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Formation of core/shell ultrafine fibers of PVDF/PC by electrospinning via introduction of PMMA or BTEAC

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ABSTRACT

Core/shell structured ultrafine fibers of poly(vinylidene fluoride) (PVDF)/polycarbonate (PC) were prepared by electrospinning their dispersions in a mixed solvent of *N*,*N*-dimethylformamide and tetrahydrofuran. The morphology of the obtained fibers viewed under a scanning electron microscope and a transmission electron microscope could be adjusted via introduction of poly(methyl methacrylate) (PMMA) or triethylammonium chloride (BTEAC). The viscosity of the dispersions increased with the increasing amount of PMMA in the range of 10–15 wt%, while the diameter of the dispersive spherical phase in the dispersions decreased. A proper amount of PMMA could decrease the resistance of the dispersive phase transformation in PVDF/PC dispersions, so that the uniform fibrous morphology and distinct core/shell structure were easily formed in the electrospun fibers. Because of the significant increase of the conductivity of the PVDF/PC dispersion, addition of 2 wt% BTEAC could also promote formation of the core/shell structure of electrospun PVDF/PC ultrafine fibers. Comparison between electrospun fibers of PVDF/PC, PVDF/PC/PMMA and PVDF/PC with BTEAC etched by chloroform showed that the core/shell structure of PVDF/PC with BTEAC was in the highest quality.

1. Introduction

Electrospinning process has been studied as an effective method to produce ultrafine fiber from polymer solutions or melts under a high electric voltage [1–12]. In recent years, different approaches have been reported to produce ultrafine fibers with two or more components, such as polymer/inorganic composite fibers or polymer blends [13–17]. Particularly, by means of electrospinning from the dispersion of polymer blends, core/shell ultrafine fibers could be prepared [18]. Also novel functional potential applications could be expected for the electrospun fibers with the particular microstructure in extensive applications such as filtration systems [19] and sensors [20]. Wei et al. [21,22] had studied that some dispersions of polymer blends, for instance polybutadiene (PB)/polycarbonate (PC) and PB/poly(methyl methacrylate) (PMMA), could be employed to fabricate core/shell ultrafine fibers by electrospinning. The researches demonstrated that formation of core/shell structure was proof to be correlative with the category, composition, and compatibility of polymers in dispersion [21,22]. However, owing to some factors, the fabrication of core/shell electrospun fibers would be only prepared by a few appropriate multi-polymer dispersions. In the other words, the core/shell structured fiber could be fabricated by electrospinning from multi-polymer dispersions with special properties [22].

Previous references had reported [23–26] that a third component was often introduced to the blended system in order to modify properties of the binary polymer blend. For example, PMMA could be added into the PC/poly(vinylidene fluoride) (PVDF) blend via melting as a compatibilizer to improve the interface adhesive in the obtained product [23,24]. However, the method to prepared core/shell structured ultrafine fibers by introducing an appropriate third component in the blended dispersions for electrospinning was not reported previously.

In this paper, PMMA and triethylammonium chloride (BTEAC) as the third component were added into the PVDF/PC dispersion, respectively. The effect of PMMA and BTEAC on electrospinning of PVDF/PC dispersions was analyzed by evaluating the properties of the multi-polymer dispersions and the morphology of the electrospun fibers. Comparison between the influences of the two third-components on the electrospun dispersions was also discussed.

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2. Experimental methods

2.1. Materials

PVDF with weight-average relative molecular mass of $3.5–4.0 \times 10^5$, was purchased from Kureha Chemical Industry (Japan). PC was supplied from General Electric Company (USA), and its weight-average relative molecular mass of 3.1×10^4 was determined by Gel Permeation Chromatography. PMMA with relative molecular mass of 3.5×10^4, Ruthenium tetroxide (RuO_4) in 0.5% aqueous solution, and BTEAC were collected from Aldrich. *N*,*N*-dimethylformamide (DMF), tetrahydrofuran (THF), and chloroform ($CHCl_3$) were solvents in chemical grade. All the reagents were used as-received.

2.2. Preparation of dispersions

PC was dissolved in a mixture solvent of DMF and THF. After that, a certain amount of PMMA or BTEAC was added into the solution under stirring at 30–45 °C for about 1 h until the PC transparent solution was formed. Meanwhile PVDF was dissolved in DMF at 30–45 °C to obtain PVDF transparent solution. And then the PC solution was dropped into the PVDF solution under stirring. The contents of polymers and solvents were separately controlled in multi-polymer dispersions as shown in Table 1. All the dispersions were kept stirring for another 1 h, finally uniform milk-like dispersions could be obtained.

The dispersions were observed under an optical microscope (OM, BX51, Japan), and the diameter of dispersive spherical phase in the OM micrographs were measured by Photoshop 9.0 to calculate the average diameter of the dispersive phase. The viscosity and surface tension of the dispersions were characterized by rotary rheometer (Stress Tech Fluids Rheometer, Stress Tech, Sweden) and a tensiometer (Data Physics, DCAT21, German) in the Wilhelmy plate method at 25 °C, respectively. The conductivity of the dispersions was measured by a conductivity instrument (DDS-11A, Shanghai, China) at room temperature.

2.3. Electrospinning

All the dispersions were used to electrospinning directly. The electrospinning setup included syringe pump, high-voltage power supply, and collector as shown in our previous paper [27]. 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 ultrafine fibers were electrospun at 12 kV voltage, 0.4 mL/h flow rate, and 15 cm capillary-collector distance. The electrospun fibers were collected on a custom-made rotating roller collector wrapped by flat aluminum foil connected to ground.

The morphology of the electrospun fibers was characterized under scanning electron microscope (SEM, Philips XL-30, the Netherlands) after gold coating. The micro-structure of the ultrafine fibers was observed using a transmission electron microscope (TEM, JEM-100CX II, Japan). For the preparation of TEM samples, the nanofibers were collected on a carbon-coated copper grid, followed by staining in RuO_4 vapor by suspending them over 0.5% RuO_4 water solution.

2.4. Etching of electrospun membranes

Electrospun membranes prepared from corresponding dispersions were dried in *vacuo* at 45–55 °C for 12 h, and then cut into square with dimensions of 20 mm × 20 mm. The square samples were accurately weighed in an electronic balance (Model BS 210S, Beijing, China) and then immerged in $CHCl_3$ for 1–2 h. After the samples were taken out of $CHCl_3$ and dried, they were weighted again. The mass loss of the electrospun membranes were calculated using the following equation:

$$\text{Mass loss}(\%) = \frac{m_b - m_a}{m_b} \times 100\% \tag{1}$$

where m_b and m_a are the masses of the membranes before and after etched in the $CHCl_3$, respectively.

Table 1
Compositions and properties of the PVDF/PC dispersions for electrospinning.

Sample No.	PVDF/PC (wt/wt)	DMF/THF (v/v)	Polymer concentration (g/mL)	PMMA (wt%)	BTEAC (wt%)	Conductivity (μ/cm)	Surface tension (mN/m)	Viscosity [a] (Pa·s)
A-1[b]	7/3	7/3	0.18	0	–	0.87	35.03	0.78
A-2	7/3	7/3	0.18	5	–	1.96	–	0.84
A-3	7/3	7/3	0.18	10	–	1.38	–	0.88
A-4	7/3	7/3	0.18	15	–	1.26	34.56	0.93
A-5	7/3	7/3	0.18	20	–	0.78	–	0.95
B-1[c]	9/1	7/3	0.18	0	–	0.64	34.83	1.31
B-2	8/2	7/3	0.18	0	–	0.62	35.08	1.20
B-3	7/3	7/3	0.18	0	–	0.87	35.03	0.78
B-4	6/4	7/3	0.18	0	–	0.93	34.83	0.60
C-1[d]	9/1	7/3	0.18	15	–	0.88	34.71	1.58
C-2	8/2	7/3	0.18	15	–	0.88	34.67	1.23
C-3	7/3	7/3	0.18	15	–	1.26	34.56	0.93
C-4	6/4	7/3	0.18	15	–	1.03	34.46	0.77
D-1[e]	7/3	7/3	0.10	–	0	1.48	34.55	0.12
D-2	7/3	7/3	0.14	–	0	0.97	34.93	0.34
D-3	7/3	7/3	0.18	–	0	0.87	35.03	0.78
E-1[f]	7/3	7/3	0.10	–	2	216.5	34.64	0.12
E-2	7/3	7/3	0.14	–	2	231.5	34.88	0.37
E-3	7/3	7/3	0.18	–	2	259.5	34.87	0.77

[a] Viscosity: values at 65 s^{-1} shear rate.
[b] Group A: PMMA ($\overline{M}_w = 3.5 \times 10^4$).
[c] Group B: PVDF/PC mass ratio.
[d] Group C: PMMA 15 wt%, PVDF/PC mass ratio.
[e] Group D: polymer concentration.
[f] Group E: BTEAC.

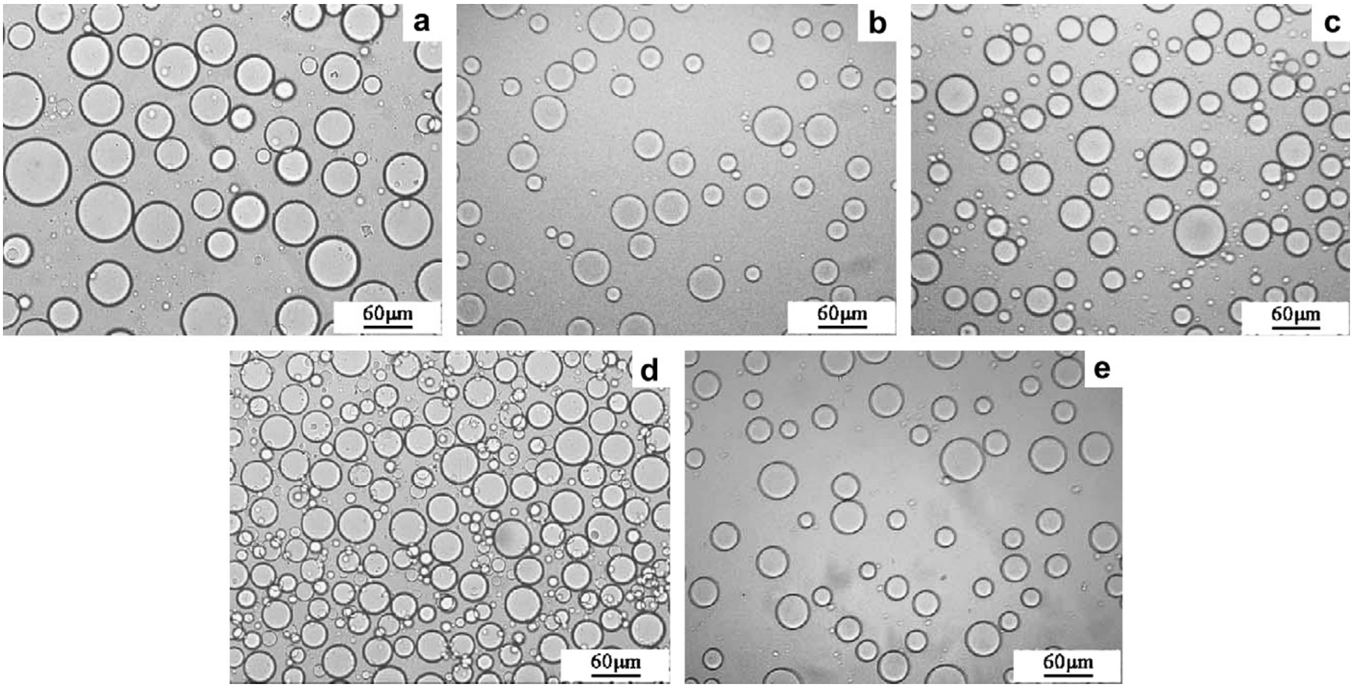

Fig. 1. Optical micrographs of PVDF/PC dispersions with different PMMA contents of 0 wt% (a), 5 wt% (b), 10 wt% (c), 15 wt% (d), and 20 wt% (e), respectively.

SEM, TEM, and Fourier transformed infrared spectroscopy (FT-IR, Perkin Elmer, Spectrum 100, USA) were carried out to evaluating the electrospun membranes before and after etched in $CHCl_3$, respectively. Specially, in order to observe the cross-section morphology, the electrospun fibers was swiftly cut off by a sharp slice and soaked in $CHCl_3$ for 1–2 h. The dried sample which were taken out of $CHCl_3$ and after gold-coated was viewed under a Field Emission SEM (FEI, NOVA NanoSEM 430, USA).

3. Results and discussions

3.1. PVDF/PC/PMMA dispersions

PMMA is compatible with both PVDF and PC [23]. When PMMA was introduced into PVDF/PC dispersion, the properties of the dispersion would be expected to change. Fig. 1 shows optical micrographs of PVDF/PC dispersions for electrospinning with different PMMA contents. Similar dispersive spheral phase was shown in PVDF/PC dispersion before and after introduced PMMA. There were many dispersive spheres existing in the heterogeneous milk-like dispersions owing to the incompatibility of PVDF and PC. Before PMMA was used, the diameter of the dispersive phase was 44.8 ± 14.5 μm, but the diameters of dispersive phase descended to 27.5 ± 9.9 μm, 25.5 ± 12.1 μm, 25.0 ± 11.9 μm, and 24.9 ± 11.2 μm with the increasing order of PMMA content from 5 to 20 wt%, respectively. Feng et al. [23] had reported, when PMMA was used as a compatibilizer to the PVDF/PC blend, the volume of dispersive phase decreased distinctly, which could be the reason that the diameters of dispersive phase in the present PVDF/PC/PMMA dispersion reduced. The viscosity and conductivity of the PVDF/PC

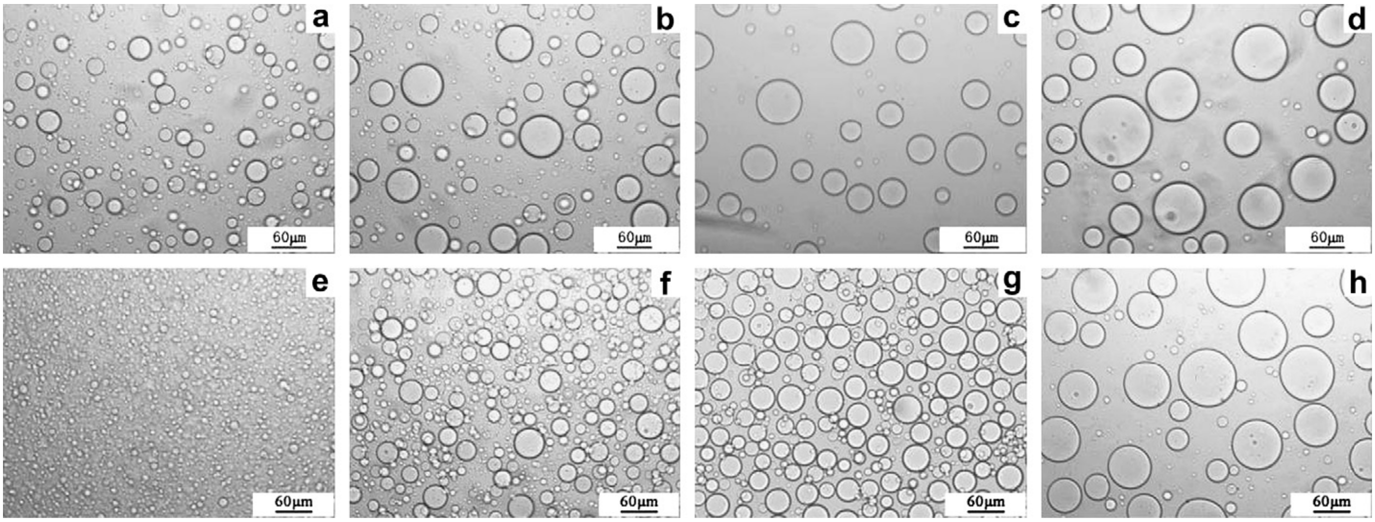

Fig. 2. Optical micrographs of dispersions with different PVDF/PC mass rations of 9/1 (a,e), 8/2 (b,f), 7/3 (c,g), 6/4 (d,h) without PMMA (a–d) and with 15 wt% PMMA (e–h), respectively.

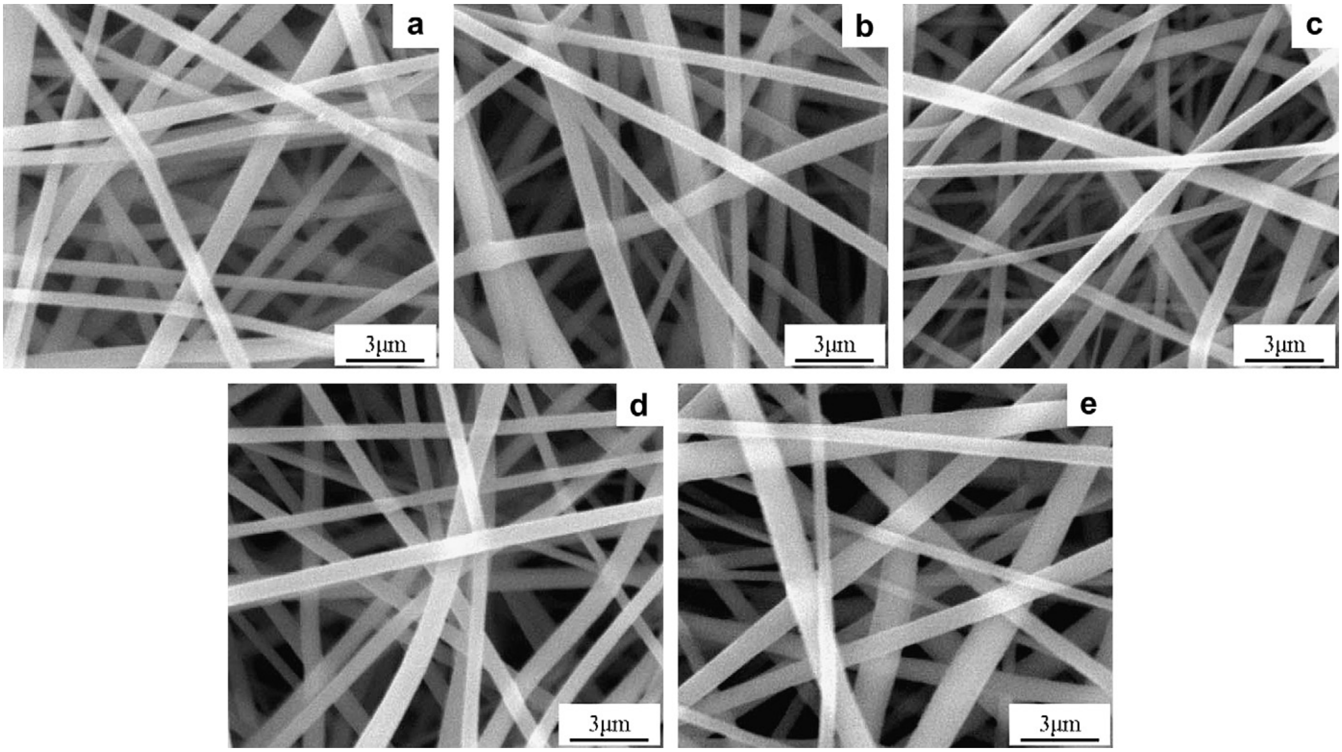

Fig. 3. SEM micrographs of electrospun PVDF/PC fibers with PMMA contents of 0 wt% (a), 5 wt% (b), 10 wt% (c), 15 wt% (d), and 20 wt% (e), respectively.

dispersions with 0–20 wt% PMMA were illustrated in Table 1 (Group A). With the increase of the PMMA content, the viscosities of the dispersions enhanced gradually. According to the scaling theory of de Gennes [28], the higher concentration of polymer solution possessed, the larger viscosity would be exhibited. So, the viscosity of PVDF/PC/PMMA dispersions increased gradually from 0.78 to 0.95 Pa s when 5–20 wt% PMMA were introduced. But the conductivities of the PVDF/PC/PMMA dispersions were lower than 2 μS/cm, due to the relatively weak conductive polymers and solvents in the dispersions.

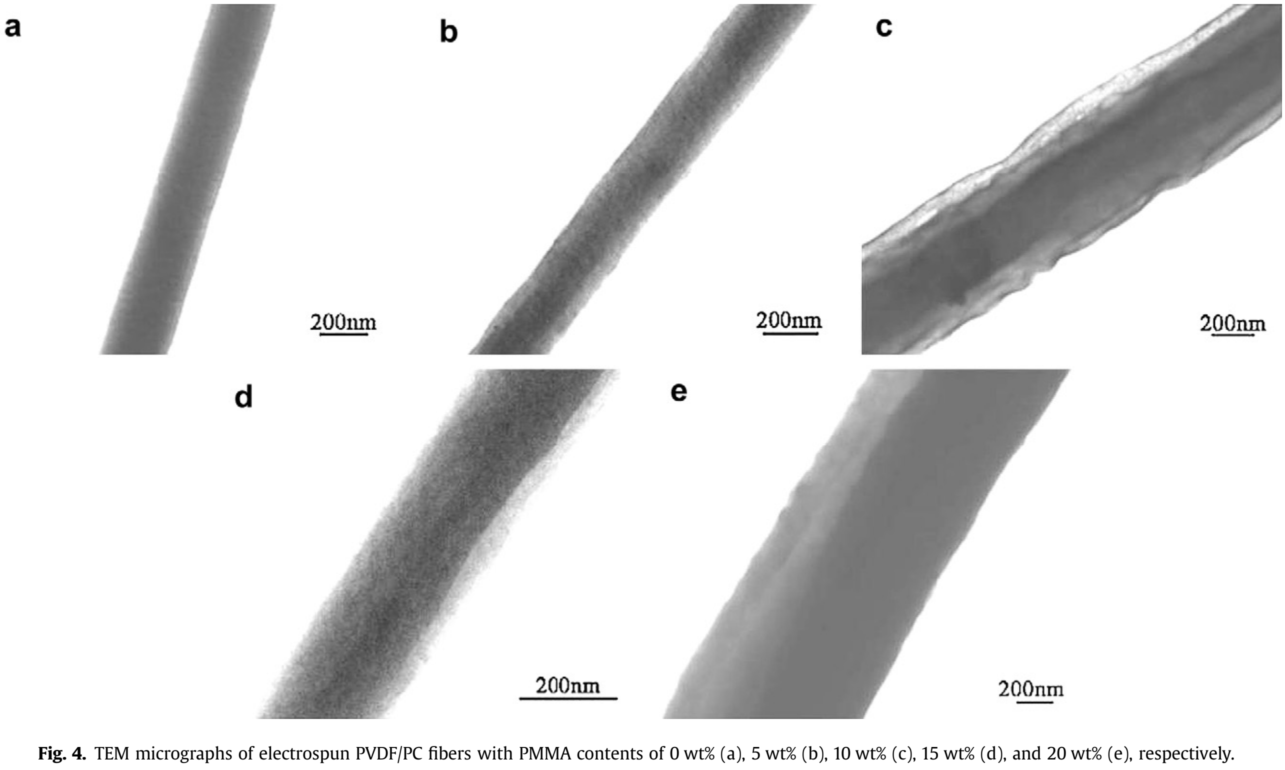

Fig. 4. TEM micrographs of electrospun PVDF/PC fibers with PMMA contents of 0 wt% (a), 5 wt% (b), 10 wt% (c), 15 wt% (d), and 20 wt% (e), respectively.

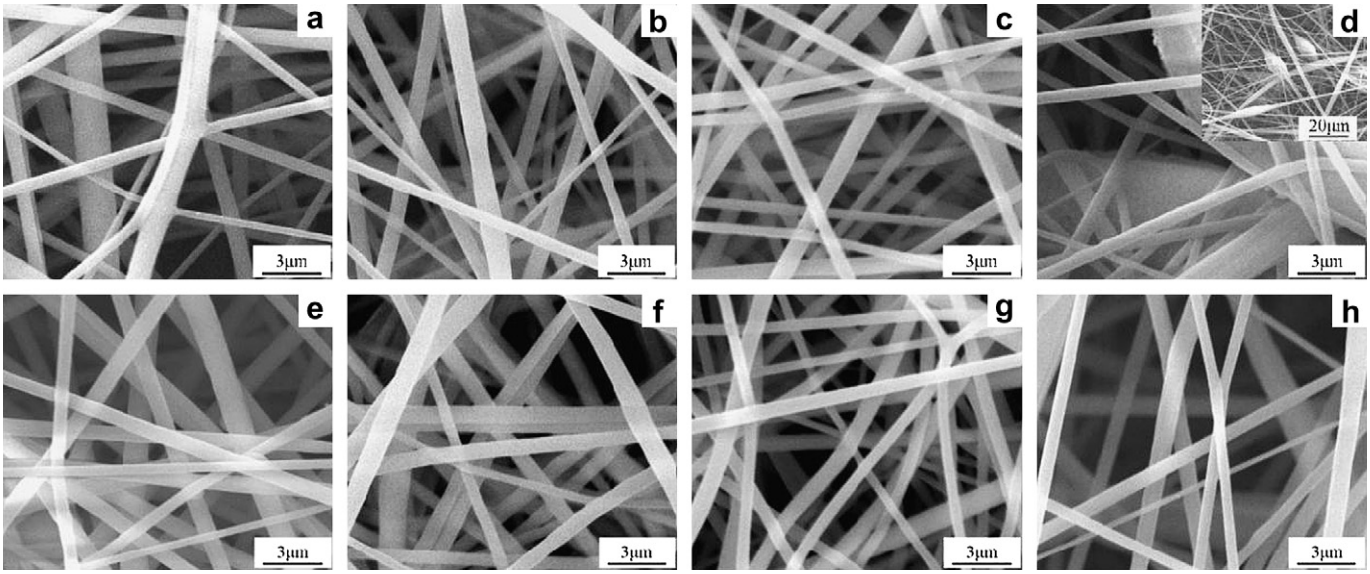

Fig. 5. SEM micrographs of electrospun fibers at different PVDF/PC mass ratios of 9/1 (a,e), 8/2 (b,f), 7/3 (c,g), 6/4 (d,h) without PMMA (a, b, c, d) or with 15 wt% PMMA (e, f, g, h), respectively.

Optical micrographs of electrospun dispersions with different PVDF/PC mass ratios are shown in Fig. 2. Dispersive spheres in the dispersions were formed and the diameters of the spheral phase were 15.4 ± 8.8 μm, 28.5 ± 18.8 μm, 36.4 ± 18.1 μm, and 52.0 ± 31.8 μm in accord with PVDF/PC mass ratios of 9/1, 8/2, 7/3, and 6/4, respectively [Fig. 2(a–d)]. After plunged 15 wt% PMMA into the PVDF/PC dispersion, the diameters of the dispersive phase were deceased distinctly to 3.6 ± 3.1 μm, 19.0 ± 11.1 μm, 26.1 ± 11.1 μm, and 48.3 ± 25.7 μm, respectively [Fig. 2(e–h)]. The viscosity, surface tension and conductivity were collected in Table 1 (Groups B and C). With the amount of PC increased, the viscosities of PVDF/PC and PVDF/PC/PMMA dispersions decreased. It may be due to the hindered entanglement ability of PC chain because of its chain rigidity, and result in lower viscosities of the dispersions. No matter what the mass ratio of PVDF/PC was, the surface tensions and conductivities of both PVDF/PC and PVDF/PC/PMMA dispersions did not change significantly. The surface tensions were around 34.5–35.0 mN/m and the conductivities were lower than 2 μS/cm.

3.2. *PVDF/PC/PMMA electrospun fibers*

Uniform electrospun PVDF/PC fibers with different PMMA contents could be obtained in electrospinning [Fig. 3], and the diameters of electrospun fibers were among 200–800 nm. Different PMMA contents could lead to different micro-structures in PVDF/PC electrospun fibers [Fig. 4]. Because all the fibers were stained by RuO_4 vapor before TEM observation, PC phase has been stained preferentially [21]. Therefore, the dark regions in the TEM micrographs of the ultrafine fibers were identified as PC while the light regions were PVDF or PMMA. Core/shell structure could be observed in these

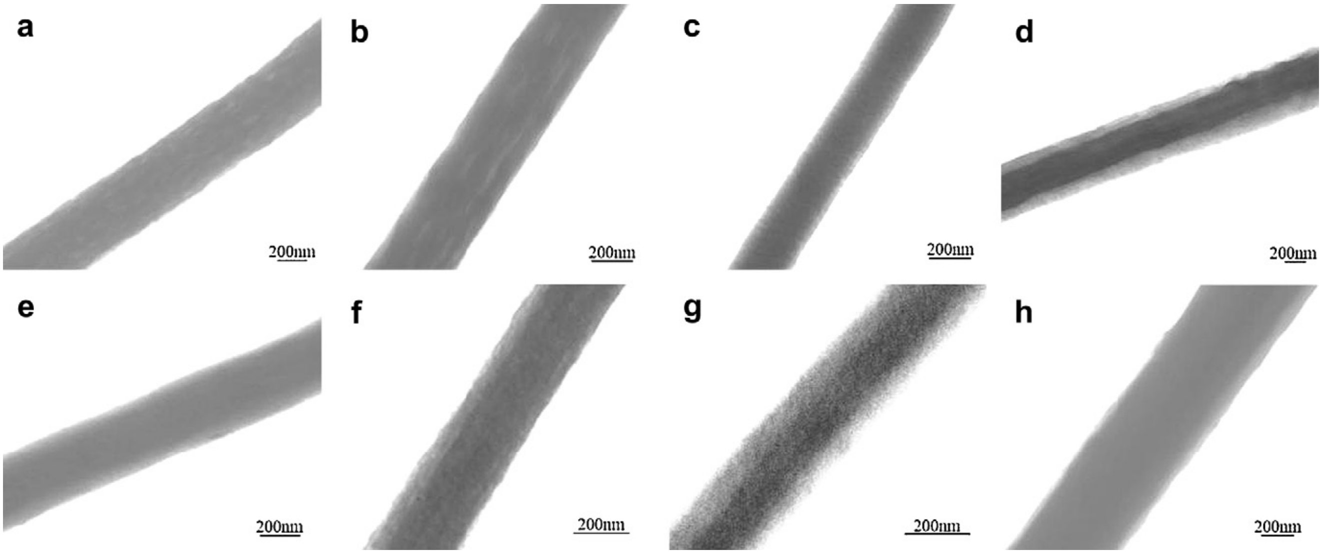

Fig. 6. TEM micrographs of electrospun fibers at different PVDF/PC mass ratios of 9/1 (a,e), 8/2 (b,f), 7/3 (c,g), 6/4 (d,h) without PMMA (a, b, c, d) or with 15 wt% PMMA (e, f, g, h), respectively.

Table 2
Comparison of the dispersive phase diameter of PVDF/PC dispersions with and without PMMA.

PVDF/PC (wt/wt)	Diameter of the dispersed phase (μm)	
	PVDF/PC	PVDF/PC/PMMA
9:1	15.4 ± 8.8	3.6 ± 3.1
8:2	28.5 ± 18.8	19.0 ± 11.1
7:3	36.4 ± 18.1	26.1 ± 11.1
6:4	52.0 ± 31.8	48.3 ± 25.7

electrospun fibers, but core/shell structure was not obvious for the sample without PMMA, and the boundary between the core and shell of the electrospun fiber was ambiguous [Fig. 4(a)]. When 5–15 wt% PMMA was added for fabricating PVDF/PC fibers, distinct core/shell structure appeared in PVDF/PC fibers, and the boundary between the core and shell of the fiber became more obvious with increasing the PMMA content [Fig. 4(b–d)]. However, when the PMMA content was improved to 20 wt%, side-by-side structure was formed [Fig. 4(e)].

Xu et al. [29] fabricated core/shell ultrafine fiber by electrospinning heterogeneous poly(ethylene oxide)/poly(ethylene glycol)-poly(L-lactic acid) emulsion. The mechanism was the inward movement of dispersive emulsion droplets that might be caused by rapid elongation and quick evaporation of the solvents during electrospinning. Similarly in the electrospinning process of the heterogeneous PVDF/PC/PMMA dispersions, the dispersive spheral phase could be transferred into the center of ultrafine fibers and form the core. In this process, the resistance of the dispersive phase transformation could be described by Stokes law [30], which could be ascertained by following equation:

$$f = -6\pi\eta r v \qquad (2)$$

where η is the viscosity of the continuous phase; r is radius of sphere; v is the velocity when the sphere pass through the viscous liquid; the minus is presented the direction of resistance is opposite to and movement of the small spheres.

Under the same electrospun condition, the transformed velocity of dispersive spheral phase would keep consistent. So the value of transformed resistance between the dispersive phase and continuous phase could be controlled by the diameter of the dispersive phase and the viscosity of the dispersion. When PMMA was introduced to the PVDF/PC dispersion, the diameters of dispersive spheral phase decreased by 0.56–0.61 times compared with which before PMMA addition, meanwhile the viscosity increased by 1.08–1.22 times. That could be calculated by the Eq. (2), with additions of 5–20 wt% PMMA, the resistance of the dispersive phase transformation dropped to 0.60–0.74 times. So PMMA could be used to decrease the resistance of the dispersive phase transformation and enhance the ability of transformation, which was helpful to the core/shell structure formation in PVDF/PC/PMMA fibers. More distinct core/shell structured ultrafine fiber could be fabricated in electrospinning with 5–15 wt% PMMA additions. However, 20 wt% PMMA in PVDF/PC dispersion would result in higher viscosity and might hinder the transformation of dispersive spheral phase, and side-by-side structure fiber was formed in electrospinning.

In order to evaluate the accelerating effect on the formation of core/shell structure of PVDF/PC dispersions, a certain amount PMMA was added in the PVDF/PC dispersion with different mass ratios. Fig. 5 shows SEM micrographs of electrospun fibers with different PVDF/PC mass ratios before and after PMMA addition. When the mass ratio of PVDF and PC was set as 9/1 to 7/3, uniform ultrafine fibers could be prepared [Fig. 5(a–c)]. But, if the PVDF/PC was equal to 6/4, only thread and bead PVDF/PC morphology could be found due to the weaker entanglement of PC chain [Fig. 5(d)]. According to the theory of chain entanglement in semidilute and concentrated polymer solution of Colby et al. [31,32], the more polymer existed in the solution, the higher ability of polymer chain entanglement could exhibit between polymers. Also McKee et al. had reported that high entanglement of polymer chain was helpful to fabricate the uniform fiber during electrospinning [33]. So with the PMMA addition, there was more polymer existed in PVDF/PC/PMMA dispersions, which could enhance the ability of polymer

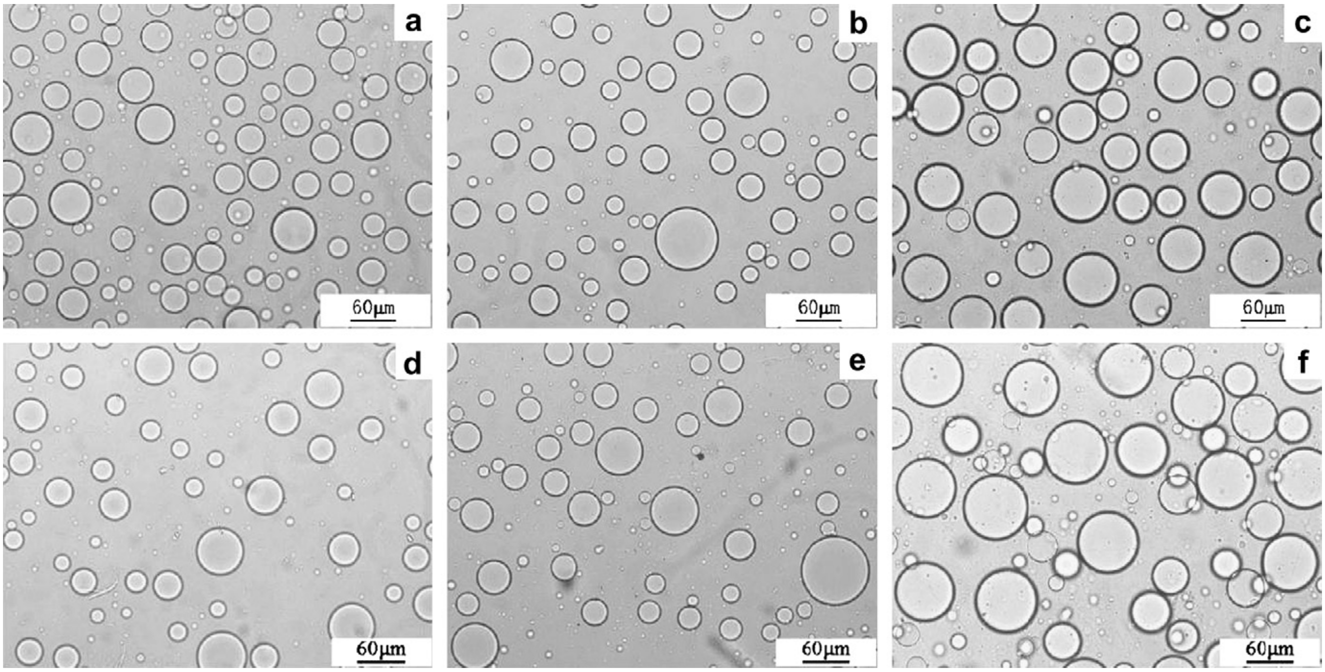

Fig. 7. Optical micrographs of PVDF/PC dispersions at different polymer concentrations of 0.10 g/mL (a, d), 0.14 g/mL (b, e), 0.18 g/mL (c, f) without BTEAC (a, b, c) or with 2 wt% BTEAC (d, e, f), respectively.

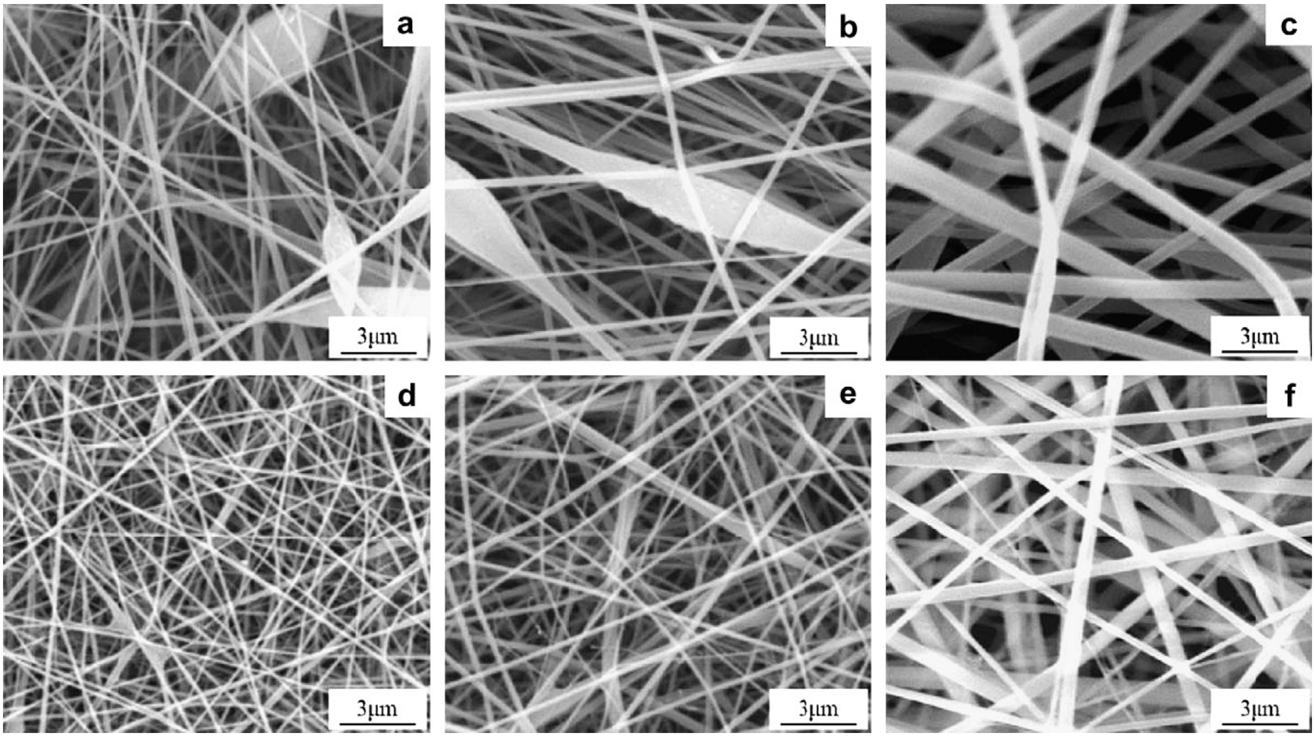

Fig. 8. SEM micrographs of electrospun PVDF/PC fibers at different polymer concentrations of 0.10 g/mL (a, d), 0.14 g/mL (b, e), 0.18 g/mL (c, f) without BTEAC (a, b, c) or with 2 wt% BTEAC (d, e, f), respectively.

chain entanglement in dispersion, so as to the ultrafine fibers could be easily formed in electrospinning.

TEM micrographs of electrospun fibers at different PVDF/PC mass ratios with and without PMMA are exhibited in Fig. 6. Without PMMA, when the mass ratio between PVDF and PC was 9/1 or 8/2, only co-continuous structured fiber could be produced. By improving the amount of PC to PVDF/PC = 7/3, ambiguous core/shell structure and less evident boundary between the core and shell generated in electrospun fiber. Until the mass ratio of PVDF and PC descended to 6/4, an obvious core/shell structure and a distinct

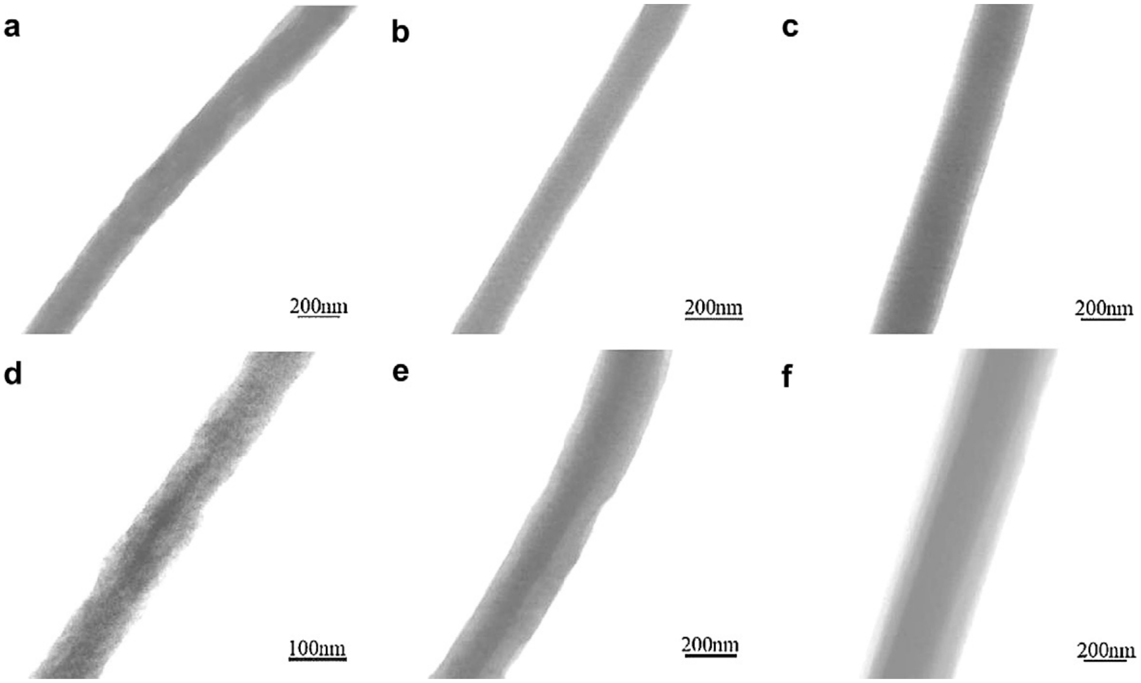

Fig. 9. TEM micrographs of electrospun PVDF/PC fibers at different concentrations of 0.10 g/mL (a, d), 0.14 g/mL (b, e), 0.18 g/mL (c, f) without BTEAC (a, b, c) or with 2 wt% BTEAC (d, e, f), respectively.

boundary between the core and shell could be found in the ultrafine fibers. After PMMA addition, the situation of the micro-structure in the electrospun fibers was different. When PVDF/PC was 9/1 to 6/4, core/shell structured fiber could easily be fabricated, and if PVDF/PC = 8/2 or 7/3, the core/shell structure was rather distinct.

Comparison of the dispersive phase diameter of PVDF/PC electrospun dispersions with and without PMMA (Table 2), the diameters of dispersive spheral phase decreased by 0.23–0.93 times with PMMA addition and the viscosities increased by 1.21–1.28 times [Table 1, Groups B and C]. According to the Eq. (2), the resistance of the dispersive phase transformation was 0.28, 0.69, 0.87, and 1.19 times after PMMA addition in accord with PVDF/PC = 9/1, 8/2, 7/3, and 6/4, respectively. So, as the PVDF/PC mass ratio was 9/1 to 7/3, the core/shell structure of PVDF/PC/PMMA fibers appeared. But, when the PVDF/PC was 6/4, the core/shell structure of the ultrafine fiber was conversed to amorphous. All the results showed that suitable amount PMMA could decrease the resistance and enhanced the ability of the dispersive phase transformation in PVDF/PC dispersions, which could accelerate the formation of core/shell structured ultrafine fibers during electrospinning.

3.3. PVDF/PC dispersions with BTEAC

Optical micrographs of PVDF/PC dispersion at different polymer concentrations with and without BTEAC are illustrated in Fig. 7. When the polymer concentration enhanced from 0.10 g/mL to 0.18 g/mL, the diameter of dispersive spheral phase increased gradually [Fig. 7(a–c)]. There was a slight discrepancy in the diameter of the spheral phase after addition of 2 wt% BTEAC in PVDF/PC dispersion [Fig. 7(d–f)]. The viscosity, surface tension, and conductivity of the dispersions with or without BTEAC are shown in Table 1 (Groups D and E). With 0.10–0.18 g/mL concentrations, the viscosity and surface tension of the PVDF/PC dispersions nearly kept invariable before and after BTEAC addition. But the conductivity of the PVDF/PC dispersion with BTEAC was increased drastically, which was over 200 μS/cm.

3.4. PVDF/PC ultrafine fibers with BTEAC

At relatively lower polymer concentration of PVDF/PC dispersion (0.10–0.14 g/mL), bead and thread was produced during electrospinning [Fig. 8(a, b)]. After adding BTEAC into PVDF/PC

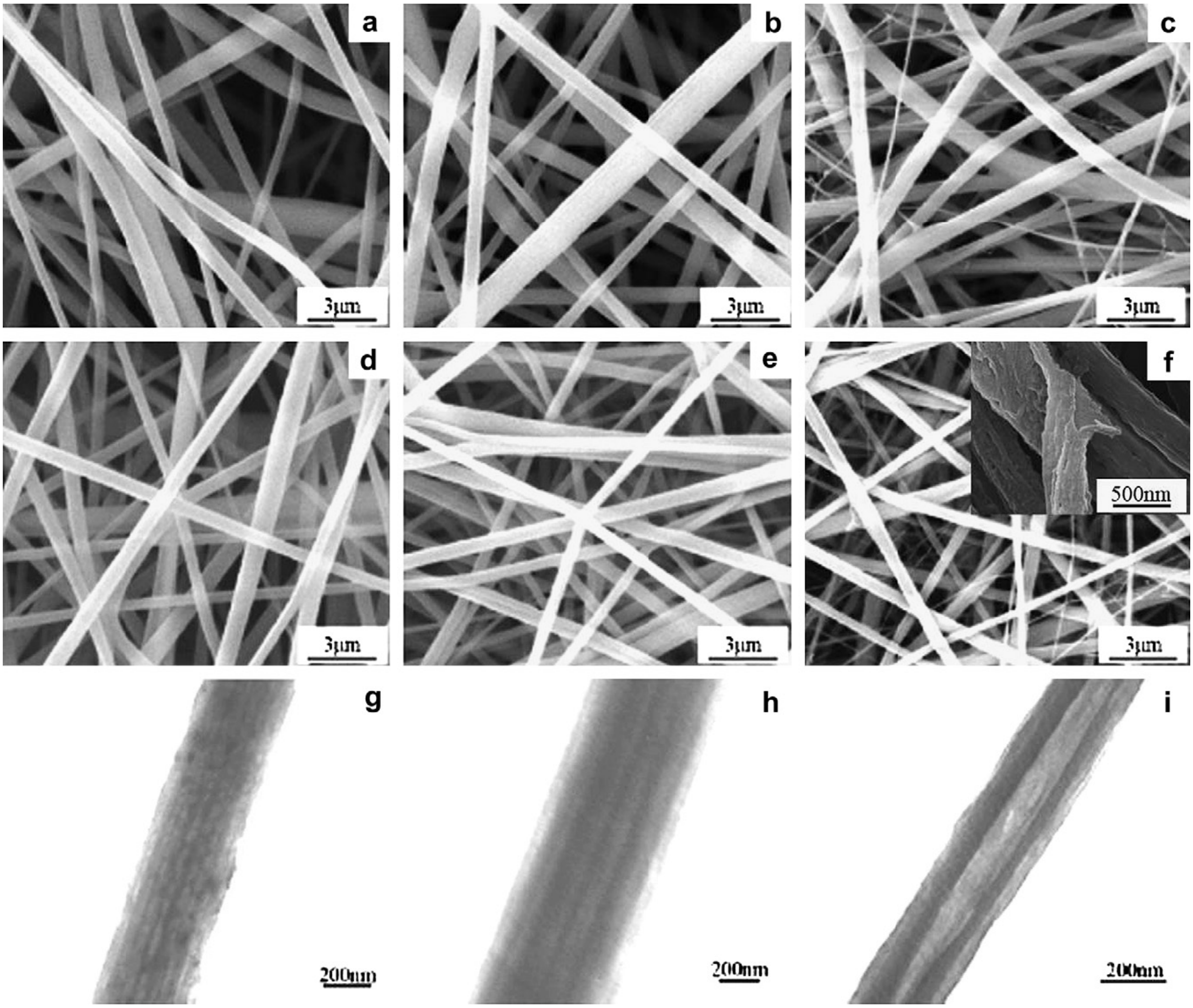

Fig. 10. SEM and TEM micrographs of electrospun fibers before (a, b, c) and after etched in $CHCl_3$ (d, e, f, g, h, i), respectively. (a, d, g) PVDF/PC; (b, e, h) PVDF/PC/PMMA; (c, f, i) PVDF/PC with BTEAC.

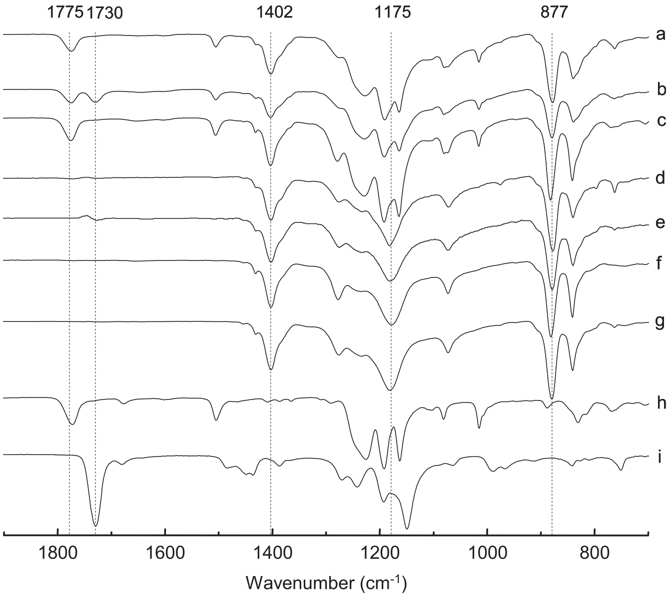

Fig. 11. FT-IR spectra of electrospun membranes before (a, b, c) and after etched in $CHCl_3$ (d, e, f), respectively. (a, d) PVDF/PC; (b, e) PVDF/PC/PMMA; (c, f) PVDF/PC with BTEAC; (g) PVDF; (h) PC; (i) PMMA.

dispersions, uniform fibers were prepared [Fig. 8(d, e)]. The addition of BTEAC could result in a higher charge density on the surface of ejected jet during spinning, thus more electric charges were carried by the electrospinning jet. The overall tension in the fibers depends on the self-repulsion of the excess charges on the jet, which would induce spindle-like thread change into uniform fiber. Similar conclusion could be drown from the investigation of Kim et al. during electrospinning of polycarbonate (PC) in chloroform solution with BTEAC [34].

Fig. 9 shows the TEM micrographs of electrospun PVDF/PC fibers at different polymer concentrations with and without BTEAC. Before introduction of BTEAC into the PVDF/PC dispersion, only ambiguous core/shell structure could be observed in PVDF/PC fibers [Fig. 9(a–c)]. After BTEAC addition, the distinct core/shell structure was found in PVDF/PC fibers at 0.14–0.18 g/mL concentrations, and the boundary between the core and shell of the fiber became more obvious. It is known that salt ions with smaller atomic radius have a higher charge density and thus a higher mobility under an external electric field [35,36]. The addition of BTEAC in PVDF/PC dispersion could accelerate the ability of dispersive phase transformation with charges in electrospinning, which was beneficial to the core/shell structure formation of the PVDF/PC ultrafine fibers.

3.5. *Comparison of PMMA and BTEAC*

The mass loss of electrospun PVDF/PC, PVDF/PC/PMMA, and PVDF/PC with BTEAC membranes after etched by $CHCl_3$, which were calculated by Eq. (1), were $27.8 \pm 0.6\%$, $37.0 \pm 1.0\%$, and $29.8 \pm 0.9\%$, respectively. In comparison with theoretical values of mass loss calculated from raw material ratio for each electrospun membrane, the practical mass losses were only a little lower than the theoretical data (30.0%, 39.1%, and 31.4%, respectively). Also the SEM morphology of PVDF/PC, PVDF/PC/PMMA, and PVDF/PC with BTEAC fibers was not changed a lot before and after etched in $CHCl_3$ [Fig. 10(a–f)].

FT-IR spectra of electrospun membranes are shown in Fig. 11. The strong peaks at 1402 cm^{-1}, 1175 cm^{-1} and 844 cm^{-1} appeared in PVDF fibrous membranes were the characteristic band of PVDF [Fig. 11(g)], and the band at 1175 cm^{-1} was attributed to the C–F stretching vibration. Fig. 11(h) showed strong peaks at 1755 cm^{-1} and 1233 cm^{-1} assigned to the C═O stretching vibration and the C–O stretching vibration, respectively. The electrospun PMMA membrane exhibited a strong peak at 1730 cm^{-1} in Fig. 11(i), that could be decided as the C═O stretching vibration in PMMA. After etched in $CHCl_3$, there were not appeared any peak at 1775 cm^{-1}, 1730 cm^{-1} or 1233 cm^{-1} in PVDF/PC, PVDF/PC/PMMA, and PVDF/PC with BTEAC membranes [Fig. 11(d–f)]. The results exhibited that PC and PMMA in the electrospun PVDF/PC, PVDF/PC/PMMA, and PVDF/PC with BTEAC membrane were all etched by $CHCl_3$.

Fig. 10(g–i) shows the TEM micrographs of electrospun PVDF/PC, PVDF/PC/PMMA, and PVDF/PC with BTEAC fibers after etched by $CHCl_3$. The black color in the center of ultrafine fibers became light, and also PVDF/PC with BTEAC fiber formed obvious cavity structure. The cross sectional SEM micrographs of electrospun PVDF/PC with BTEAC membrane after etched in $CHCl_3$ was indicated in the inset of Fig. 10(f). After etched in $CHCl_3$, an obvious hollow structure was exhibited in the ultrafine fiber, that was shown a specific core/shell which had already been produced in the fibers formation during the electrospinning. Due to the cutting process used to prepare the sample by a sharp slice, unsmooth cross surface was formed in the rupture section of the fiber.

All the results indicated that core/shell structured ultrafine fibers could be prepared by electrospun PVDF/PC, PVDF/PC/PMMA, and PVDF/PC with BTEAC dispersions, and the core/shell structure of PVDF/PC with BTEAC fiber was of the highest quality.

4. Conclusions

The core/shell structured PVDF/PC ultrafine fiber could be prepared by electrospinning of PVDF/PC dispersed solutions. When PMMA were added into the PVDF/PC dispersion, the diameter of dispersive spheral phase decreased obviously. The resistance of the dispersive phase transformation in PVDF/PC dispersions decreased, and also the ability of dispersive phase transformation could improve in electrospinning with an appropriate PMMA content. When 10–15 wt% of PMMA were used, uniform fibrous morphology and distinct core/shell structure ultrafine fibers could be fabricated, and the boundary between core and shell of the fiber was rather obvious. After addition of 2 wt% BTEAC into the PVDF/PC dispersions with polymer concentrations of 0.14–0.18 g/mL, the ability of dispersive phase transformation with charges could be enhanced in electrospinning, therefore electrospun fibers with uniform morphology and distinct core/shell structure could easily be formed.

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