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Formation of PVP hollow fibers by electrospinning in one-step process at sub and supercritical CO_2

Wahyudiono[a], Siti Machmudah[a,b], Hideki Kanda[a], Satoko Okubayashi[c], Motonobu Goto[a,*]

[a] Department of Chemical Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan
[b] Department of Chemical Engineering, Sepuluh November Institute of Technology, Kampus ITS Sukolilo, Surabaya 60111, Indonesia
[c] Department of Advanced Fibro-Science, Kyoto Institute of Technology, Kyoto 606-8585, Japan

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ABSTRACT

It was well known that electrospinning is one of the simple technical methods for the production of polymer nanoparticles and nanofibers. Various polymers have been successfully electrospun into ultrafine particles and fibers in recent years mostly in solvent solution and some in melt form. In this work, hollow fibers with walls made of organic polymer composites have been formed by electrospinning in a single processing step under pressurized carbon dioxide (CO_2). The experiments were conducted at 313 K and ~8 MPa. The capability and feasibility of this technique was demonstrated by the production of polyvinylpyrrolidone (PVP) fibers whose size and wall thickness could be independently varied by controlling a set of experimental parameters. The PVP fibers had an average pore diameter 2–4 μm. At low pressures (<5 MPa; subcritical conditions), the solid fibers were formed, the baloon-like structures of PVP was formed with increasing pressure of CO_2 at 8 MPa (supercritical condition)

1. Introduction

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 [1–8]. 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 [1,9,10]. Recently there has been a great deal of progress in the potential applications of hollow fibers in microfluids, photonics, and energy storage [3,11–13]. However, the fabrication of hollow fibers was still by template processes or using coaxial capillary. In this case, the hollow fibers are produced by electrospinning and then coated with a precursor material which prepared by various deposition methods. Subsequently, the inner section of electrospun nanofiber is removed by selective dissolution or thermal degradation, and the hollow fibers can be obtained. This template process only works best for relatively short structures because the overlapping or entanglement between long, flexible templates inevitably causes interconnections between the resulting fibers [14–17]. In the coaxial electrospinning process, two different solutions are spun simultaneously, using a spinneret with two coaxial capillaries, to produce core/shell fibers. The core of the above fibers is then selectively removed, and hollow fibers are formed [18–22]. There were some difficulties on these processes, such as the choosing of preferable a core solution consisting of a nonsolvent to the shell polymer so that a solid film can be instantaneously formed at the interface and how to accurately control electrospinning parameters, and so forth. It causes the limitation of applied materials which used as starting materials especially when a water-soluble polymer was incorporated in the inner core. It was also noted that the equipment design and electrohydrodynamic behaviors of these process were complex.

In the present work, the one step generation of PVP hollow fibers by electrospinning under pressurized CO_2 would be described. 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 are widely used as excipients and are particularly suited to the preparation of solid dispersions for improving the dissolution rates of poorly water-soluble drugs in traditional pharmaceutical technologies [23–25]. As a starting material, PVP was dissolved in dichloromethane (DCM) and directly electrospuned at sub and supercritical CO_2. It was well known that sub and supercritical CO_2 is a very poor solvent for virtually polymers [26], even, PVP was not dissolved in pure CO_2 up to 480 K and 290 MPa [27,28],

* Corresponding author. Tel.: +81 52 789 3392; fax: +81 52 789 3392.
E-mail address: mgoto@nuce.nagoya-u.ac.jp (M. Goto).

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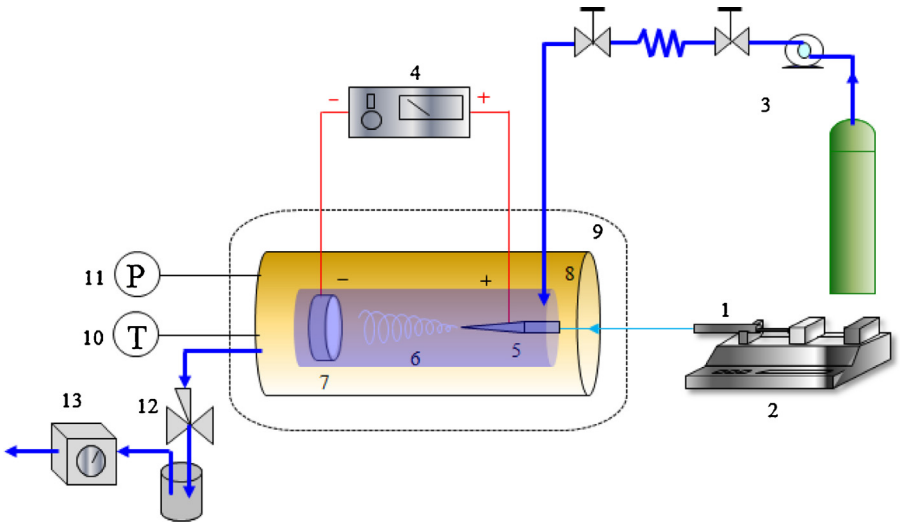

Fig. 1. Schematic diagram of the electrospinning system. (1. Polymer solution; 2. Syringe pump; 3. CO_2 cylinder & pre-heater; 4. High voltage power source; 5. Nozzle; 6. Polymer jet/fiber; 7. Collector; 8. PEEK autoclave; 9. Heater; 10. Temperature monitor; 11. Pressure gauge; 12. Back Pressure Regulator (BPR); 13. Flow-meter).

while at the same operating conditions CO_2 can solubilize most organic solvents, such as acids, alcohols, and other low volatility solvents. The phase compositions for the system CO_2-DCM at various temperatures and pressures was reported by previous researcher [29]. The CO_2 apparently had sufficient affinity to carry a portion of the DCM. As the pressure of the CO_2 was increased the amount of DCM displaced increased. This is, of course, a beneficial effect in terms of removing the solvent from the polymer. Shen et al. [30] introduced the application of CO_2 as an electrospinning processing aid at near-critical point to create fibers polymer. They used 6.5 wt% PVP in DCM as a polymer solution feed with 20 kV peak voltage applied. At 3.45, 4.96, and 5.10 MPa, the fibers spun which had porous internal structure with a coherent external skin have produced clearly. Similar experiments with 6.5 wt% PVP in DCM in supercritical CO_2 resulted also the fibers spun with porous internal structure [31]. Liu et al. [31] concluded that the fibers created with 2.5 cm distance of the nozzle-to-collector had a much different morphology than the fibers obtained with three times longer nozzle-to-collector distance (8.5 cm) which housed in a nonconductive poly(ether ether ketone) (PEEK) tube. They reported also that the polymer jet experiences longer flight times due to the longer nozzle-to-collector distance, which allows more time for the fibers to stretch and elongate before depositing on the collector.

2. Experimental

2.1. Materials

PVP (MW 1,300,000) was 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 was dissolved in DCM at a concentration of 4 wt%. This concentration was selected to accomplish the previous researcher's reports [30,31]

2.2. Experimental setup and procedure

Fig. 1 shows our apparatus for electrospinning under pressurized CO_2. 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 aluminum foil. The tip-to-collector distance was 8 cm. Prior to electrospinning (Fig. 1), a nonconductive PEEK vessel was heated to a desired temperature of 313 K (in fact the temperature ranges were 310–318 K). A thermocouple was inserted in the inside of PEEK vessel and contacted directly with the space of PEEK vessel to control the temperature electrospinning process. K-type thermocouples were also set into the PEEK vessel wall to measure the radial temperature distribution. After the desired temperature was reached, CO_2 is pumped into the PEEK vessel through PEEK capillary tube to a desired pressure. A BPR was used to maintain a constant pressure. The polymer solution was injected into PEEK vessel when the desired condition was reached. High pressure stainless steel syringe which placed in the high pressure syringe pump was used to inject polymer solution via PEEK capillary tube. The flow rate of polymer solution was 0.05 mL/min. At the same time, the high voltage power supply was applied to generate electrostatic force. In this apparatus, the polymer solution and CO_2 was transferred separately through the nozzle which placed in the stainless steel flange (anode electrode). The experiments were carried out at 15 min. In order to provide more reliable results, each experiment was conducted two to four times.

2.3. Fibers characterization

The morphologies of the electrospun fibers were observed using a scanning electron microscope (SEM; JEOL JSM-6390LV) after gold coating and the fiber diameter was measured from the SEM image using image analyzer software (ImageJ 1.42). It was well known that SEM had capability for detecting fiber diameters and morphologies, but the resolution is lost at extreme magnifications. Also, SEM requires the samples to be electrically conductive, therefore, for most of the electrospun polymers produced, a gold or platinum coating must be applied that may alter the diameter readings at higher magnifications. However, SEM remains a quick method for observing the fibers produced and it requires a very small sample size to operate.