade. All the reagents were used as received.

### Electrospinning

PVDF was dissolved in DMF at 30–45°C and PC was dissolved in a mixture of DMF and THF (7/3, v/v) to form clear solutions, separately. After then, the PC solution was dropped into the PVDF solution under stirring to obtain the dispersed PVDF/PC (7/3,wt/wt) solutions with 0.18 g/mL concentration for electrospinning. For introduction of PMMA or BTEAC, 15 wt % PMMA or 2 wt % BTEAC with respect to the total mass of PVDF and PC was added in the PC solution. Three different polymer composite (PVDF/PC, PVDF/PC/PMMA PVDF/PC with BTEAC) dispersions were obtained and used to prepare electrospun fibers.

The electrospinning setup including syringe pump, high-voltage power supply, and collector was shown in our previous article.<sup>19</sup> A hypodermic stainless steel needle with inner diameter of 0.7 mm and 3 cm in length was fixed to the syringe as a capillary, the tip of which had been cut flat. The metal capillary was connected to the high-voltage power supply (Model DW-P503-4AC, Tianjin,

China). Generally, the electrospun membranes were prepared at 12 kV voltage, 0.4 mL/h flow rate, and 15 cm working distance and collected on a custom-made roller rotating at 0.42 m/s speed wrapped by flat aluminum foil connected to ground. After about 25 h, the membrane was removed from the aluminum foil and vacuum-dried at 45–55°C for 12 h for further use.

### Hot-press

The electrospun membranes were treated in monolayer at 130°C in a continuous hot-presser (Photoart-24LSI, South Korea), and the schematic diagram of the continuous hot-press process for treating the electrospun membranes was shown in our previous article.<sup>14</sup> The electrospun membranes were continuously turned into the machine from the inlet and collected at the outlet. The hot-press speed was controlled at 0.43 m/min. Each membrane was treated twice for both upper and inverse surface.

### Characterizations

The morphology of the electrospun membranes was observed under a scanning electron microscope (SEM, Philips XL-30, the Netherlands) after gold coating. The average diameter of the electrospun fibers was measured in the SEM micrographs (5000 $\times$ ) by Photoshop 9.0 software. For Fourier transformed infrared spectroscopy (FT-IR, Perkin-Elmer, Spectrum 100, USA) measurement, the samples were placed on top of the attenuated total reflection set and scanned from 4000 to 650  $\text{cm}^{-1}$ . X-ray diffraction (XRD) patterns of the electrospun membranes were obtained using an X-ray diffractometer (Rigaku D/max 2500, Japan) with Cu  $K_{\alpha}$  radiation ( $\lambda = 1.5405$ ). The samples were scanned at 3°/min in the range of 10–45° of  $2\theta$  at room temperature. Differential scanning calorimeter (DSC) measurements were performed in a Perkin-Elmer Diamond apparatus at a heating rate of 10°C/min. Each sample of the electrospun membranes was about 5–10 mg. The melting temperature ( $T_m$ ) was noted as the temperature at the maximum value of the endothermic peak.

The tensile properties of the electrospun membranes were tested in a tensile machine (Instron 5848, USA). The samples were cut into 60  $\times$  10  $\text{mm}^2$  with a gauge length of 40 mm. The tests were conducted at a crosshead speed of 5 mm/min at room temperature by using a 100N load cell. The reported tensile modulus, tensile strength, and elongation represented average results of five tests.

For the porosity measurement, three pieces of the electrospun membranes were cut into a square shape in 20  $\times$  20  $\text{mm}^2$ . Each of them was accurately

weighed in an electronic balance with a resolution of 0.1 mg. The length and the width of the electrospun membranes were accurately measured in a vernier caliper with a resolution of 0.005 mm, and their thickness was ascertained by a micrometer with a resolution of 0.002 mm. The apparent density ( $\rho$ ) of the electrospun membranes were calculated from the obtained mass and the volume. Then, the porosity of the electrospun membranes was determined using the following equation:

$$\text{Porosity (\%)} = \frac{(\rho_0 - \rho)}{\rho_0} \times 100\% \quad (1)$$

where,  $\rho$  was the apparent density of PVDF/PC electrospun membranes, and  $\rho_0$  was the average density of materials used in electrospinning which could be obtained according the following equation:

$$\frac{1}{\rho_0} = \frac{\omega_1}{\rho_1} + \frac{\omega_2}{\rho_2} + \frac{\omega_3}{\rho_3} \quad (2)$$

where,  $\rho_1$ ,  $\rho_2$ , and  $\rho_3$  were the density of PVDF, PC and of PMMA, that is, 1.76, 1.20, and 1.19 g/cm<sup>-3</sup>, respectively.  $\omega_1$ ,  $\omega_2$ , and  $\omega_3$  were the mass fractions of PVDF, PC, and PMMA in electrospun membranes, respectively. So  $\rho_0$  was 1.54 or 1.49 g/cm<sup>3</sup> under the mass ratio of PVDF/PC and PVDF/PC/PMMA equaling to 70/30 or 70/30/15, respectively.

Alternately, three pieces of the above electrospun membranes were placed into glass beakers containing diethyl carbonate after weighing. After 1 h, the samples were removed from diethyl carbonate and weighted again immediately after absorbing surface liquid with a piece of filter paper. The liquid absorption of the electrospun membranes in diethyl carbonate was calculated using the following equation:

$$\text{Liquid absorption (\%)} = \frac{(m_1 - m_0)}{m_0} \times 100\% \quad (3)$$

where,  $m_0$  and  $m_1$  were the masses of the membranes before and after immersion in the medium, respectively.

The diameter of electrospun fibers and the results of tensile properties, porosity, and liquid absorption were analyzed statistically by Student's *t*-test method. To estimate the significant difference in these properties, *P* (*P*-value) was detected by the value less than 0.05.

## RESULTS AND DISCUSSTION

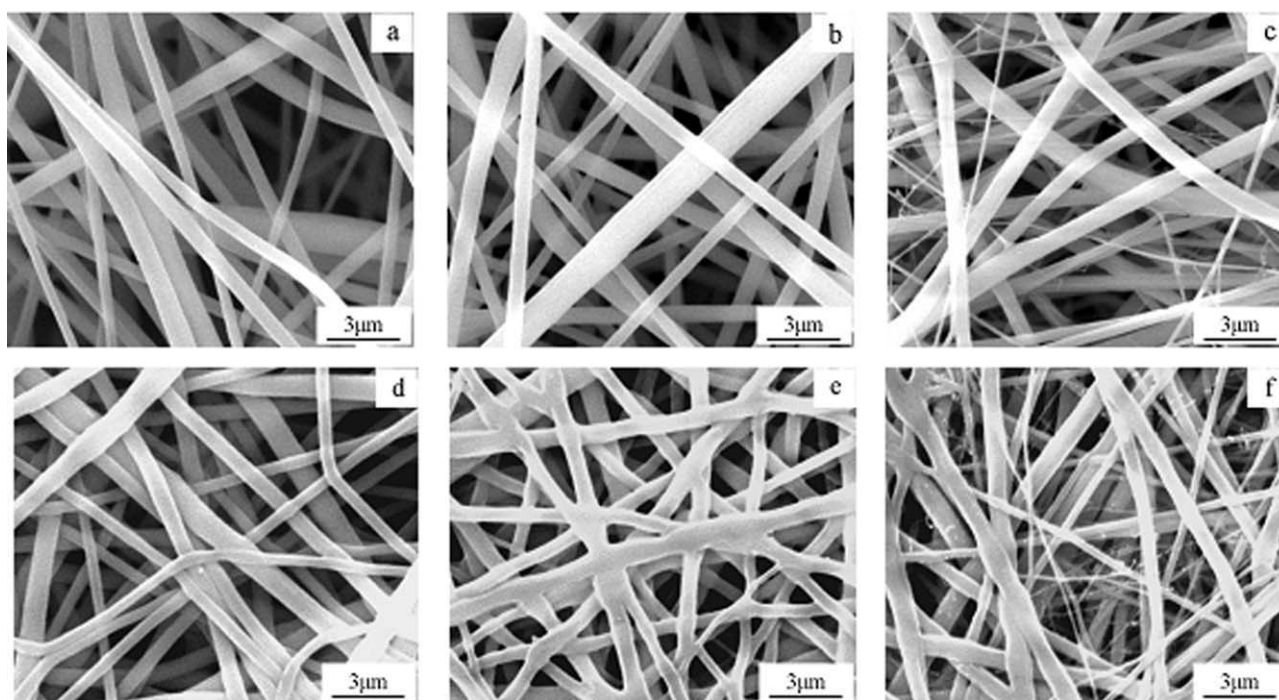
### Morphology

In electrospinning, different additives could be introduced in the multi-component polymeric dispersions

to facilitate the formation of ultrafine fibers. In our previous work, the morphology and microstructure of electrospun PVDF/PC fiber were detailed discussed in variation of polymer compositions and solvent mixtures, and the core/shell structure in electrospun PVDF/PC fibers was prepared.<sup>20</sup> To prepare more distinct core/shell structured ultrafine fiber in electrospinning, PMMA or BTEAC was added in the PVDF/PC dispersion, respectively, in our previous work, it was shown that both the PMMA and BTEAC could promote the formation of core/shell structure of PVDF/PC ultrafine fiber in electrospinning. Under suitable amount PMMA and BTEAC addition, more distinct core/shell structured electrospun fiber could be obtained in experiment, even more it was found that BTEAC improved the generation of the core/shell structure of the ultrafine fibers more easily than PMMA.<sup>18</sup>

Figure 1 shows the SEM micrographs of electrospun PVDF/PC fibrous membranes with and without PMMA or BTEAC before and after hot-press. The electrospun PVDF/PC fibers exhibited uniform fibrous morphology [Fig. 1(a)], and the average diameter of the ultrafine fibers was  $626 \pm 199$  nm. After addition of 15wt% PMMA into the PVDF/PC dispersions, the average fiber diameter increased significantly to  $769 \pm 288$  nm ( $P = 0.047$ ) [Fig. 1(b)]. However, after added 2 wt % BTEAC, there formed some thin fiber with tiny diameter in PVDF/PC fibers which lead the average diameter of electrospun PVDF/PC fibers with BTEAC decreased to  $556 \pm 288$  nm [Fig. 1(c)], and there was no significant differences in the average diameter of PVDF/PC fibers with and without BTEAC ( $P = 2.02$ ).

When continuous hot-press was applied to PVDF membrane in our previous work at 130°C, the morphology of electrospun fibers did not change too much, basically maintained the primary uniform fibrous morphology.<sup>17</sup> However, after increasing the hot-press temperature above 145°C, the PVDF fiber began to get merge in hot-press process. It could be supposed if the PVDF/PC fibers were hot-pressed above 145°C, PVDF might begin to melt and the fibers merged together. Not only could the fibrous morphology but also the micro-structure of the multi-component fibers be destroyed in hot-press. After hot-pressed at 130°C, the uniform fibrous morphology of PVDF/PC electrospun fibers with and without BTEAC did not change significantly [Fig. 1(d,f)] owing to the high melting temperature of PVDF (160–169°C) and the flow temperature of PC at around 230°C.<sup>19,21</sup> However, because of the low flow temperature of PMMA (around 150°C),<sup>22</sup> it might fuse during hot-press. When PVDF fibrous membranes were hot-press at different temperature in our previous work,<sup>17,18</sup> if the hot-press temperature was 20°C lower than the flow melting point, the



**Figure 1** SEM micrographs of the electrospun membranes before (a–c) and after (d–f) hot-press. (a,d) PVDF/PC; (b,e) PVDF/PC/PMMA; (c,f) PVDF/PC with BTEAC.

electrospun fibers could not fully melt, and the fibrous morphology of the electrospun membrane would not change too much. Figure 1(e) shows the fiber morphology of PVDF/PC/PMMA did not change a lot, only the cross point of the PVDF/PC/PMMA fibers at the surface of the electrospun membrane merged together after hot-pressed at 130°C.

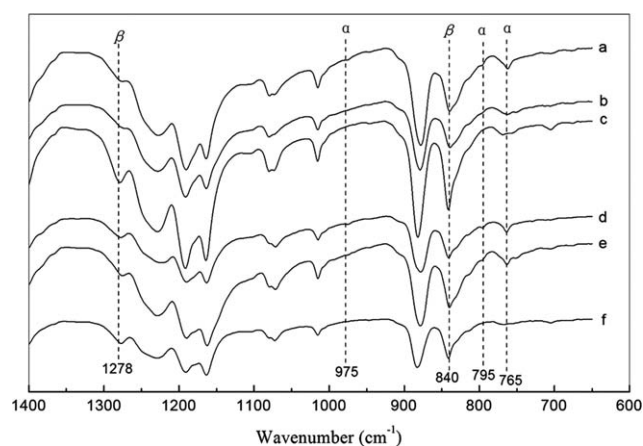
### Crystallinity of PVDF

FT-IR spectra of electrospun PVDF/PC membranes with and without PMMA and BTEAC before and after hot-press are illustrated in Figure 2. The strong peaks at 840 and 1278  $\text{cm}^{-1}$ , which were the characteristic band of  $\beta$ -type crystallite form of PVDF, appeared in the FT-IR spectra of electrospun PVDF/PC membranes before and after hot-press.<sup>23</sup> Meanwhile, the weak peaks at 975, 795, and 765  $\text{cm}^{-1}$ , assigned to the characteristic bands of  $\alpha$ -type crystallite form of PVDF, indicated that a little amount  $\alpha$ -type crystallite form of PVDF also appeared in electrospun membranes.<sup>23</sup>

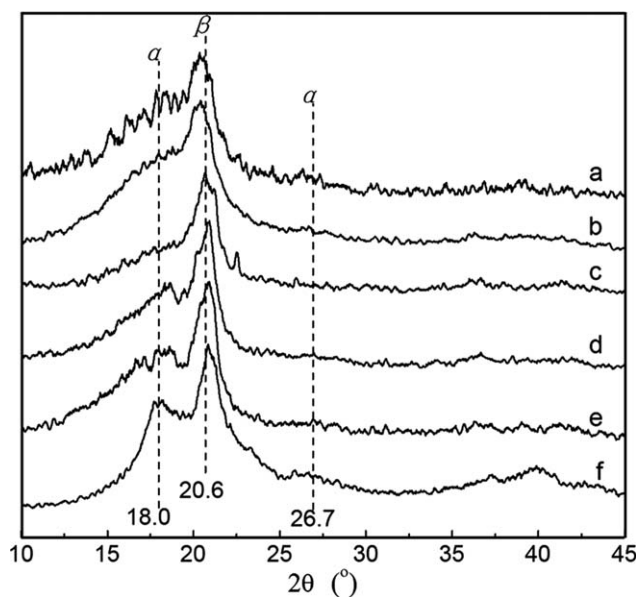
Figure 3 shows XRD diffraction patterns of electrospun membranes before and after hot-press. The electrospun PVDF/PC, PVDF/PC/PMMA, and PVDF/PC with BTEAC membranes before and after hot-press showed similar crystalline structures including one major peak at 20.6° of  $2\theta$ , which was recognized as the characteristic peak of  $\beta$ -type crystallite form of PVDF.<sup>23</sup> The minor peak at 18.0° in XRD diffraction pattern of electrospun membranes

could be considered as the presence of a little amount  $\alpha$ -type crystallite form of PVDF.<sup>23</sup> That was to say, similar crystallite form was observed in the electrospun PVDF/PC membranes with or without PMMA or BTEAC and the  $\beta$ -type crystallite form of PVDF was the main crystallite form accompanied with a little amount  $\alpha$ -type crystallite form. The crystallite form of PVDF in all the electrospun fibers did not vary obviously before and after hot-press, which was coincided with the results of FT-IR.

It is well known that PVDF held one of three crystalline structures depending on the preparation and post-treatment conditions, that is, Form I ( $\beta$ -type



**Figure 2** FT-IR spectra of the electrospun membranes before (a–c) and after (d–f) hot-press. (a,d) PVDF/PC; (b,e) PVDF/PC/PMMA; (c,f) PVDF/PC with BTEAC.



**Figure 3** XRD patterns of the electrospun membranes before (a–c) and after (d–f) hot-press. (a,d) PVDF/PC; (b,e) PVDF/PC/PMMA; (c,f) PVDF/PC with BTEAC.

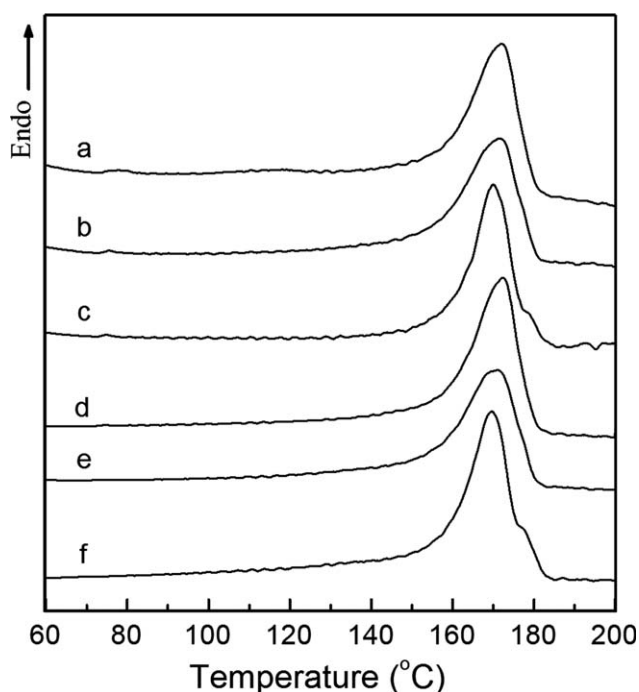
crystalline in planar zigzag conformation, orthorhombic), Form II ( $\alpha$ -type crystalline in TGTG, monoclinic) and Form III ( $\gamma$ -type crystalline in TTTGTTT, monoclinic).<sup>24</sup> The  $\beta$ -type crystallite form of PVDF was generally formed in the tensile process, while blending process was easy to induce  $\alpha$ -type crystallite form.<sup>25</sup> Therefore, the main crystallite form of PVDF in the electrospun membranes was the  $\beta$ -type crystallite form in the PVDF/PC fibers with or without introduction of PMMA and BTEAC. After hot-pressed at 130°C, PVDF in the electrospun PVDF/PC membranes did not undergo a real melting, so the crystallite form of PVDF did not change remarkably.

DSC thermograms of electrospun PVDF/PC membranes with and without PMMA and BTEAC before and after hot-press are presented in Figure 4. The PVDF/PC membrane before hot-press showed an endothermic peak with a melting temperature at 172.1°C as shown in Figure 4(a). With 15 wt % PMMA addition, the melting temperature of the membrane was 171.4°C [Fig. 4(b)]. After added 2 wt % BTEAC to PVDF/PC fibers, the melting temperature of the electrospun membrane shifted to 170.1°C [Fig. 4(c)], and around 180°C there appeared an endothermic peak which was assigned to the thermal decomposition of BTEAC. After hot-press, the PVDF/PC, PVDF/PC/PMMA and PVDF/PC with BTEAC exhibited endothermic peaks at 172.4, 171.4, and 169.7°C [Fig. 4(d–f)], respectively. The melting temperatures of all the electrospun PVDF/PC membranes with or without PMMA and BTEAC were about 170°C before and after hot-pressed at 130°C,

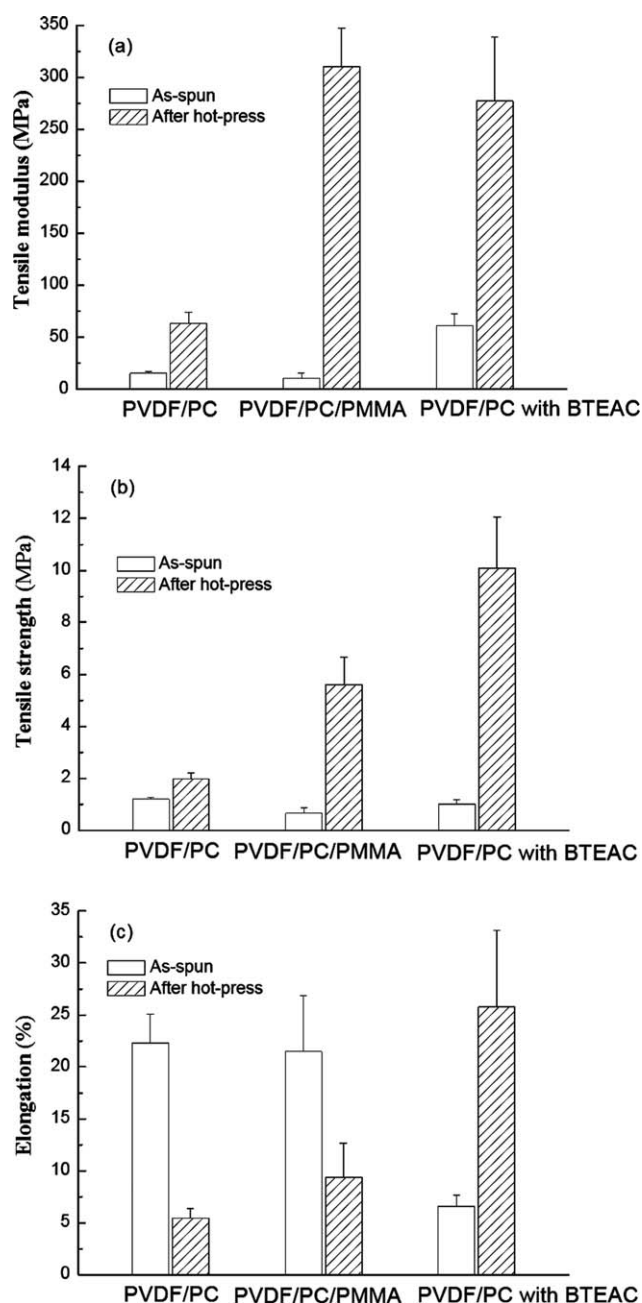
indicating little alternation of PVDF crystallite form in PVDF/PC fibers before and after hot-press.

### Tensile properties

Figure 5 illustrates the tensile properties of the electrospun membranes before and after hot-press. Before hot-press, the tensile modulus of the PVDF/PC membrane was  $15.3 \pm 1.4$  MPa, and with addition of PMMA and BTEAC, the tensile modulus values were  $10.6 \pm 4.5$  MPa and  $61.2 \pm 11.2$  MPa, respectively, [Fig. 5(a)]. The tensile strength of PVDF/PC, PVDF/PC/PMMA, and PVDF/PC with BTEAC were  $1.20 \pm 0.06$  MPa,  $0.65 \pm 0.21$  MPa, and  $1.01 \pm 0.18$  MPa, respectively, [Fig. 5(b)]. After hot-pressed at 130°C, the tensile modulus and tensile strength of the electrospun membranes were sharply enhanced because of the structural perfection improvement of the fibers aggregates after hot-press. The tensile modulus values of the electrospun membranes, PVDF/PC, PVDF/PC/PMMA and PVDF/PC with BTEAC, were increased to  $63.3 \pm 11.2$  MPa,  $310.5 \pm 37.1$  MPa, and  $277.0 \pm 61.3$  MPa, respectively, [Fig. 5(a)], whereas the tensile strengths of the membranes were improved to  $1.99 \pm 0.21$  MPa,  $5.59 \pm 1.06$  MPa, and  $10.19 \pm 1.98$  MPa, respectively, [Fig. 5(b)]. Similar results were detected in our previous work, when the PVDF electrospun membranes were examined before and after hot-press,<sup>17</sup> i.e., when the electrospun PVDF membrane was treated by continuous hot-press, the tensile strength and



**Figure 4** DSC thermograms of the electrospun membranes before (a–c) and after (d–f) hot-press. (a,d) PVDF/PC; (b,e) PVDF/PC/PMMA; (c, f) PVDF/PC with BTEAC.

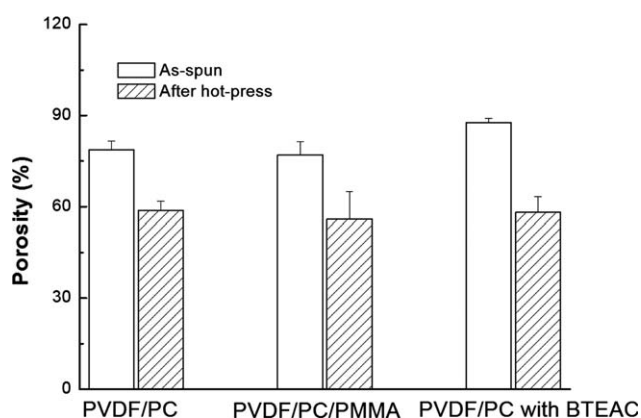


**Figure 5** Tensile properties of the electrospun membranes before and after hot-press. (a) Tensile modulus; (b) tensile strength; (c) elongation.

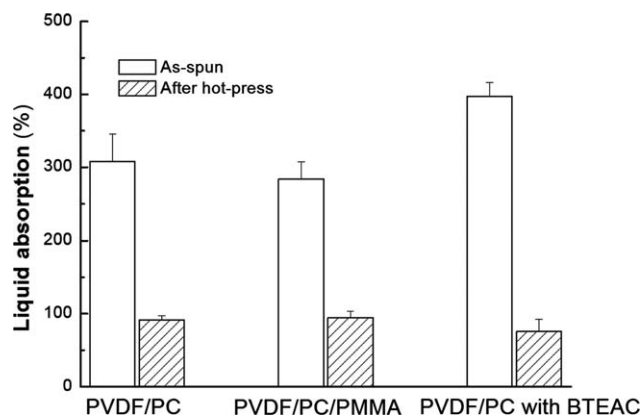
tensile modulus of the membrane were heavily enhanced.

In the present study, significant differences of the tensile modulus and tensile strength between the hot-pressed PVDF/PC electrospun membrane with and without PMMA or BTEAC could be noticed in Figure 5(a,b). When 2 wt % BTEAC was added in PVDF/PC, the tensile strength of the membrane was the highest in all three fibrous membranes. In the case of no significant changes of PVDF crystal structure from FT-IR, XRD, and DSC results, it was assumed that the improvement of tensile modulus

and tensile strength of the electrospun membranes after hot-press owing to the changes of the morphology and microstructure in the electrospun fibers. In our previous work,<sup>17</sup> when the electrospun membrane was treated at a rather high temperature in continuous hot-press, the tensile modulus and tensile strength of the electrospun membranes could be increased because of the merge of electrospun fibers at the cross points. Therefore, after hot-press at 130°C, a few of PVDF/PC/PMMA fibers could be merged at the cross points [Fig. 1(e)], so that the tensile strength and tensile modulus of the hot-pressed PVDF/PC/PMMA membrane was higher than those of the PVDF/PC membrane. However, the merged cross point points might not be the only factor for the improvement of the tensile strength. The tensile strength of the hot-pressed PVDF/PC with BTEAC membrane was  $10.19 \pm 1.98$  MPa, higher than the tensile strength of the PVDF/PC/PMMA membrane ( $5.59 \pm 1.06$  MPa), and there were no merged points in cross section of PVDF/PC with BTEAC fibers. The increase of tensile strength of PVDF/PC with BTEAC membrane was attributed to the formations of distinct core/shell structure. Mukherjee and Satyanarayana<sup>26</sup> had ever established an empirical relationship between the structure and properties of lignocellulosic fibers through computer analysis, and the results showed fracture mode could also be dictated by defect parameter, and the presence of defects in fibers reduced the elongation and thus lead to intercellular fracture irrespective of other structural parameter. More distinct core/shell structure means fewer defects in electrospun fibers, so the distinct core/shell fiber structure was helpful to the physical connection in the ultrafine fiber structure during hot-press, which could be well contributed to the tensile modulus and tensile strength of the electrospun membranes. The more distinct core/shell structure in ultrafine fibers, the higher tensile



**Figure 6** Porosity of the electrospun membranes before and after hot-press.



**Figure 7** Liquid absorption of the electrospun membranes before and after hot-press.

modulus and tensile strengths exhibited in the electrospun membranes.

From Figure 5(c), it could be seen that the elongations of the PVDF/PC membranes with and without PMMA and BTEAC before and after hot-press are different. After hot-press, the enhancement of tensile modulus of the electrospun membranes with PMMA and BTEAC lead to the increase of the stiffness and decrease in the elongation of the PVDF/PC membranes. After addition of 2 wt % BTEAC in the PVDF/PC fibers which lead to small fiber diameter, the elongation decreased from  $22.3 \pm 2.7\%$  to  $6.6 \pm 1.0\%$ . After hot-press, structural perfection of the fibers aggregates was improved, so the elongation of electrospun membranes impacted by the microstructure of electrospun fibers. From the empirical relationship between the structure and properties of lignocellulosic fibers which established by Mukherjee and Satyanarayana,<sup>26</sup> the defects which existed in fibers could reduce the elongation. It could be deduced that the less defected distinct core/shell structured fiber was also helpful to enhance the elongation of the PVDF/PC membrane with BTEAC by the better connection of ultrafine fibers, so the value of elongation reached to  $25.8 \pm 7.4\%$ . The best distinct regular core/shell structure was not only propitious to the tensile strength but also good for the elongation of multi-component membranes.

### Porosity

The porosity of PVDF/PC electrospun membranes with and without PMMA and BTEAC before and after hot-press is exhibited in Figure 6. Before hot-press, the porosity of PVDF/PC and PVDF/PC/PMMA was  $78.7 \pm 2.8\%$  and  $77.0 \pm 4.4\%$ , respectively, without significant differences ( $P = 0.61$ ), but BTEAC addition lead to a higher porosity ( $87.6 \pm 1.4\%$ ) because of the thinner diameter of the ultra-

fine fibers. After hot-press, the thicknesses of PVDF/PC, PVDF/PC/PMMA, and PVDF/PC with BTEAC membranes decreased. It leads to the increase of the apparent density of multi-component electrospun membranes, so that the porosity of all the three PVDF/PC membranes was dropped to around 58%, and there were no significant differences between them ( $P = 0.63$ ).

### Liquid absorption

Figure 7 shows the liquid absorption in diethyl carbonate of the PVDF/PC membrane was  $308 \pm 37\%$ , and after introduction of 15 wt % PMMA, the liquid absorption decreased to  $284 \pm 24\%$  but no significant differences ( $P = 0.37$ ). However, the liquid absorption of the PVDF/PC membrane with BTEAC was  $398 \pm 19\%$ , significantly larger than that of the PVDF/PC membrane ( $P = 0.02$ ). After hot-press, the liquid absorption of the three electrospun membranes was decreased to  $91.0 \pm 6.0\%$ ,  $93.9 \pm 9.0\%$ , and  $75.9 \pm 16.6\%$ , respectively, with no significant differences ( $P = 0.22$ – $0.67$ ). The changes of the liquid absorption of the hot-pressed membranes were related with their porosity, and the liquid absorption of all the three membranes dropped to 75–90%.

### CONCLUSION

Electrospun PVDF/PC ultrafine fibers before and after introduction of PMMA or BTEAC exhibited uniformly fibrous morphology and the morphology of the electrospun fibers was retained in good conditions after hot-press. Similar crystallite form of PVDF was observed in all the electrospun PVDF/PC membranes before and after hot-press. Both the change of morphology and micro-structure of the electrospun fibers were helpful to improve mechanical properties. After hot-press, the tensile strength of the electrospun PVDF/PC membrane with 2 wt % BTEAC highly reached to  $10.1 \pm 2.0$  MPa for the distinct core/shell structured fibers and the connection of PVDF at the fiber junction during hot-press. Core/shell microstructure of the ultrafine fibers did not influence the porosity and liquid absorption of the electrospun PVDF/PC membrane after hot-press.

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