

## Study on the preparation of hyperbranched polyethylene fibers and hyperbranched polyethylene composite fibers via electrospinning

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**ABSTRACT:** This contribution mainly studied the preparation of hyperbranched polyethylene (HBPE) fibers and HBPE/multiwalled carbon nanotube (MWCNT) composite fibers via electrospinning for the first time. Firstly, the effects of solvents, solution concentration, voltage, and rotating speed of collector on the morphology of HBPE fibers were studied. Among the factors, solvent type, concentration, and voltage showed notable influence on the morphology of HBPE fibers. HBPE has an excellent dispersion effect on CNT in organic solvents. Through ultrasonic dispersion, the HBPE solutions with dispersed MWCNT were obtained. Then HBPE/MWCNT composite fibers were obtained with different contents of MWCNT via electrospinning. The effects of voltage and working distance on the morphology of HBPE/MWCNT composite fibers were investigated. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42517.

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### INTRODUCTION

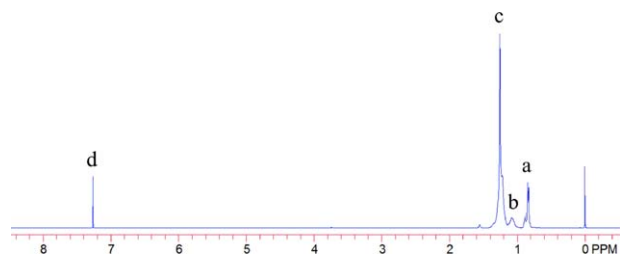
Polymer fibers have potential applications in a variety of fields including filtration devices, vascular grafts, solar cells, etc.<sup>1</sup> Conventional methods to prepare polyethylene (PE) fibers involved melt extrusion,<sup>2</sup> gel spinning technology,<sup>3</sup> etc. Mackay and coworkers<sup>4</sup> reported the preparation of polyethylene fibers via melt extrusion using hyperbranched polymers as processing aid. Influences of the processing aid on the rheological properties and fiber surfaces were studied. However, how to efficiently prepare nanofibers/microfibers is still a challenge for the conventional methods. Electrospinning is famous as a continuous, effective, and versatile method to prepare polymeric fibers. Abundant polymeric fibers have been obtained with diameters ranging from nanometers to micrometers.<sup>5–16</sup> Though significant progress has been made in the preparation of polymeric fibers via electrospinning, only a few of works involved the preparation of polyethylene fibers due to the insolubility of traditional polyethylene at room temperature.<sup>3,17,18</sup>

Larrondo and Manley<sup>2,19,20</sup> made creative work on the preparation of polyethylene and polypropylene fibers via electrospinning. The influences of various experimental parameters on the width of fibers, the morphology, and the flow field in an electrically driven jet were investigated. The electrospun fibers need to

be washed with xylene to remove xylene that acted as the solvent, which is a complication in the production process. Chase and coworkers<sup>21</sup> studied the preparation of linear low density polyethylene (LLDPE) fibers via electrospinning using *p*-xylene that has a higher volatility as the solvent. The obtained fibers possess diameters of 2–7  $\mu\text{m}$  and roughened surfaces. Zussman and coworkers<sup>3</sup> reported the electrospinning of ultrahigh-molecular-weight polyethylene (UHMWPE) solution with *p*-xylene and cyclohexanone as the mixed solvent. It was found that solvent composition and concentration has notable influences on the morphology of fibers.

In the previous work, electrospinning processes of PE were performed at high temperatures ( $>100^\circ\text{C}$ ) due to the poor solubility. Hyperbranched polyethylene (HBPE) prepared by Ni-based and Pd-based catalysts possess high branching degree. As a result, HBPE shows an excellent solubility in organic solvent [e.g., tetrahydrofuran (THF) and chloroform] together with excellent film-forming ability even at room temperature. Hence, HBPE is fairly proper to be used in electrospinning to prepare HBPE fibers. However, preparation of HBPE fibers via solution electrospinning at room temperature has not been reported.

Furthermore, carbon nanotube (CNT) has become a novel generation of filler to prepare polymeric composites due to its



**Figure 1.**  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum of HBPE sample [ $\text{CDCl}_3$ , 400 MHz, room temperature, a: 0.83 ppm ( $\text{CH}_3$ ); b: 1.07 ppm ( $\text{CH}$ ); c: 1.25 ppm ( $\text{CH}_2$ ); d: 7.26 ppm ( $\text{CHCl}_3$ )]. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

outstanding properties. CNT could impart many excellent properties to the polymeric composites, including enhanced mechanical properties, thermal conductivity, electrical conductivity, rheological property, etc.<sup>22–25</sup> Composite fibers containing CNT have also been obtained via electrospinning, including polystyrene/CNT fibers,<sup>26,27</sup> polycarbonate/CNT fibers,<sup>28</sup> etc. Researches by Ye and coworkers<sup>29</sup> and Kontopoulou and coworkers<sup>30</sup> indicated that HBPE has an excellent dispersion ability for CNT in solution. It is reasonable to infer that HBPE/CNT composite fibers could be obtained via electrospinning of HBPE/CNT solution.

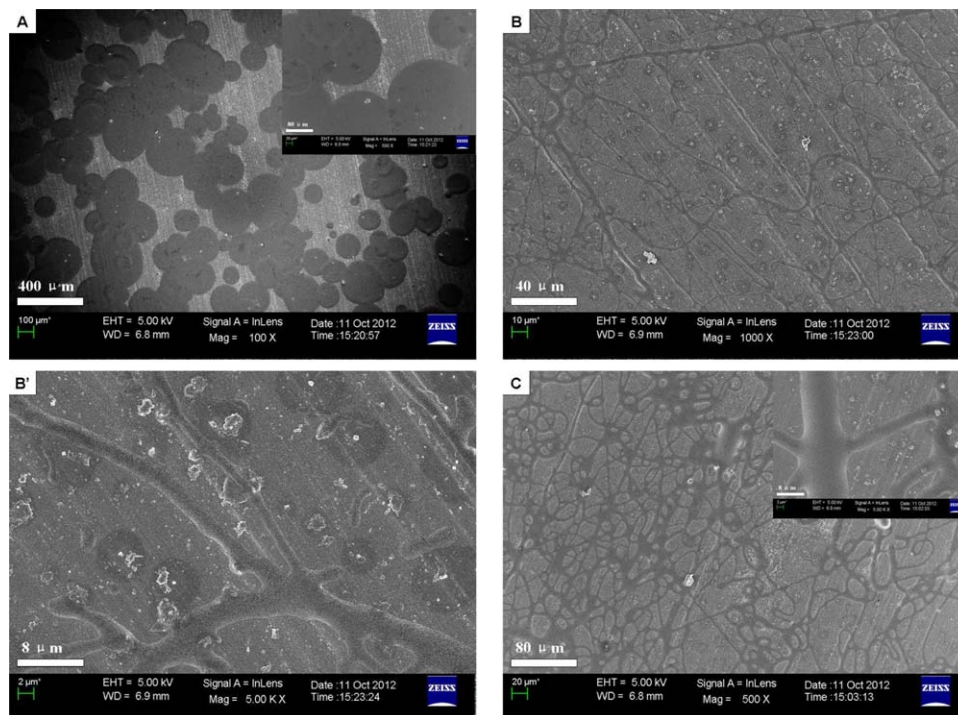
This contribution explored the preparation of HBPE fibers and HBPE/multiwalled carbon nanotube (MWCNT) composite

**Table I.** Electrospinning of HBPE Solutions Under Different Conditions<sup>a</sup>

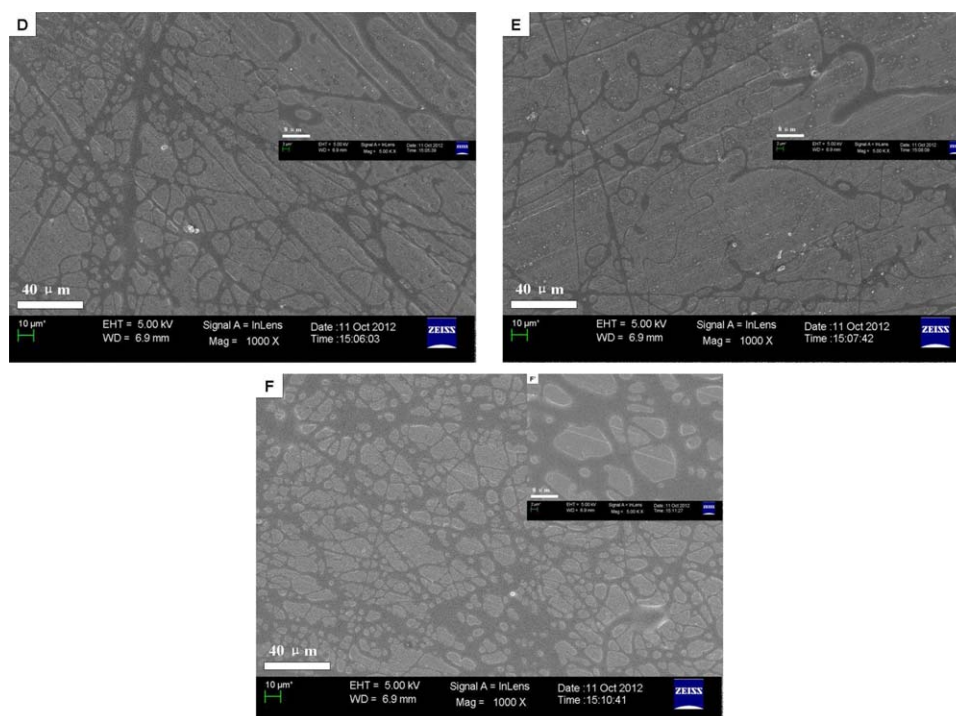
Run	Solvent	Voltage (kV)	Speed (mm/min)	Feed rate (mL/h)	Temperature (°C)	Average diameters ( $\mu\text{m}$ )
1 <sup>b</sup>	<i>p</i> -Xylene	7–15	0.20	0.76	50	251
2	THF	7–8	0.15–0.20	0.57–0.76	35	2.8
3	$\text{CHCl}_3$	7–10	0.15	0.57	35	7.0
4	THF	9	0.20	0.76	35	2.8
5	THF	12	0.20	0.76	35	3.2
6	THF	15	0.75	2.86	35	3.1

<sup>a</sup>Other conditions: 5 mL solvent; concentration of HBPE: 5 wt %; 15 cm working distance; 2 mL of disposable syringes with a inner diameter of 9.0 mm.

<sup>b</sup>9 mg of cetyltrimethylammonium bromide (CTAB) was added after PE dissolving in *p*-xylene and heating for another 15 min.



**Figure 2.** SEM images of PE fibers prepared via electrospinning in different solvents as summarized in Table I (A: Run 1, *p*-xylene; B: Run 2, THF; C: Run 3,  $\text{CHCl}_3$ ). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3.** SEM images of PE fibers prepared via electrospinning in THF at  $\sim 35^{\circ}\text{C}$  under different voltages (D: 9 kV; E: 12 kV; F: 15 kV). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

fibers via electrospinning. To the best of our knowledge, this is the first time to prepare HBPE fibers via electrospinning.

## EXPERIMENTAL

### Materials

HBPE was prepared from ethylene polymerization catalyzed by  $\alpha$ -diimine Ni complex/MAO according to the previous reports.<sup>31,32</sup> The structure data of HBPE are:  $M_n = 6.05 \times 10^4$  g/mol, PDI = 1.93, branching degree = 111.3 branches/1000 carbons [calculated from  $^1\text{H}$  NMR spectrum (Figure 1) using Eq. (1)],  $T_g = -62.7^{\circ}\text{C}$ . THF ( $\epsilon = 7.58$ ), chloroform ( $\epsilon = 4.81$ ), *p*-xylene ( $\epsilon = 2.3$ ), and cetyltrimethylammonium bromide (CTAB) (added to improve the conductivity of polymer solution) were

provided by Sinopharm Chemical Reagent Co., Ltd and used as received. MWCNT with diameter of 10–30 nm was provided by Bill Technology Development Co., Ltd in Shenzhen and used as received.

$$\text{Branching degree} = \frac{\text{CH}_3 \text{ integral}}{\text{Total integral}} \times \frac{2}{3} \times 1000 \quad (1)$$

Branching degree: branches per 1000 carbons;  $\text{CH}_3$  integral: integral of resonance peak of H in  $\text{CH}_3$ ; Total integral: integral of resonance peak of all H.

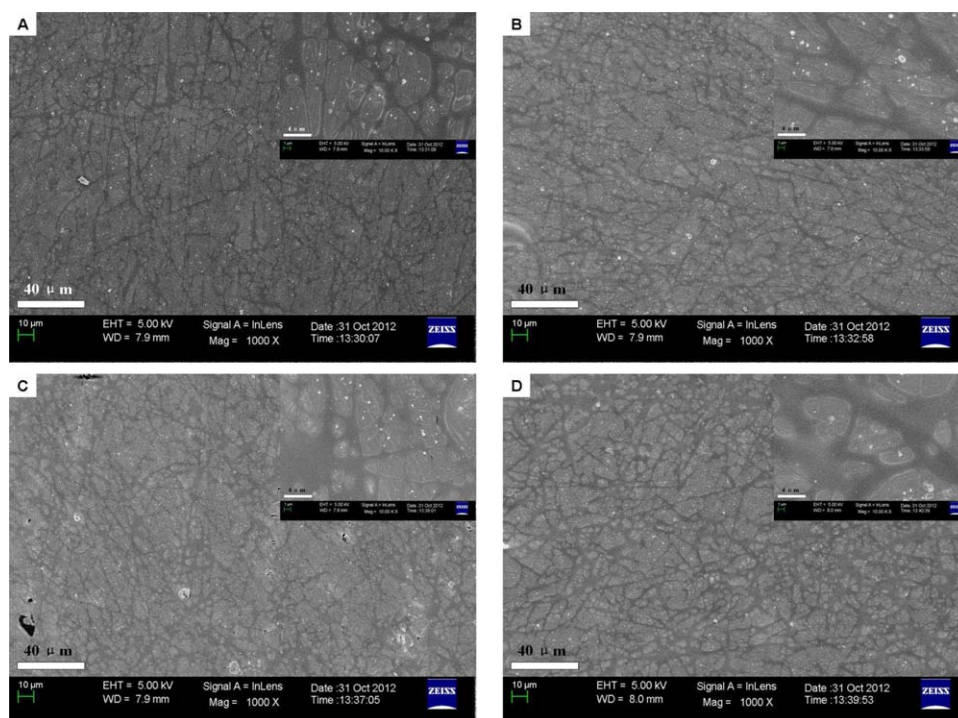
### Preparation of HBPE Solutions for Electrospinning

Typical process: 0.234 g HBPE was weighted and added into a round-bottom flask containing 5 mL of THF ( $\rho = 0.889$  g/mL).

**Table II.** Electrospinning of HBPE Solutions with Different Concentrations<sup>a</sup>

Run	THF (mL)	HBPE (mg)	HBPE (wt %)	Voltage (kV)	Rotate speed (m/min)	Time (min)
1	4.0	0.1108	3%	9	2	25
2	4.0	0.1108	3%	9	4	25
3	4.0	0.1108	3%	9	8	25
4	4.0	0.1108	3%	9	16	25
5	4.0	0.1484	4%	9	2	20
6	4.0	0.1484	4%	9	4	20
7	4.0	0.1484	4%	9	8	20
8	4.0	0.1877	5%	9	2	20
9	4.0	0.1877	5%	9	4	20
10	4.0	0.1877	5%	9	8	20

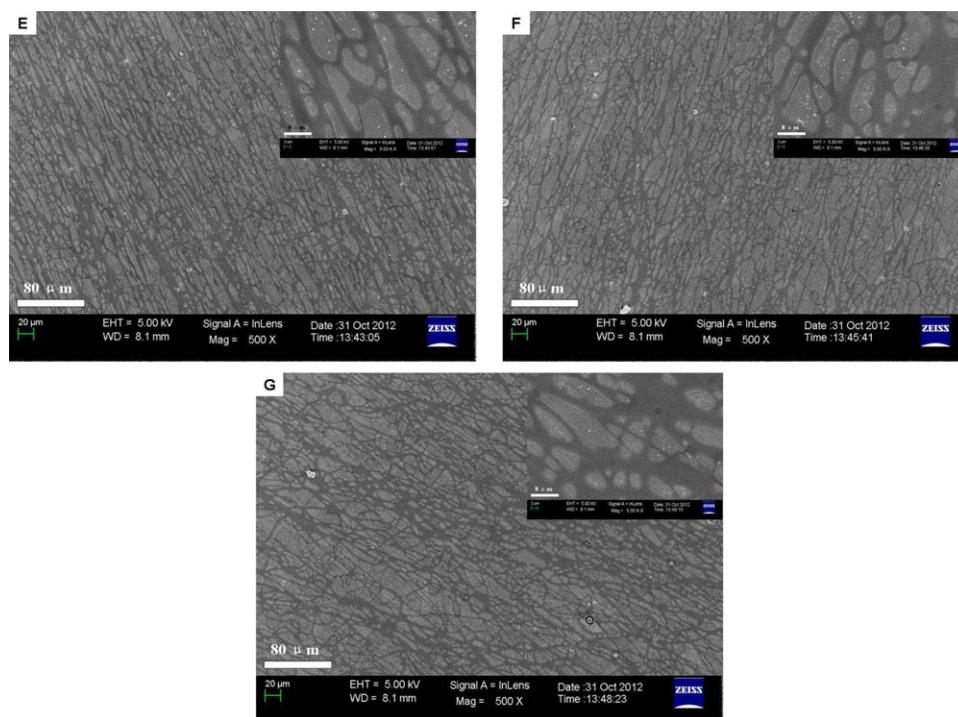
<sup>a</sup>Working distance = 15 cm,  $25^{\circ}\text{C}$ , speed = 0.25 mm/min, feed rate = 0.95 mL/h, electrospinning for 20–25 min.



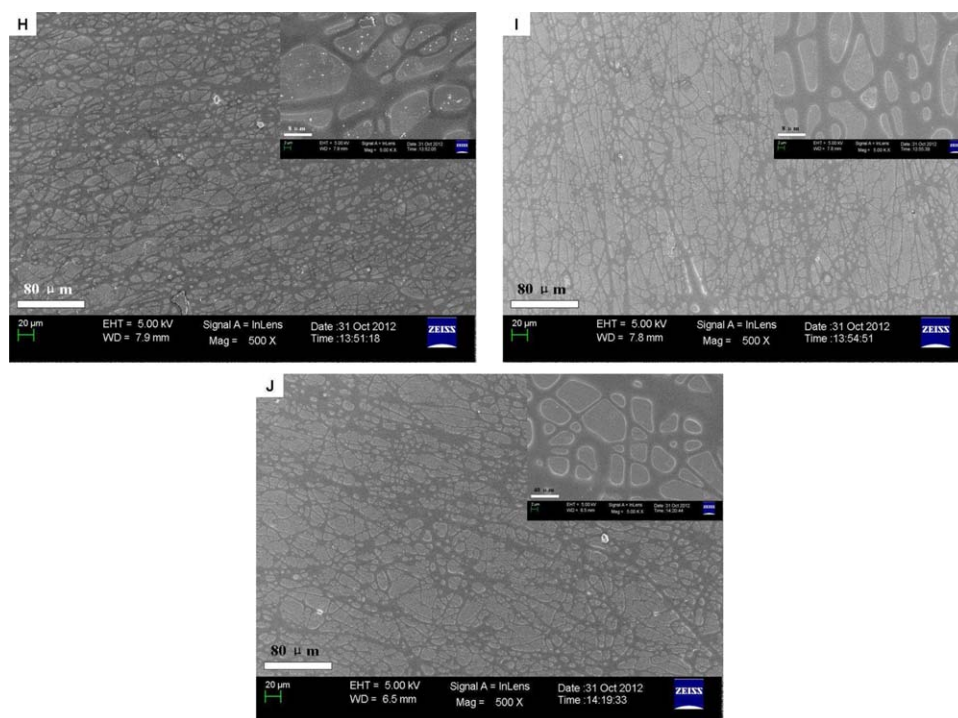
**Figure 4.** SEM images of PE fibers prepared via electrospinning of PE solution in THF with a concentration of 3 wt % at different rotating speeds of collector. (A: 2 m/min; B: 4 m/min; C: 8 m/min; D: 16 m/min). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

After refluxing for 2 h under stirring condition, HBPE was dissolved completely in THF to provide polymer solution with a weight percentage of 5%.

**Preparation of HBPE/MWCNT Solution for Electrospinning**  
Typical process: HBPE and MWCNT with a weight ratio of 10 : 1 were added into a flask equipped with magnetic stirrer. After



**Figure 5.** SEM images of PE fibers prepared via electrospinning of PE solution in THF with a concentration of 4 wt % at different rotating speeds of collector (E: 2 m/min; F: 4 m/min; G: 8 m/min). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 6.** SEM images of PE fibers prepared via electrospinning of PE solution in THF with a concentration of 5 wt % at different rotating speeds of collector. (H: 2 m/min; I: 4 m/min; J: 8 m/min). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

adding certain amount of THF, the HBPE was dissolved by refluxing under stirring condition for 1 h. Then the mixture was treated with ultrasonic dispersion for 1 h. Then the rest HBPE was added into the flask as demanded in Table V. The mixtures were refluxed for another 2 h and treated with ultrasonic dispersion for 1 h. After cooling to room temperature, the solution was taken for electrospinning.

#### Electrospinning of HBPE or HBPE/MWCNT Solutions

All electrospinning works were performed on Electrospinning Equipment SS-2534 (Beijing Ucalery technology development co., LTD). The anode of high-voltage power supply was connected to the metal needle anchored on syringe containing polymer solution and the cathode was connected to the collector. To ensure the fibers arriving at the collector, the cathode voltage was set at  $-2$  kV. After setting the feed rate, rotate speed of collector and working voltage, starting the syringe pump to begin electrospinning. After a period, turn off the power and syringe pump to end the electrospinning.

#### SEM Characterization of HBPE or HBPE/MWCNT Fibers

Scanning electron microscopy (SEM) images of the fibers were recorded on Ultra 55 SEM equipment (CarlzeisD, Germany). The samples for SEM observation were prepared as following: a small piece of aluminium foil covered with dense HBPE fibers was pasted onto copper holder through conductive adhesive. The average diameters of fibers were measured by software Nano Measurer.

## RESULTS AND DISCUSSION

This contribution explored the possibility of preparation of HBPE fibers via electrospinning. Then using the dispersion effect of HBPE on MWCNT in solvents, HBPE/MWCNT fibers were obtained via electrospinning of HBPE/MWCNT solutions.

#### Effects of Solvent Type and Voltage on HBPE Fiber Morphology

The effects of solvent type and voltage which are two important influencing factors in electrospinning on the fiber morphology

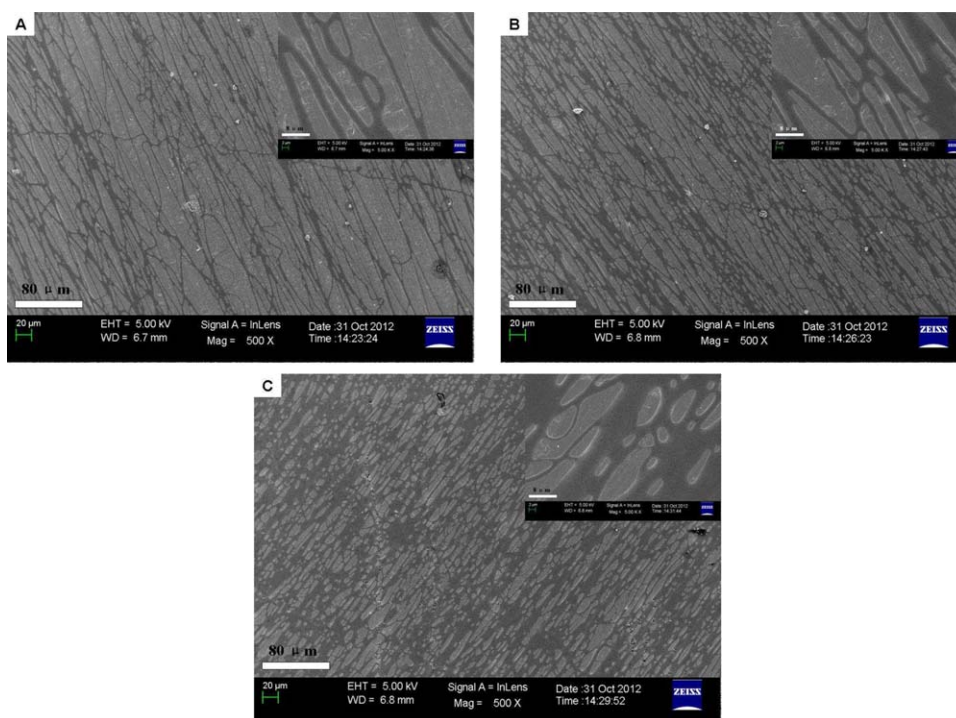
**Table III.** Electrospinning of HBPE Solutions for Different Times<sup>a</sup>

Run	Solvent	Concentration (wt %)	Voltage (kV)	Working distance <sup>b</sup> (cm)	Rotate speed (m/min)	Feed rate <sup>c</sup> (mL/h)	Time (min)
1	THF	4%	9	15	4	0.95	10
2	THF	4%	9	15	4	0.95	20
3	THF	4%	9	15	4	0.95	30

<sup>a</sup> Other conditions: 25°C, 2 mL of disposable syringe (inner diameter  $\sim$ 9.0 mm).

<sup>b</sup> The vertical distance from needle to the collector.

<sup>c</sup> Calculated from the advancing speed of syringe pump and the inner diameter of syringe.



**Figure 7.** SEM images of PE fibers prepared via electrospinning of PE/THF solution of 4 wt % for different times (A: 10 min; B: 20 min; C: 30 min). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

were firstly investigated. The detailed electrospinning conditions were summarized in Table I.

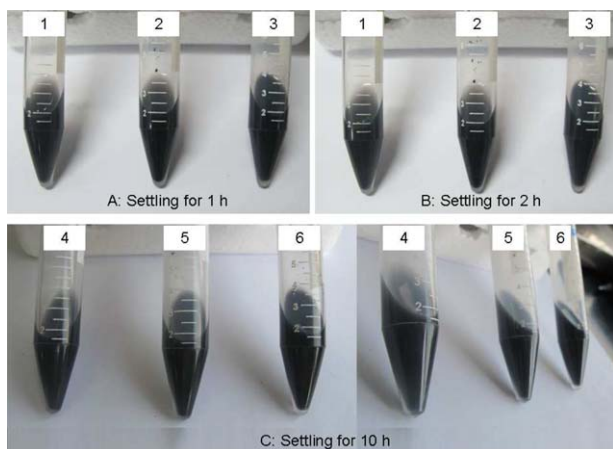
SEM images of HBPE fibers prepared by electrospinning with different solvents were collected in Figure 2. It could be found that the solvent type has a significant influence on HBPE fiber morphology. In case of *p*-xylene, no fibers were formed in the voltage range of 7–15 kV at 50°C. HBPE solution arrived at the aluminium foil (covered around the collector) in form of small droplets. SEM image approved that the electrospinning product was formed from droplets of polymer solution. The size of the droplet is dependent on the voltage. The ejection of droplets indicated the medium conductivity of solution containing CTAB. HBPE fibers could not be formed in electrospinning due to two aspects: (1) low viscosity of HBPE solution and (2) low conductivity providing lower electrostatic repulsion than surface tension.

HBPE/THF solution could form HBPE fibers via electrospinning at 7 kV through the solution solidified easily at the end of the spinning jet. When electrospinning was performed at 8 kV, solution solidification did not appear and a stable spinning process was obtained. From Figure 2(B and B'), branched HBPE fibers were obtained with semicircular cross sections due to the viscous property of HBPE. The fibers had a relatively uniform diameter of 1–3 μm. Using chloroform as solvent, fibers with a larger diameter (3–8 μm) than the other cases were obtained at the same HBPE weight concentration. This is because chloroform has a higher density (1.49 g/mL) than THF (0.89 g/mL) which results in much more HBPE contained in the same volume of chloroform. At 5 wt % concentration, the viscosity of HBPE/chloroform solution is larger than that of HBPE/THF solution. Another feature of HBPE fibers from HBPE/chloroform solution is the enhanced tortuosity morphology which could be attributed to the higher solution viscosity.

**Table IV.** Electrospinning of HBPE/MWCNT Solutions of 1.9 wt %<sup>a</sup>

Run	THF (mL)	HBPE (mg)	MWCNT (mg)	Voltage (kV)	Working distance (cm)	Speed (mm/min)	Feed rate (mL/h)
1A	3.0	50.6	1.0	9	15	0.25	0.95
1B	3.0	50.6	1.0	15	25	0.25	0.95
1C	3.0	50.6	1.0	21	35	0.25	0.95
2	3.0	50.4	2.1	/	/	/	/
3B	3.0	50.4	3.5	9	15	0.20	0.76

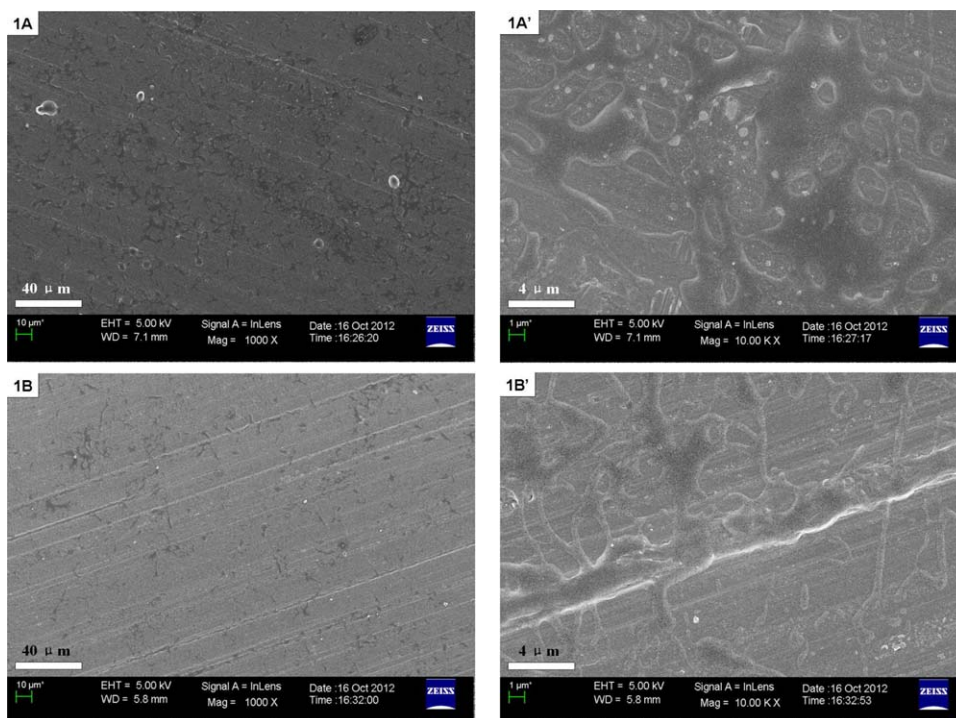
<sup>a</sup>Other conditions: 24°C, 2 mL of disposable syringes with an inner diameter of 9.0 mm, inner diameter of needle (21G) = 0.5 mm, linear speed of cylindrical collector = 4 m/s.



**Figure 8.** Photo pictures of PE/MWCNT suspensions in THF with different compositions as summarized in Tables IV and Table V. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 9.** Photo picture of electrospinning of MWCNT/HBPE/THF solution under the conditions of Run 1A in Table IV. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 10.** SEM images of PE fibers prepared via electrospinning of HBPE/MWCNT/THF solutions (HBPE/MWCNT = 50 : 1) under different conditions as shown in Table IV (1A and 1A': 9 kV, 15 cm; 1B and 1B': 15 kV, 25 cm). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Figure 3 showed the SEM images of HBPE fibers obtained at different voltages. At 9 kV, electrospinning products mainly contain crosslinked or branched fibers and a few of beaded HBPE. At 12 kV, distinctively tortuouse HBPE fibers were obtained with a diameter of 1–4  $\mu\text{m}$ . When voltage increased to 15 kV, the spinning speed increased and the feed rate was increased to keep the spinning processing smoothly. More thin fibers were obtained under the electrospinning conditions. However, obvious agglomeration appeared in HBPE fibers, which is due to the high feed rate and more solvent which could not vaporize completely before arriving at the collector.<sup>16</sup>

The effect of voltage on the diameter of fibers is attributed to the increase of electrostatic repulsion on the fibers. Also the higher voltage will cause stronger electrostatic interaction which results in the increase of tortuosity of HBPE fibers.<sup>16</sup>

#### Effects of Solution Concentration and Rotating Speed of Collector on HBPE Fiber Morphology

In this section, the effects of solution concentration and rotating speed of collector on the fiber morphology were discussed. Solutions with a concentration of 3 wt %, 4 wt %, and 5 wt % were electrospun at different rotating speeds of collector as summarized in Table II.

SEM images of electrospun fibers from HBPE solution of 3 wt % were collected in Figure 4. The prepared fibers contain thick fibers (diameter of 2–3  $\mu\text{m}$ ) and thin fibers (diameter <1  $\mu\text{m}$ ). At low rotating rates of collector (2 and 4 m/min), the thick fibers are short and connected by many thin fibers. With the increase of rotating rate, the fraction of thick fibers increased. No obvious difference was observed at varying rotating rates of collector.

**Table V.** Electrospinning of HBPE/MWCNT Solutions at Room Temperature<sup>a</sup>

Run	THF (mL)	HBPE (mg)	MWCNT (mg)	Voltage (kV)	Working distance (cm)	Feed rate (mL/h)	Average diameters ( $\mu\text{m}$ )
4A	3.0	100.2	1.0	9	15	0.76	3.7
4B	3.0	100.2	1.0	12	20	0.76	1.9
4C	3.0	100.2	1.0	15	25	0.76	2.5
5A	3.0	100.1	2.2	9	15	0.76	3.4
5B	3.0	100.1	2.2	12	15	0.76	2.7
5C	3.0	100.1	2.2	15	15	0.95	2.2

<sup>a</sup>Other conditions: room temperature, inner diameter of needle (21G) = 0.5 mm, 2 mL of disposable syringes with a inner diameter of 9.0 mm, linear speed of cylindrical receptor = 4 m/s.

From Figure 5, branched HBPE fibers were obtained with a diameter of 1–4  $\mu\text{m}$  via electrospinning of solution containing 4 wt % of HBPE at different rotating speeds. The fibers showed distinctive meshy morphology. In addition, also some thick fibers with a breadth of 6–10  $\mu\text{m}$  were formed via agglomeration of thin fibers.

At a rotating speed of 2 m/min, net-like fibers were obtained with a relatively regular arrangement, indicating the deposition of fibers has an orientation on the collector. Fibers obtained at 4 m/min for collector rotating have a reduced orientation degree. When rotating speed increased to 8 m/min, tanglesome fibers were obtained. The results indicated that low rotating speed of collector makes for the preparation of orientated fibers.

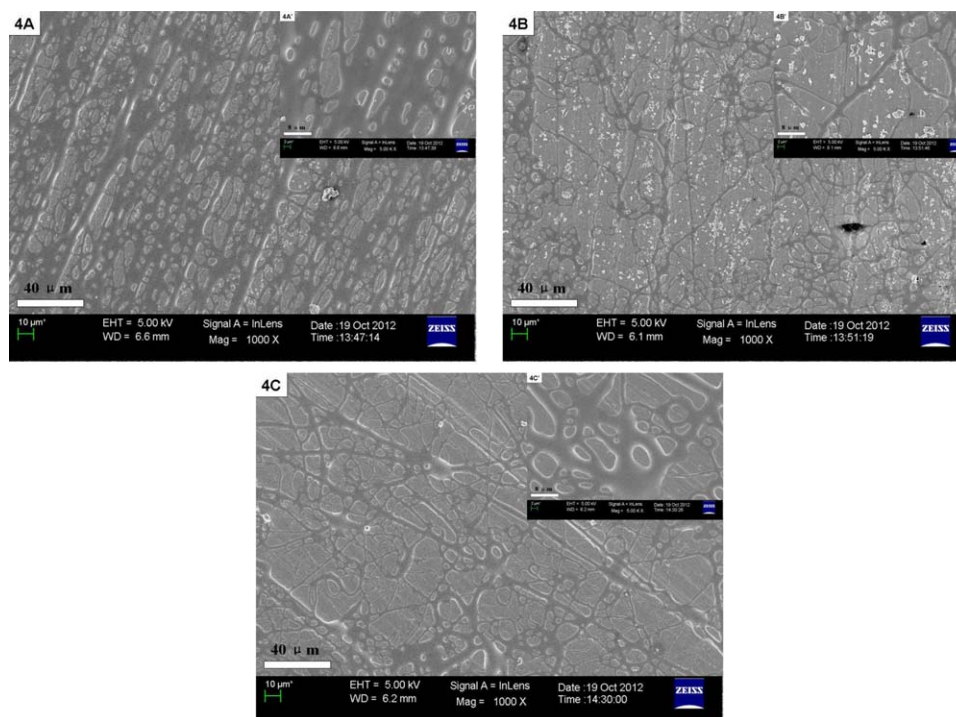
Figure 6 showed the HBPE fibers obtained from electrospinning of the solution with 5 wt % of HBPE. Different with the

products from solution with 4 wt % HBPE, tanglesome HBPE fibers were obtained at a rotating speed of 2 m/min. At higher rotating speeds, more tortuouse HBPE fibers were obtained. An enhanced agglomeration of fibers was observed at a rotating speed of 8 m/min.

The results manifested that the concentration has significant influences on the morphology of electrospun HBPE fibers. Only when the concentration of solution is equal to or above 4 wt %, long fibers could be obtained. Solider fibers and narrower deposition width can be obtained from the electrospinning of solution with higher concentration. However, high concentration is adverse to prepare orientated fibers.

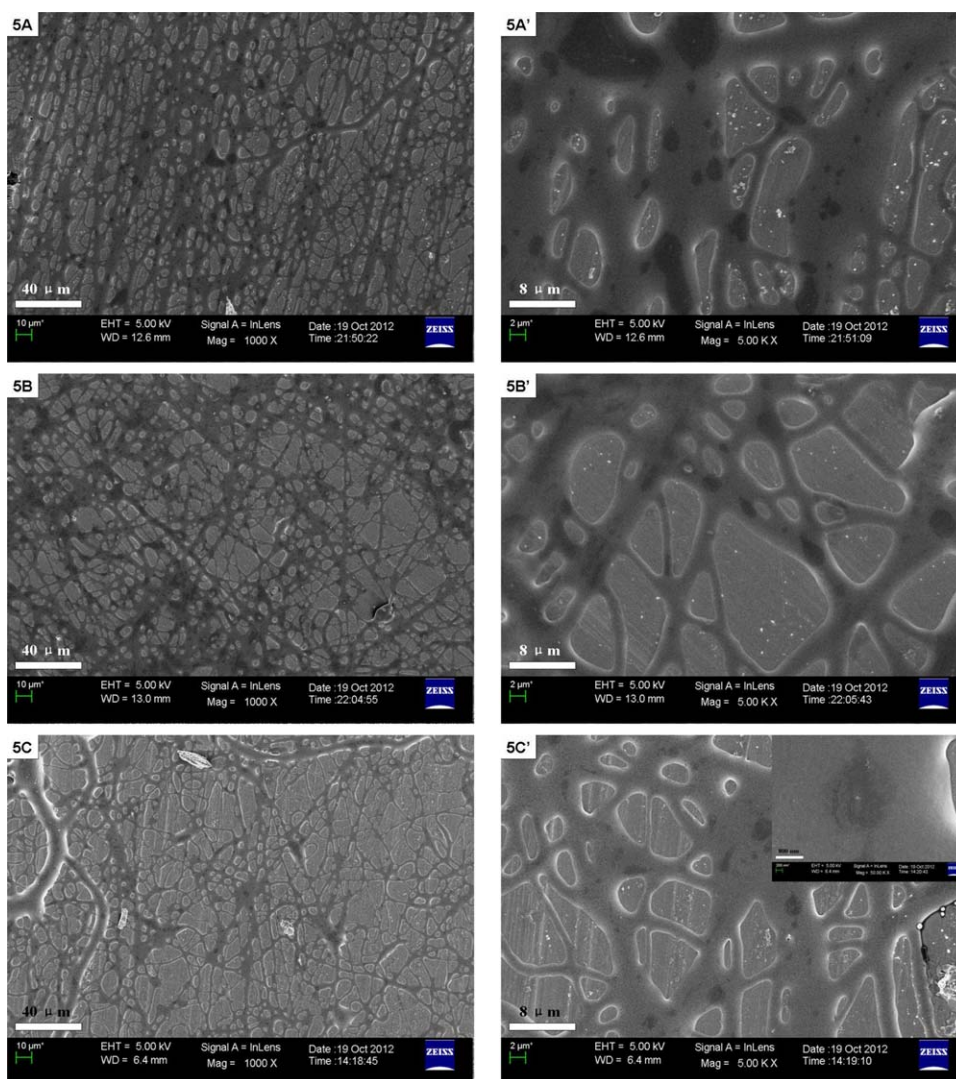
#### Effects of Electrospinning Time on HBPE Fiber Morphology

Agglomeration tends to occur between the contiguous HBPE fibers due to its unique viscosity property. Electrospinning time has direct influence on the fiber density. The effect of



**Figure 11.** SEM images of PE fibers prepared via electrospinning of HBPE/MWCNT/THF solution under different conditions (4A: 9 kV, 15 cm; 4B: 12 kV, 20 cm; 4C: 15 kV, 25 cm). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 12.** SEM images of PE/MWCNT fibers prepared via electrospinning of HBPE/MWCNT/THF solution with HBPE/MWCNT = 50 : 1 under different voltages (5A, 5A': 9 kV; 5B, 5B': 12 kV; 5C, 5C': 15 kV). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

electrospinning time on fiber morphology was investigated for two solutions with different concentrations. The detailed conditions were summarized in Table III. The SEM images of fibers were shown in Figure 7.

For the solution of 4 wt %, 10 min of electrospinning provided fibers with a uniform diameter of 1–3  $\mu\text{m}$ . Meanwhile, a few of fiber agglomerations exists. Increasing electrospinning time, the fiber density together with fiber agglomeration increased. Also, the fibers showed an orientation.

#### Preparation of HBPE/MWCNT Composite Fibers

The previous report<sup>29</sup> indicated that MWCNT solubility in HBPE/THF solution would increase with the HBPE/MWCNT ratio. At HBPE/MWCNT = 10 : 1, the solubility reached a maximum of 920 mg/L. To make sure the completely soluble of HBPE and MWCNT, solutions with low HBPE concentration (50 mg HBPE in 3 mL THF) were prepared with HBPE/MWCNT of 50 : 1, 25 : 1, and 15 : 1, as summarized in Table

IV. The solutions as shown in Figure 8(A, B) showed a uniform color and no precipitation occurred after settling for 2 h, indicating the excellent solubility of MWCNT in the solutions.

The solutions were used for electrospinning under the conditions as summarized in Table IV. Figure 9 showed the stable and continuous electrospinning process of Run 1A in Table IV and a large quantity of fibers were obtained. The SEM images of the prepared fibers were collected in Figure 10.

Only short fibers were prepared together with many agglomerations for sample 1A. This is because the concentration (1.9 wt %) and subsequent viscosity of solution are too low to form long fibers. Electrospinning with a longer working distance (between the spinneret and collector) produced short fibers with fewer agglomerations. Higher MWCNT content also reduced the fiber agglomerations. The effect of MWCNT might come from its conductivity, which increased the conductivity of the solution.

To get “real” HBPE/MWCNT fibers with larger length, solutions with higher HBPE concentration (3.6 wt %) were prepared and used for electrospinning under the conditions in Table V. The solutions with a stable MWCNT dispersion were obtained, indicated by the absence of precipitation after settling for 10 h [Figure 8(c)].

Firstly, the effect of working distance at a constant electric intensity on the fiber morphology was studied for the electrospinning of solution 4. The SEM images of electrospinning results were collected in Figure 11. Dense fibers which formed a fibrous membrane were obtained with apparent agglomerations for Run 4A (9 kV, 15 cm). The single fibers have a diameter of 1–3  $\mu\text{m}$ . For Run 4B (12 kV, 20 cm), the prepared fibers have a tortile morphology and no apparent agglomeration was observed. The fibers obtained from Run 4C (15 kV, 25 cm) show a similar morphology to that from Run 4B. This is because it takes longer time for fibers to arrive the collector. As a result, the electrostatic repulsion acts at the fibers for longer time, which facilitates the formation of thin fibers. Though MWCNT is not visible in the fibers, the fibers should contain MWCNT since they were obtained from stable solution containing MWCNT.

The electrospinning of solution with HBPE/MWCNT = 50 : 1 was performed at different voltages. The SEM images of obtained fibers were shown in Figure 12. At three voltages, crosslinked fibers were obtained with visible black spots on the surface. Since the fibers were obtained from solution containing considerable MWCNT, it is reasonable to regard the black spots as the accumulation areas of MWCNT. Fibers obtained at 9 kV have large and dark colored spots with distinct boundaries. With the increase of voltage, the color of spots became lighter, implying that the voltage has an effect on the dispersion of MWCNT in the composite fibers.

The voltage also showed a notable influence on the fiber morphology. Fibers obtained at 9 kV showed certain orientation which was not observed for the fibers prepared at 12 kV and 15 kV. Fewer agglomerations were formed for fibers obtained at 15 kV than those at 9 kV and 12 kV. This is because higher voltage results in stronger electrostatic repulsion on the surface. Also high-voltage facilitates the vaporization of solvent and relatively dry fibers could be formed to avoid agglomeration.

## CONCLUSIONS

Electrospinning of HBPE solutions to prepare HBPE fibers was reported for the first time. Branched or crosslinked HBPE fibers and HBPE/MWCNT composite fibers were prepared successfully via electrospinning. The effects of solvent type, solution concentration, voltage, working distance on the morphologies of HBPE, and HBPE/MWCNT fibers were investigated.

THF and chloroform are suitable solvents to prepare HBPE solutions for electrospinning. HBPE fibers were obtained from both of HBPE/THF solution and HBPE/chloroform solution via electrospinning, respectively. Voltage showed notable influences on the diameter and tortuosity of fibers. High voltage facilitates the formation of thin and tortuose fibers. The HBPE/THF solution only with a high concentration ( $\geq 4$  wt %) could provide

long fibers via eletrospinning. High voltage and high rotating speed of collector are adverse to produce fibers with orientation. Electrospinning for longer time produced fibers with more agglomerations.

Also, HBPE/MWCNT composite fibers were prepared from solutions (100 mg HBPE in 3 mL THF) containing MWCNT via electrospinning. The dark spots on the fiber surfaces implied the uneven distribution of MWCNT in the fibers. Higher voltage makes for the uniform dispersion of MWCNT in the prepared fibers.

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## REFERENCES

1. Lyons, J.; Li, C.; Ko, F. *Polymer* **2004**, *45*, 7597.
2. Larrondo, L.; St. John Manley, R. *J. Polym. Sci. Polym. Phys.* **1981**, *19*, 909.
3. Rein, D. M.; Shavit-Hadar, L.; Khalfin, R. L.; Cohen, Y.; Shuster, K.; Zussman, E. *J. Polym. Sci. B Polym. Phys.* **2007**, *45*, 766.
4. Hong, Y.; Cooper-White, J. J.; Mackay, M. E.; Hawker, C. J.; Malmström, E.; Rehnberg, N. *J. Rheol.* **1999**, *43*, 781.
5. Deitzel, J. M.; Kosik, W.; McKnight, S. H.; Tan, N. C. B.; DeSimone, J. M.; Crette, S. *Polymer* **2002**, *43*, 1025.
6. Ding, B.; Kim, H. Y.; Lee, S. C.; Shao, C. L.; Lee, D. R.; Park, S. J.; Kwag, G. B.; Choi, K. J. *J. Polym. Sci. B Polym. Phys.* **2002**, *40*, 1261.
7. Wang, X. Y.; Lee, S. H.; Ku, B. C.; Samuelson, L. A.; Kumar, J. *J. Macromol. Sci. Pure Appl. Chem.* **2002**, *A39*, 1241.
8. Fridrikh, S. V.; Yu, J. H.; Brenner, M. P.; Rutledge, G. C. *Phys. Rev. Lett.* **2003**, *90*, 144502-1.
9. Yao, L.; Haas, T. W.; Guiseppi-Elie, A.; Bowlin, G. L.; Simpson, D. G.; Wnek, G. E. *Chem. Mater.* **2002**, *15*, 1860.
10. Huang, Z. M.; Zhang, Y. Z.; Kotaki, M.; Ramakrishna, S. *Compos. Sci. Technol.* **2003**, *63*, 2223.
11. Gururajan, G.; Sullivan, S. P.; Beebe, T. P.; Chase, D. B.; Rabolt, J. F. *Nanoscale* **2011**, *3*, 3300.
12. Devarayan, K.; Hanaoka, H.; Hachisu, M.; Araki, J.; Ohguchi, M.; Behera, B. K.; Ohkawa, K. *Macromol. Mater. Eng.* **2013**, *298*, 1059.
13. Frontera, P.; Busacca, C.; Trocino, S.; Antonucci, P.; Lo Faro, M.; Falletta, E.; Della Pina, C.; Rossi, M. *J. Nanosci. Nanotechnol.* **2013**, *13*, 4744.
14. Li, Q. S.; Guan, L. L.; Hong, W.; Liu, J.; Xing, G. Z. *Integr. Ferroelectrics* **2013**, *144*, 48.
15. Miao, Y. E.; Fan, W.; Chen, D.; Liu, T. X. *ACS Appl. Mater. Interfaces* **2013**, *5*, 4423.

16. Seeram Ramakrishna, K. F.; Teo, W.-E.; Lim, T.-C.; Ma, Z. *An Introduction to Electrospinning and Nanofibers*; World Scientific Publishing Co. Pte. Ltd.: Singapore, **2005**.
17. Givens, S. R.; Gardner, K. H.; Rabolt, J. F.; Chase, D. B. *Macromolecules* **2007**, *40*, 608.
18. Deng, R. J.; Liu, Y.; Ding, Y. M.; Xie, P. C.; Luo, L.; Yang, W. M. *J. Appl. Polym. Sci.* **2009**, *114*, 166.
19. Larrondo, L.; St. John Manley, R. J. *Polym. Sci. Polym. Phys.* **1981**, *19*, 933.
20. Larrondo, L.; St. John Manley, R. J. *Polym. Sci. Polym. Phys.* **1981**, *19*, 921.
21. Givens, S. R.; Gardner, K. H.; Rabolt, J. F.; Chase, D. B. *Macromolecules* **2006**, *40*, 608.
22. Kalakonda, P.; Iannacchione, G. S.; Daly, M.; Georgiev, G. Y.; Cabrera, Y.; Judith, R.; Cebe, P. *J. Appl. Polym. Sci.* **2013**, *130*, 587.
23. Qian, H.; Greenhalgh, E. S.; Shaffer, M. S. P.; Bismarck, A. *J. Mater. Chem.* **2010**, *20*, 4751.
24. Peng, R. G.; Wang, Y. Z.; Tang, W.; Yang, Y. K.; Xie, X. L. *Polymers* **2013**, *5*, 847.
25. Song, K. A.; Zhang, Y. Y.; Meng, J. S.; Green, E. C.; Tajaddod, N.; Li, H.; Minus, M. L. *Materials* **2013**, *6*, 2543.
26. Sen, R.; Zhao, B.; Perea, D.; Itkis, M. E.; Hu, H.; Love, J.; Bekyarova, E.; Haddon, R. C. *Nano Lett.* **2004**, *4*, 459.
27. Sundaray, B.; Subramanian, V.; Natarajan, T. S. *J. Nanosci. Nanotechnol.* **2007**, *7*, 1793.
28. Kim, G. M.; Michler, G. H.; Pötschke, P. *Polymer* **2005**, *46*, 7346.
29. Xu, L.; Ye, Z.; Cui, Q.; Gu, Z. *Macromol. Chem. Phys.* **2009**, *210*, 2194.
30. Petrie, K.; Docoslis, A.; Vasic, S.; Kontopoulou, M.; Morgan, S.; Ye, Z. *Carbon* **2011**, *49*, 3378.
31. Zhao, Y.; Wang, L.; Yu, H.; Zhang, L.; Li, C.; Ding, W.; Jing, G. *J. Polym. Res.* **2013**, *20*, 1.
32. Zhao, Y.; Wang, L.; Zhang, L.; Yu, H.; Chen, Z.; Tai, Y. *J. Macromol. Sci. A* **2013**, *50*, 685.