Research Article

Producing Polymer Fibers by Electrospinning in Supercritical Fluids

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Nanofibers have a wide range of applications, including filtration and biomedical engineering. Porous or hollow fibers with large surface-to-volume ratios are more popular in some fields than the common nanofibers. Porous nanofibers can be obtained through electrospinning with highly volatile solvents or through special treatment following electrospinning. A new process where electrospinning is conducted in supercritical or near-critical CO₂ to produce porous or hollow nanofibers has been summarized. In addition, a process entailing compressed N₂-assisted electrospinning was attempted to produce PVP nanofibers in this work, but it was proved to be unsuccessful. Since the fiber morphologies are dependent on the phase behavior of organic solvents in supercritical fluids, ASPEN PLUS 2006 was used to simulate the phase equilibrium of the solvent-supercritical fluid system to explain why porous or hollow fibers can be obtained in compressed CO₂, but not in compressed N₂.

1. Introduction

Electrospinning is one of the most intriguing and efficient processes used to produce a variety of polymer fibers. Besides, fiber diameters can range from several microns to tens of nanometers, and as small as 10 nm [1–3]. The electrospinning process uses a high electrical field to induce charged polymer droplets. As the solution jet travels, it is elongated and whipped continuously by the electrical force, accompanied by the evaporation of solvent. The fibers are formed when they are deposited on the oppositely charged collector [4–6].

In general, fibers, produced by electrospinning, have a smooth surface and solid-core cross-section. These fibers have been used in protective clothing, filtration, catalysis, biosensors, tissue engineering, and so forth [7–9]. In addition, the special performance of nanofibers can be enhanced as specific surface area increases. Consequently, fibers that possess specific structures, such as hollow, core-sheath, and porous surface, can offer advantage for a number of applications. For instance, these “special fibers” are ideal alternatives in drug delivery, tissue engineering scaffolds,

filter applications, or as templates for forming functional nanotubes [10–13].

Nowadays, porous polymer fibers or fibers with a large specific surface area have been produced using a special electrospinning process [14, 15]. Bognitzki et al. [16] initially reported that porous nanofibers could be directly fabricated by electrospinning. The mechanism that generates the pore structure of the fibers during electrospinning is a phase separation caused by rapid evaporation of the system's solvent leading to the subsequently rapid solidification of polymer [16, 17]. However, a second mechanism responsible for formation of pores in these fibers is under consideration is the “breath figure” [18–20]. It has been demonstrated that the humidity of the experimented environment directly affects the surface morphology of electrospun fibers [19, 20]. Meanwhile, porous polymer fibers can also be produced through electrospinning polymer blends, followed by selective removal of one of the components [21]. In conclusion, the after processing is usually solvent extraction [22–24], thermal treatment [25], light crosslinking [26, 27], and chemical reaction [10, 28].

FIGURE 1: SEM images of PVP fiber morphologies obtained by electrospinning into a CO_2 bath at 295 K and (a) 3.45; (b) 4.83; and (c) 4.96 MPa [41].

Supercritical fluid has been successfully exploited to form microstructure in polymer processing. Process examples include, supercritical foaming [29, 30] and emulsion templating [31]. It is noticeable that nonsolvent-induced phase separation (NIPS) is another versatile method that can be employed to form porous polymer fibers and polymeric membranes [32, 33]. It has been suggested that compressed gas or supercritical fluid can be good alternatives to nonsolvent in polymer processing of porous materials [34].

2. Electrospinning in Supercritical or Near-Critical CO_2

In addition to being a good solvent for most of organic polymers [35], supercritical CO_2 (scCO_2) is also inexpensive, environmentally safe, and readily available. scCO_2 facilitates the absorption of desirable additives under appropriate conditions [36]. Therefore, scCO_2 or near-critical CO_2 offer great potential as nonsolvent in electrospinning processes for preparing porous or nanofibers with novel morphologies [30]. This approach is analogous to the process, known as “precipitation with a compressed fluid antisolvent” (PCA). Some researchers have reported that an organic polymer solution can be sprayed through a capillary tube into compressed carbon dioxide to generate porous or hollow fibers [37–39]. Levit and Tepper [40] firstly proposed a scCO_2 -assisted electrospinning process in which the needleless electrospinning system was placed into a vessel filled with scCO_2 . The solid poly(dimethylsiloxane) (PDMS) and poly(D, L-lactic acid) (PLA) fibers were obtained against gravity in a bath of scCO_2 , whereas no fibers were obtained when the electrospinning was performed in air. It is explained that the supercritical solvent softens rather than dissolving or liquefying the polymer, which reduces the viscosity of the undissolved polymer for electrospinning.

Based on their pioneering work, Shen et al. [41] developed and patented [42] a vessel in which the polymer solution could be electrospun in a near-critical CO_2 . Using this device, the authors prepared PVP nanofibers with a porous internal structure and a coherent external skin. These materials were produced, when a PVP/dichloromethane (DCM) solution was electrospun at 3.45, 4.83, and 4.96 MPa, as seen in

Figure 1. However, under ambient conditions, with a PVP/DCM solution, electrospun PVP nanofibers with solid core were produced [20]. Presence of scCO_2 or near-critical CO_2 accelerates the solution phase separation. The compressed CO_2 extracts solvent (DCM), enhancing mass transfer and rapid drying of the polymer. As a result, the coherent external skin takes shape on the polymer fibers. In addition, due to the rapid diffusion of CO_2 into the polymer solution jet, compressed CO_2 also plays the role as a porogen facilitating the formation of the interior porous structure in this process.

Lee et al. [43] proposed a similar procedure to produce PVP nanofibers by electrospinning in a bath of compressed CO_2 . Hollow PVP fibers were produced, with diameter ranging from 400 to 900 nm. The presence of CO_2 contributes to removal of organic solvent, which effectively eliminates the formation of beads. Since scCO_2 is a potential swelling agent for polymers [36], the diameters of fibers that are electrospun in near-critical or supercritical CO_2 are larger than those obtained under atmosphere conditions. In addition, Liu et al. [44] improved the experimental apparatus by increasing the nozzle-to-target distance. To demonstrate the impact of compressed CO_2 on the fiber morphology, several polymer solutions were tested. Nanofibers obtained from PVP/ethanol solution exhibited a single hollow core and a ribbon-like morphology when the pressure exceeded 5.6 MPa. Porous PVDF fibers were formed from poly(vinylidene fluoride) (PVDF)/dimethylacetamide (DMAc) solution and PVDF/dimethylformamide (DMF) solution electrospun into a saturated CO_2 vapor. It was suggested that the morphologies of fibers depend not only on the operating conditions (pressure and temperature) of CO_2 , but also on phase behavior of the organic solvent in CO_2 . It is now understood that the saturated CO_2 has two important impacts on scCO_2 -assisted electrospinning process. The first is the rapid diffusion of CO_2 in the solution jet which induces phase separation of the polymer solution. The second involves excess CO_2 which extracts solvent from the solution jet. These two effects are responsible for the porous or hollow nanofibers being formed when a polymer/solvent solution was electrospun in compressed CO_2 , but not in ambient air.

Wahyudiono et al. [45] developed an apparatus similar to that of Liu et al. [44] to electrospin PVP-DCM solution

FIGURE 2: SEM of PVP fibers created by electrospinning a 5 wt% PVP-DCM solution into N₂ at 298 K and (a) 2.5 MPa; (b) 5 MPa; (c) 7.5 MPa, and (d) simulated binary phase equilibrium for N₂-DCM and air-DCM solutions.

into pressurized CO₂ (at 2, 4, and 8 MPa), but it was unsuccessful in producing hollow or porous PVP fibers. Generally speaking, as CO₂ pressure rises, the diameter of nanofibers increases, and the formation of polymer beads ends. This effect results from rapid evaporation of DCM in CO₂ which influences the polymer solution's concentration and phase separation progress [46]. In addition, the polymer is swelled by scCO₂ [47]. In this vein, Wahyudiono et al. [48] used FT-IR spectroscopy to analyze the polymer product, and they found that the structural properties of PVP fibers do not change after electrospinning in pressurized CO₂. This suggests that near- or scCO₂ offers great potential to improve devolatilization of solvents during electrospinning.

In conclusion, near- or scCO₂-assisted electrospinning has been used to produce hollow and porous fibers. It has been found that the state of the CO₂ affects the miscibility of solvent-CO₂ system and the rate of solution phase separation during the electrospinning jet's flight time [44]. As a result, it is possible to produce fibers with different morphologies by regulating CO₂ pressure and temperature of the electrospinning process.

3. Electrospinning in Compressed Nitrogen (N₂)

3.1. Materials and Methods. Poly(vinylpyrrolidone) (PVP, average molecular weight: 1,300,000) was obtained from Aldrich Chemical Co. Dichloromethane (DCM, ≥99.5%) and ethanol (absolute, ≥99.5%) were purchased from Sigma-Aldrich Chemical Co. (USA). The electrospinning apparatus (developed by Institute of Separation Science & Technology, Erlangen-Nuremberg University, Erlangen, Germany) is identical to that used in our previous work [49].

3.2. Results and Discussions. In our previous study, compressed N₂ was applied as an antisolvent in the electrospinning process, but no hollow or porous PVP fibers were obtained [49]. In this work, there were some supplements to the original efforts, but the same electrospinning apparatus and polymer solutions were employed. It is known that the phase behavior of the experimental solvent in N₂ intimately affects the formation of PVP fibers. However, to date, only the solubility data of N₂ in ethanol has been reported [50].

FIGURE 3: SEM of PVP fibers created by electrospinning a 5 wt% solution into N₂ at 298 K and 0.1 MPa: (a) N₂-ethanol solution; (b) N₂-DCM solution; and (c) simulated binary phase equilibrium for N₂-ethanol and N₂-DCM solutions.

The Peng-Robinson equation of state (EOS) was successfully applied to simulate the phase equilibrium for the binary system of N₂ and the solvent [49]. In this work, ASPEN PLUS 2006 was also used together with the Peng-Robinson EOS for simulating the binary phase behavior.

Figure 2 shows the PVP fibers produced by electrospinning a PVP-DCM solution into compressed N₂. Polymer fibers are seen to fuse with polymer beads at 2.5 MPa and 5 MPa (Figures 2(a) and 2(b)). Figure 2(d) shows that little DCM diffused into the N₂-rich phase and small quantities of N₂ appear near the surface of the jet saturated with DCM under low operating gas pressure. It appeared that there was not sufficient time for the evaporation of DCM before it reached the oppositely charged collector. At 7.5 MPa (Figure 2(c)), PVP fibers readily formed without beads, even though some fibers fused together. This suggested that the jet remained liquid-like when it hit the target [44]. At 7.5 MPa and 298 K, the simulated solubility of N₂ in the DCM-rich phase was found to be about 5 wt%, and the simulated

solubility of DCM in N₂-rich phase was only 2 wt% (Figure 2(d)), which is higher than that at 2.5 MPa and 5 MPa. That is why PVP fibers without beads can be produced at 7.5 MPa, but not at 2.5 MPa and 5 MPa. In addition, the solubility of N₂ in the DCM-rich phase was obviously lower than that of air. This could explain why fibers without beads can be produced under an ambient air environment. In our previous work, the phase equilibrium of CO₂-DCM binary system was simulated [49]. The binary critical pressure at 298 K for the CO₂-DCM system was found to be 6.5 MPa, at which DCM and CO₂ are mutually miscible. However, in this present study, we found that the binary critical pressure of DCM-N₂ and DCM-air systems' is more than 100 MPa, which is higher than the operating pressure used in this study. This fact may explain why porous or hollow fibers can be obtained in a bath of compressed CO₂, but not in N₂ or air.

Since evaporation of the solvent during the electrospinning process changes the viscoelastic properties of

the polymer solutions [51], we chose to use ethanol and DCM in this study. Figure 3 shows the morphology of PVP fibers created from electrospinning PVP-ethanol and PVP-DCM solution into N_2 bath at 298 K and 0.1 MPa. Compared with PVP-ethanol, PVP-DCM system results in a wider distribution of fiber diameters and fewer spindles or beads. Also, the fibers are solid core without any porous structure on the surface (Figure 3(a)). Figure 3(c) shows that the miscibility of N_2 and DCM is obviously better than that of N_2 and ethanol, which may explain why there are fewer beads in N_2 and DCM binary systems. The diffusion of gas into the polymer jet may induce phase separation and some special internal structures (hollow or porous). However, there is no binary critical pressure, under which the composition in liquid and vapor is similar, even though the pressure is higher than 200 MPa (Figure 3(c)). The relative immiscibility of both binary systems demonstrates why porous or hollow fibers cannot be produced in compressed N_2 . The binary critical pressure at 298 K for CO_2 -DCM is about 6 MPa, and for CO_2 -ethanol is 6.5 MPa, which indicates that the two systems are miscible, and that the diffusion of CO_2 into polymer solution jet easily induces phase separation [49].

Based on the experimental results and phase equilibrium simulation, it can be concluded that N_2 is not a good choice as an antisolvent for producing hollow or porous nanofibers. The miscibility of the solvent in near-critical or supercritical fluids has an important influence on the inner structure of polymer fibers.

4. Conclusions and Perspectives

Electrospinning is one of the most popular methods for producing polymer nanofibers. Supercritical fluid-assisted electrospinning is still a new process, representing an evolution of traditional electrospinning. This new method is advancing the techniques for producing hollow or porous nanofibers in a single step. The fibers' morphology can be easily controlled by regulating the temperature and pressure of supercritical fluids. It can completely eliminate employment of an organic solvent, as demonstrated by the work of Levit and Tepper [40].

In the future, it is conceivable that the use of supercritical fluid-assisted electrospinning to produce nanofibers with specific microstructures will have great impact on technologies such as, filtration, tissue engineering, and drug delivery. It has been shown that the phase behavior of the solvent and polymer in supercritical fluids has great influences on the morphologies of the fibers. Consequently, more fundamental efforts must be exerted in exploiting phase separation under the supercritical conditions. This work provides the necessary information for designing electrospinning processes in supercritical fluids.

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