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Direct generation of electrospun interconnected macroporous nanofibers using a water bath as a collector

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Abstract

Porous nanofibers are of great significance to different applications. Herein, interconnected macroporous nanofibers were electrospun from polystyrene (PS)/chlorobenzene (CB)/N’N-dimethylformamide (DMF) using a bath collector. The effects of the solvent ratio and bath collector temperature on the structure of PS fibers are studied. The results showed that the presence of CB is essentials for the formation of porous fibers. Furthermore, the size of the pores on the surface of fibers increases by increasing the ratio of CB as well as decreasing the temperature of the bath collector. The formation mechanism of the interconnected macroporous structure is discovered. The BET test showed that these fibers had an outstanding specific surface area (SSA) of ~44.27 m² g⁻¹. We believe our findings can be used as a good reference for the generation of electrospun nanofibers with interconnected macroporous using a water bath as a collector.

1. Introduction

Electrospinning is a technique for generating fibers with a diameter ranging from few nanometers to several micrometers [1, 2]. Electrospun fibers can be formed in different morphologies resulting in their ability to be used in different applications such as oil cleanup, energy harvesting, biomedical applications, self-cleaning surfaces, keeping food fresh, and so on [3–17].

The performance and efficiency of electrospun webs can be substantially enhanced by further increasing their specific surface area (SSA) which can be achieved through various approaches such as fabricating fibers with porous structure [18–20]. To date, a variety of methods have been developed to generate porous fibers such as sacrificial templating and phase separation [3, 21]. These methods have drawbacks because occasionally processes are not accessible, not suitable for certain polymers, and have no adjustment over the orientation and diameter of the fibers. Nevertheless, phase separation (e.g., thermally induced phase separation (TIPS), vapor-induced phase separation (VIPS), and non-solvent induced phase separation (NIPS)) is the most widely used method [3, 22, 23]. Pores can be formed on the surface of fibers via TIPS, however, the spinnability of fibers using high volatile solvents is a big problem [3]. While fibers with porous interior can be obtained by VIPS, whereas both surface and interior pores are produced through the combination of TIPS and VIPS [3, 24]. NIPS can create macroporous by mixing a non-solvent into a polymer-solvent solution prior to electrospinning [25, 26]. It is known that water is insoluble for most non-polar polymers, and it can be served as an excellent non-solvent for many polymers. When a water bath is used as the receiving collector of an electrospinning process, water will instantly precipitate polymer throughout the jet if the solvent system is completely water-soluble, as a result, no phase separation occurs between solvents. Therefore, a water-insoluble solvent for phase separation is necessary in the solvent system.

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Polystyrene (PS) is an amorphous, non-crystalline thermoplastic polymer that has excellent formability and is insoluble in water, therefore, it was selected as a model. Previously, we reported the fabrication of ultrafine PS fibers with tunable macro-pore structures and distributions for oil-water separation by using a microfluidic nozzle comprising three channels that allows for liquid mixing from two input channels and synchronized electrospinning of the resulting mixture from the other output channel [27]. Moreover, we studied the effect of the polymer solution parameters and ambient parameters on the formation of micro, meso, and macropores electrospun PVDF nanofibers [3, 5, 24]. In addition, we generated a novel PVDF spindle porous bowl like beads which showed unexpectedly high oil cleanup capacity [4]. It is worth mentioning that due to the high porosity and outstanding specific surface area of porous structure, it can be used in various applications such as tissue engineering [28, 29], drug delivery [30], water treatment applications [31–34], sensors [35, 36], photocatalysis [37, 38], lithium-ion batteries [39, 40], energy harvesting [6], and so on [41–43]. To the best of our knowledge, few studies have investigated the generation of porous fibers using a bath collector [44–46]. In this work, the possibility of generating electrospun interconnected macroporous nanofibers from PS/chlorobenzene (CB)/N’N-dimethylformamide (DMF) solution at different solvent ratios (0:1, 1:3, 1:2, 1:1, 2:1, 3:1, and 4:1) and different temperatures of the bath collector (3, 25, and 40 °C) were demonstrated. We hope our study can spot the light on the importance of producing interconnected macroporous fibers using a water bath as a collector.

2. Experimental

2.1. Materials
PS (Mw = 300,000 g mol⁻¹) was purchased from Sigma-Aldrich, USA; DMF and CB were purchased from Shanghai Chemical Reagents Co., Ltd, Shanghai, China.

2.2. Methods
Electrospinning: 15% PS was added into combination solvents of CB/DMF with different solvent ratios (0:1, 1:3, 1:2, 1:1, 2:1, 3:1, and 4:1), and then stirring them at 50 °C until the polymer is completely dissolved. The spinning solution is delivered through a tube to a vertical needle (18 G) which was fixed on a syringe pump (KDS 100, KD Scientific Inc.) connected to a high-voltage supplier (Tianjin Dongwen Co., Ltd, China). The electrospinning process was performed at the needle to bath collector distance of 5 cm, applied voltage of 12 kV, flow rate of 0.8 ml h⁻¹, temperature of 25 °C, and relative humidity of 60 ± 5% (figure 1). The fibers were electrospun for 5 min on a metal net which immersed in the bath collector (height of 8 cm and diameter of 24 cm). The obtained fibers were then transferred to a vacuum drying oven (DHG-9053A, Yiheng Scientific Instrument Co., Ltd, Shanghai, China) and dried at 36 °C for 2 h.

2.3. Characterization
The surface morphology and cross-section of the electrospun PS fibers were observed under the field emission scanning electron microscopy (FE-SEM, S-4800 Hitachi, Japan). The diameter of the fibers was analyzed and observed by a picture software (Adobe Acrobat X Pro 10.1.2.45) according to the SEM images. N₂ physical adsorption-desorption isotherms (JW-BK132F, Beijing Science and Technology Co., China) were measured to determine the SSA and pore distribution.
Surface porosity of nano decreased due to the shortened time of NG of 0.8 ml h⁻¹, applied voltage of 12 kV, bath collector temperature of 3 °C, relative humidity of 60 ± 5%, and temperature of 25 °C [27]. No pores were observed on the fiber's surface when DMF was used as a solvent (figure 2(A)), while the porous structure was found at CB/DMF = 1:3 (figure 2(B)). With the increase of CB ratio, the size of the pore surface increased (figures 2(B)–(F)) and that should be attributed to the nucleation mechanism (NG) [3]. While deformed fibers were produced at CB/DMF = 4:1 (figure 2(G)) due to the poor conductivity of CB [47]. Considering a narrow distribution of fiber diameter and high porosity, fibers formed at CB/DMF = 2:1 are optimum. Therefore, their cross-section was checked (figure 2(H)). The average diameter and surface porosity of obtained fibers are shown in table 1.

3. Results and discussion

3.1. The effect of the solvent ratio on the morphology of PS
Herein, different solvent ratios of CB/DMF (0:1, 1:3, 1:2, 1:1, 2:1, 3:1, 4:1) were tested at PS concentration of 15%, applied voltage of 12 kV, bath collector temperature of 3 °C, needle to collector distance of 5 cm, flow rate of 0.8 ml h⁻¹, relative humidity of 60 ± 5%, and temperature of 25 °C [27]. The results showed that by increasing the bath collector temperature from 3 °C to 40 °C, the size of the surface and interior pores of fibers decreased due to the shortened time of NG (figures 3(A)–(C)) [48]. Importantly, only interior pores were found using a static collector because of VIPS (figure 3(D)) [5].

The formation of the interconnected macroporous structure should be ascribed to this hypothesis. When the jet enters the water bath, water acts as a non-solvent to initiate phase separation, the polymer-rich and polymer-poor regions appear in the jet. Due to the large contact area between the jet and water, water can enter the jet easily, subsequently expansion of the phase separation region caused by NG resulting in the formation of interconnected macroporous structure. Therefore, it is worth mentioning that the formation of the macroporous structure requires the participation of a water bath, and the low-temperature condition is more suitable for generating macropores. The average diameter and surface porosity of produced fibers are shown in table 2.

3.2. The effect of bath collector on the morphology of PS
Herein, PS fibers were electrospun on a bath collector and static collector (figure 3). The results showed that by increasing the bath collector temperature from 3 °C to 40 °C, the size of the surface and interior pores of fibers decreased due to the shortened time of NG resulting in the formation of interconnected macroporous structure. Therefore, it is worth mentioning that the formation of the macroporous structure requires the participation of a water bath, and the low-temperature condition is more suitable for generating macropores. The average diameter and surface porosity of produced fibers are shown in table 2.

3.3. The ternary phase diagram of PS/(CB + DMF)/water
To further investigate the mechanism of pores formation, the phase diagram of the PS/(CB + DMF)/water ternary system is drawn (figure 4). The bimodal curve will tend to move towards a lower water concentration when the ratio of CB increases (figures 4(a)–(d)), leading to accelerating the phase separation [24]. Therefore,
bigger macropores on the surface of fibers can be generated. In addition, at the temperature of 25 °C, the binodal curve moves toward high water concentration, which represents that decreasing the temperature will be preferable for phase separation (figure 4(e)).
3.4. The nitrogen adsorption isotherms of PS macroporous microfibers

Herein, to quantify the surface area and pore structure of the PS fiber (figure 2(E)), the nitrogen adsorption isotherms were carried out (figure 5). It can be found that there is a small rising tendency at the beginning of the adsorption curve. The second half of the isotherm showed a sharp increasing trend when the relative pressure is gradually increased, in addition, no peak value was found throughout the isotherm, which indicates that the material is macroporous structure according to the IUPAC standard [49]. The pore size distribution of the studied fibers can be calculated from the adsorption and desorption curve. The results exhibited that the average pore diameter is ~64.4 nm. The BET test showed that the macroporous PS fibers have an outstanding SSA (44.27 m² g⁻¹) compared with the SSA of the smooth PS fibers formed using a static collector (7.36 m² g⁻¹) (figure 3(D)).

It is worth mentioning that since the electrospun macroporous fibers produced using a bath collector have multiple advantages (e.g. cost-effective, a variety of porous structures, high SSA, and so on), they can be used successfully in different applications such as oil-water separation, filtration, medical fields and so on.

4. Conclusions

Electrospun interconnected macroporous fibers were generated from PS/CB/DMF using a bath collector. The effects of the solvent ratio and bath collector temperature were investigated. The results showed that the presence of CB is the key factor for the formation of the porous structure. Furthermore, the porosity of fibers can be enhanced by increasing the ratio of CB and decreasing the temperature of the bath collector. The formation mechanism of the interconnected macroporous structure was explored. Considering a narrow distribution of fiber diameter and high porosity, the SSA of optimal PS fibers which electrospun at the polymer concentration of 15%, CB/DMF = 2/1, bath collector temperature of 3 °C, applied voltage of 12 kV, needle to collector distance of 5 cm, flow rate of 0.8 ml h⁻¹, relative humidity of 60 ± 5% was 44.27 m² g⁻¹, which is ~6 times higher than the SSA of the smooth fibers which were electrospun using a static collector. This study has the ability to provide researchers with an efficient and simple method for the preparation of interconnected macroporous polymer nanofibers using a bath collector.

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Author contributions

B Zaarour and L. Zhu contributed equally to this work. B Zaarour, L. Zhu, and X. Jin conceived the original concept. B Zaarour and L. Zhu designed, conducted the experiments, and analyzed the data. B Zaarour and L. Zhu wrote the manuscript. B Zaarour, L. Zhu, and X. Jin revised the manuscript. There are no conflicts to declare.

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