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Fabrication of Micro-Hollow Fiber by Electrospinning Process in Near-Critical Carbon Dioxide

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Abstract. Electrospinning is a simple technique that has gained much attention because of its capability and feasibility in the fabrication of large quantities of fibers from polymer with diameters ranging in nano-microscale. These fibers provided high surface area to volume ratios, and it was of considerable interest for many applications, such as nanoparticle carriers in controlled release, scaffolds in tissue engineering, wound dressings, military wear with chemical and biological toxin-resistance, nanofibrous membranes or filters, and electronic sensors. Recently there has been a great deal of progress in the potential applications of hollow fibers in microfluids, photonics, and energy storage. In this work, electrospinning was conducted under high-pressure carbon dioxide (CO_2) to reduce the viscosity of polymer solution. The experiments were conducted at 313 K and ~8.0 MPa. Polymer solution containing 5 wt% polymers which prepared in dichloromethane (DCM) with polyvinylpyrrolidone (PVP) to poly-L-lactic acid (PLLA) ratio 80:20 was used as a feed solution. The applied voltage was 15 kV and the distance of nozzle and collector was 8 cm. The morphology and structure of the fibers produced were observed using scanning electron microscopy (SEM). Under pressurized CO_2, PVP electrospun was produced without bead formation with diameter ranges of 608.50 - 7943.19 nm. These behaviors hold the potential to considerably improve devolatilization electrospinning processes.

Keywords: Electrospinning, Hollow fibers, Sub and Supercritical CO_2, Polyvinylpyrolidone (PVP), Dichloromethane (DCM).
PACS: 87.85.jj

INTRODUCTION

Since a high voltage electric field between a nozzle containing a polymer solution and a ground collector, electrospinning is a unique process by which ultrafine fibers with diameter ranging from nanometers to micrometers can be prepared [1-6]. This process is also a simple and low-cost method for manufacturing polymer ultrafine fibers. However, there is a number of processing parameters can greatly influence the properties of the generated fibers, such as viscoelastic force and surface tension which has been found to depend on solution concentration [7-10]. Recently there has been a great deal of progress in the potential applications of hollow fibers in microfluids, photonics, and energy storage [2,3,6,11,12]. However, the fabrication of hollow fibers was still by template processes or using coaxial capillary.

Supercritical fluid can be defined as a substance for which both pressure and temperature are above the critical point. The special combination of gas-like viscosity and liquid-like density of a supercritical fluid makes it an excellent solvent for various applications. Supercritical fluids have been used successfully as solvents, antisolvents, or plasticizers in polymer processings; e.g., polymer modification, polymer composites, polymer blending, microcellular foaming, particle production, and in polymer synthesis [9,10,12,13]. Carbon dioxide (CO_2) is the most commonly used supercritical fluid because of its low critical temperature (T_c = 304 K) and pressure (P_c = 7.38 MPa), low toxicity and high purity at a low cost. It was a good solvent for many nonpolar compounds and polymers. Its solvent power depends on temperature and pressure and also on weak interactions with the chain groups in the polymer.

Furthermore, it is non-flammable and its use does not contribute to the net global warming effect. Being a gas under ambient conditions favours its easy removal from polymeric products, thus saving costs on other secondary operations such as drying and solvent removal.

In this work, polymer solution containing PVP and PLLA will be electrospunned under pressurized CO_2 to produce hollow fibers. PVP is an environmental friendly synthetic polymer, with good performance and biocompatibility. PVP exhibits unique properties, including solubility in water or in organic solvent. It has also very low toxicity, high complexing ability, good film forming characteristics and adhesive properties. Therefore PVP is widely used as excipients and is particularly suited to the preparation of solid dispersions for improving the dissolution rates of poorly water-soluble drugs in traditional pharmaceutical technologies [14-16] PLLA is also one of the most promising biodegradable polymers owing to its mechanical property profile, thermoplastic processibility and biological properties, such as biocompatibility and biodegradability. This polymer has been approved by the Federal Drug Administration (FDA, USA) for use as a suture material because of features that offer crucial advantages [17]. Due to its good biocompatibility, biodegradability, and minimal inflammatory reaction, PVP and PLLA were used to prepare composite material. However, the application of PLLA fiber in biomedical materials was hindered by its hydrophobicity. Therefore, PVP might improve hydrophilicity of PLLA which increasingly used as the scaffold of tissue engineering by the blends of them.

EXPERIMENTAL SECTION

PVP (MW 1,300,000) and PLLA (MW 300,000) were purchased from Sigma-Aldrich and used as received. As a solution solvent, DCM (99.0%) was obtained from Wako Pure Chemical Industries, and was used without further purification. As a polymer solution, PVP and PLLA were blended in DCM at a concentration of 5 wt%.

The main apparatus consisted of a nonconductive PEEK autoclave (AKICO PEEK) including cartridge heaters coupled with an electric fan, a high voltage (HV) power supply (Matsusada Precision HARb-30P1), a high pressure pump (JASCO PU-1586), a high pressure syringe pump (Harvard Apparatus PHD-Ultra 4400), a back-pressure regulator (BPR; AKICO HPB-450 SUS-316), and a stainless steel syringe with a volume of 8 mL. The PEEK autoclave consisted of two stainless steel flanges and a PEEK vessel with a 6.0 cm inner diameter, 15.0 cm outer diameter, and 20.0 cm length. One flange was connected by a high voltage power supply as an anode electrode; the other flange was used as a cathode electrode to collect fiber products and was wrapped with aluminium foil. The tip-to-collector distance was 8 cm. The detailed experimental setup and procedure have been described extensively elsewhere [3-6]. The flow rate of polymer solution was 0.05 mL/min. The experiments were carried out at 15 min. In order to provide more reliable results, each experiment was conducted two to four times.

The morphologies of the electrospun fibers were observed using a scanning electron microscope (Hitachi S4300) after gold coating and the fiber diameter was measured from the SEM image using image analyzer software (Image J 1.42).

RESULTS AND DISCUSSION

Figure 1 showed SEM images of fibers obtained at room temperature and at various CO_2 pressures with a power supply of 15 kV. One of the challenges faced when applying electrospinning fiber formation to the surface of a collector is solvent evaporation. In this case, DCM as a polymer solvent was removed before the solution achieved the target within the short distance between the nozzle and collector. At room temperature (a), the fibers have been generated clearly; however, the polymer solvent seems clear, resulting in the wet appearance of the fibers obtained. It indicates that the evaporation process of polymer solvent was slow. On the contrary, the fibers produced under pressurized CO_2 (b-d) were dry, with no remaining apparent polymer solvent; this indicates that CO_2 may assist the evaporation process of the polymer solvent by depressurization at the end of the experiment, allowing the evaporation of the polymer solvent to occur more quickly.
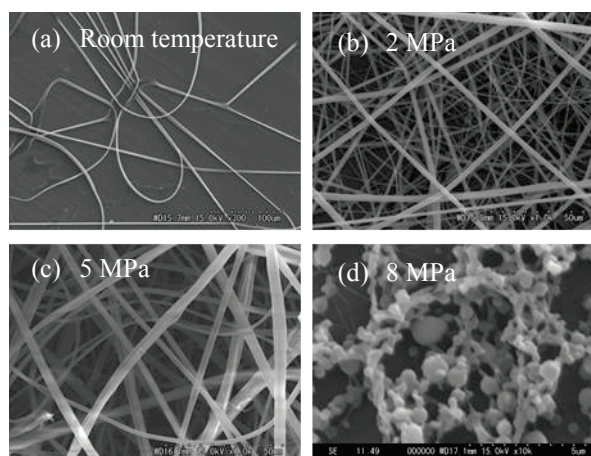
FIGURE 1. SEM images of fiber obtained.

As shown in Figure 2, when the pressures of CO_2 increased, the diameter of PVP fibers seemed to increase in tandem with the pressures of CO_2. This may be due to an increase in the solubility of the polymer solvent in CO_2 which subsequently affected the concentration of polymer. The CO_2 apparently had sufficient affinity to carry a portion of the DCM. As the pressure of the CO_2 increased, the amount of DCM displaced increased [18]. This is, of course, beneficial in terms of removing the solvent from the polymer. Some reports have shown that, within the optimal range of polymer concentrations, fiber diameter increases with increasing polymer concentration [19,20]. Deitzel et al. reported that the diameters of fibers electrospun from polyethylene oxide (PEO)/water solution increased with increasing polymer concentration according to a power law relationship [19]. Megelski et al. also suggested that by increasing the concentration of polystyrene/tetrahydrofuran (THF) solution, the fiber diameters increased and the distribution of pore sizes narrowed [20]. When the experiments were prepared at 8 MPa [Figure 1(c)], the particle in nano-microscale was almost formed although the chain among of them still occurred. This may be attributable to the fact that, under these conditions, temperature and pressure are two competing effects influencing physical and chemical properties of CO_2, which commonly intermediates between gas and liquid states. An increase in pressure resulted in an increase in the CO_2 density. Hence, it induced an increase in the acceleration of the mass transfer of PVP solution in supercritical CO_2. James et al. explained that the reaction can be run either in the presence of the supercritical CO_2 solution or subsequent to removal of the solution by depressurization [21].

Supercritical CO_2 offers several distinct advantages; for example, it increases diffusion rates of penetrants in solid polymers by manipulating temperature and pressure. CO_2 is a gas at atmospheric pressure; thus, the solvent will rapidly dissipate upon release of pressure, causing the electrospun to break apart. Therefore, processing parameters such as temperature and pressure played an important role in determining electrospun morphology by electrospinning at near and supercritical CO_2. The increase in pressure led the diffusion coefficient of the supercritical CO2 to be comparable to the high volumetric expansion of DCM, causing a fast diffusion of CO_2 into the solvent and a fast precipitation. As a result, particles were not precipitated individually; this led to bigger particle size and heavier agglomeration [22].
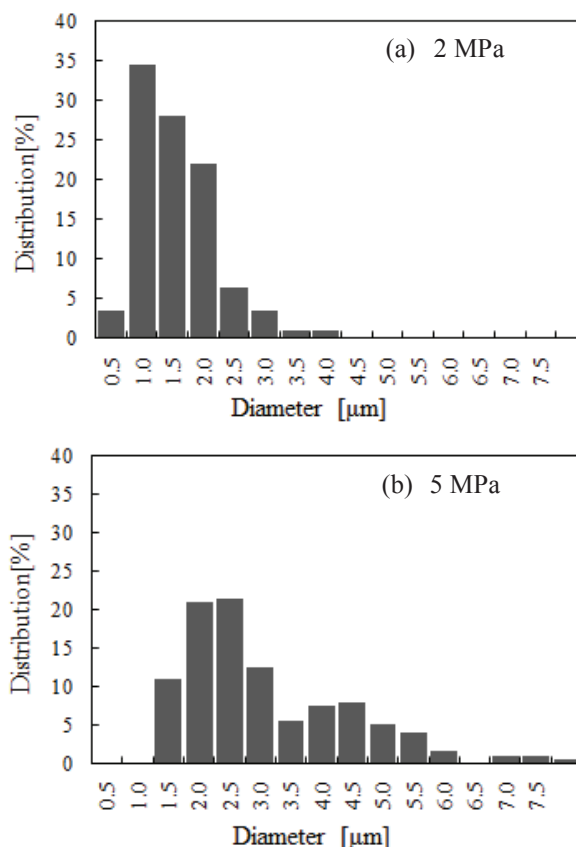

FIGURE 2. Diameter distribution of fibers. They are produced at 2 and 5 MPa of CO_2 pressures with 15 kV of power supply.

Figure 3 shows the morphology of the electrospun fibers obtained when the electrospinning process was performed at subcritical condition of CO_2. Some of these fibers are cylindrical while other fibers seem a litle flattened. It is most likely due to the collapse of rapidly solidified outer shell of electrospun jets. The skin had little influence during the early part of the jet path, where the jet diameter was much larger than the thickness of the skin. Another possible mechanism is non-axisymmetric jet instability originating from a perturbation of jet cross-sectional shape. When they were cut with a blade to investigate the internal fiber morphology, some of them have multiple pores. Porosity could possibly occur by occlusion of the solvent phase as the fibers agglomerate. Another perhaps more likely possibility is that the solvent phase forms porous regions by nucleation and growth in the polymer rich phase as more CO_2 is transferred into the fibers. The depressurization ensures that the fibers retain their porous nature without collapsing or foaming [23]. Watkins and McCarthy reported also that the presence of CO_2 could remove solvents from polymer blends by depressurization [21]. They

described that the infusion of CO_2 into a variety of semicrystalline and glassy polymer substrates and thermally-initiated radical polymerizations within the swollen substrates to generate polystyrene-substrate polymer blends. Cooper was also suggested that microspheres and microballoons of polymer (hollow microspheres) were produced by spraying of polymer in a liquid solvent through a capillary into CO_2 vapor to form droplets, which then fell into liquid CO_2 where they were rapidly dried and vitrified [24]. In addition, annealling leads to a decomposition of PLLA but also to a flow out of the blend fibers in the areas between PVP fibers. Therefore, the fibers obtained become porous or hollow structure in asymmetrically.
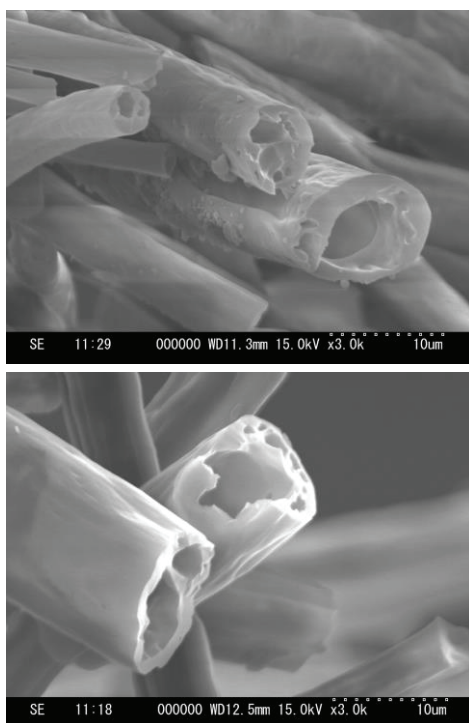
FIGURE 3. SEM cross-sectional view of a fiber obtained at 5 MPa of CO_2 pressure with 15 kV of power supply.

CONCLUSIONS

The fabrication of electrospun by electrospinning at 15 kV from PVP-PLLA blended solution was studied at a temperature and pressure of 313 K and ~ 8 MPa, respectively. The polymer solution was prepared with a concentration of 5 wt% using DCM as a solvent. The results thus show that the depressurization of CO_2 at the end of experiment assists the removal process of the polymer solvent. In supercritical CO_2 (8.0MPa), particles in nano-microscale (427.19–2593.42 nm diameters) were formed dominantly, although the

chain among them was still present. These behaviors show the potential of near- and supercritical CO_2 to considerably improve devolatilization during electrospinning processes.

REFERENCES

1. Z. M. Huang, Y. Z. Zhang, M. Kotaki and S. Ramakrishna, *Compos. Sci. Technol.* 63, 2223–2253 (2003).
2. J. Doshi and D. H.Reneker, *J. Electrostat,* 35, 151-160 (1995).
3. Wahyudiono , K. Murakami, S. Machmudah, M. Sasaki and M. Goto, *High Pressure Res.: Int. J.* 32, 54-59 (2012).
4. Wahyudiono, K. Murakami, S. Machmudah, M. Sasaki and M. Goto, *Jpn. J. Appl. Phys.* 51, 08HF07 (2012).
5. Wahyudiono, S. Machmudah, S. Okubayashi and M. Goto, *Int. J. Ind. Chem.* 4, 1-6 (2013).
6. Wahyudiono, S. Machmudah, H. Kanda, S. Okubayashi and M. Goto, *Chem. Eng. Process. Process Intensif.* in press.
7. M. Cloupeau and B. Prunet-Foch, *J. Electrostat.* 25, 165-184 (1990).
8. M. M. Demir, I. Yilgor, E. Yilgor, B. Erman, *Polymer* 43, 3303-3309 (2002).
9. P. K. Baumgarten, *J. Colloid and Interface Science* 36, 71-79 (1971).
10. H. Fong, I. Chun and D. H. Reneker, Polymer 40, 4585-4592 (1999).
11. L. Wannatong, A. Sirivat and P. Supaphol, *Polym. Int.* 53, 1851-1859 (2004).
12. S. P. Nalawade, F. Picchioni, J. H. Marsman and L. P. B. M. Janssen, *J. Supercrit. Fluids* 36, 236-244 (2006).
13. B. Bungert, G. Sadowski and W. Arlt, *Ind. Eng. Chem. Res.* 37, 3208-3220 (1998).
14. C. Leuner and J. Dressman, *Eur. J. Pharm. Biopharm.* 50, 47-60 (2007).
15. G. Van den Mooter, P. Augustijns, N. Blaton and R. Kinget, *Int. J. Pharm.* 64, 67-80 (1998).
16. G. Verreck, A. Decorte, K. Heymans, J. C. D. Adriaensen, A. Jacobs, D. Liu, D. Tomasko, A. Arien, J. Peeters, P. Rombaut, G. Van den Mooter and M. E. Brewster, *Eur. J. Pharm. Sci.* 26, 349-358 (2005).
17. B. Gupta,˘ N. Revagade and J. Hilborn, *Prog. Polym. Sci.* 32 455–482 (2007).
18. I. Tsivintzelis, D. Missopolinou, K. Kalogiannis and C. Panayiotou, *Fluid Phase Equilibria* 224, 89-96 (2004).
19. J. M. Deitzel, J. D. Kleinmeyer, J. K. Hirvonen, and N. C. Beck Tan, *Polymer* 42, 8163-8170 (2001).
20. S. Megelski, J. S. Stephens, D. B. Chase, and J. F. Rabolt, *Macromolecules* 35, 8456-8466 (2002).

21. J. W. James and T. J. McCarthy, *Macromolecules* 27, 4845-4847 (1994).
22. A. Z. Chen, Y. Li, F. T. Chau, T. Y. Lau, J. Y. Hua, Z. Zhao and D. K. Mok, *Acta Biomater.* 5, 2913-2919 (2009).
23. D. J. Dixon, R. A. Bodmeier and K. P. Johnston, *AIChE J.* 39, 127-139 (1993).
24. A.I. Cooper, *J. Mater. Chem.* 10, 207-234 (2000).