ELECTROSPINNING IN NEAR-CRITICAL AND SUPERCRITICAL FLUIDS

Liu, K, Wu, Y, and M. A. McHugh*, Department of Chemical and Life Science Engineering, Virginia Commonwealth University, 601 W. Main St., Richmond, VA 23284 USA, mmchugh@vcu.edu, 804-828-3648

Electrospinning (ES) is coupled with PCA, precipitation with a compressed fluid antisolvent (PCA), to create a hybrid technique, ES-PCA, capable of creating micro- and nano-size polymeric fibers from polymers that are difficult to electrospin in any other way. The formation of internal fiber microstructure is controlled by spinning into a CO_2 bath at different operating pressures and temperatures to rapidly remove the polymeric solvent and, thus, create the fiber morphology. The benefit of this ES-PCA process is that interesting fiber morphologies can be created at pressures less than 135 bar and at temperatures well below 100 °C. Typically solid-core polymeric fibers are created by electrospinning a polymer-liquid solvent solution at ambient conditions although it is possible to create hollow-core fibers if a co-axial nozzle is used in the spinning process. Alternatively, it is possible to use the ES-PCA process to create fibers with an open cell microstructure or even hollow core fibers in near-critical CO_2 using just a single nozzle.

INTRODUCTION

There are numerous reviews available on the electrospinning of polymer solutions to make nanofibers with a desired structure, morphology, and orientation [see, for example, 1, 2]. Although there has been a great deal of progress with electrospinning technology, it still remains a challenge to electrospin highly refractory polymers for several reasons. Many times refractory polymers form very high solution viscosities that will clog the spinning nozzle. In addition, typically very nonvolatile solvents are needed to dissolve a refractory polymer and then it becomes difficult to remove the solvent from the polymer solution jet to create the fiber. Some success at processing refractory polymers has been realized by electrospinning at high-temperatures, but high-temperature electrospinning has its own challenges since fibers are most easily formed at operating temperatures below the glass transition (T_g) or melting temperatures. The present study describes the application of near-critical CO_2 as an electrospinning processing aid to create fibers with novel morphology readily varied by adjusting the operating pressure and temperature.

There is continued interest in using supercritical fluid (SCF) solvents to process polymers for a variety of market applications [3-7]. However, it has been shown that many times it takes kilobar pressures to dissolve most polymers in an SCF solvent [8]. Rather than operate at kilobar pressures and try and dissolve the polymer, the ES-PCA process described in this talk takes advantage of the high solubility of an SCF solvent in most polymer-solvent solutions. In this case the polymer-solvent-SCF solvent solution now has a very modest solution viscosity so that it is possible to electrospin with very small diameter nozzles. Another characteristic of the ES-PCA process is that the polymer solution jet is electrospun into a bath of SCF solvent which is used to extract the low molecular weight solvent from the solution jet. Again, no attempt is made to dissolve the polymer from the solution jet. By way of example of the ES-PCA process, results are shown when using near-critical CO_2 to electrospin poly(vinyl pyrrolidone) (PVP) from PVP-dichloromethane (DCM) solutions. The formation of PVP fibers is directly related to the DCM-CO_2 phase behavior since the

electrospinning operating pressures are well below those needed to dissolve neat PVP in CO_2. Details on the apparatus used for the ES-PCA process will be described in the talk. An exemplary result of the process is presented here with more details on other polymer-solvent systems presented in the talk.

RESULTS

There are a variety of process variables that can be fixed during the electrospinning process including the applied voltage, the nozzle diameter, the distance from the nozzle to the target, the operating temperature and pressure, the concentration of polymer in solution, and the flow rate of solution to the nozzle. For the example presented here the applied voltage is set at 20 kV and the nozzle to target distance is very short at ~2.5 cm. Although a variety of SCF solvents could be used in this ES-PCA process, here only results with CO_2 are presented. The solutions are 6.5 wt% poly(vinyl pyrrolidone) (PVP, weight average molecular weight of 1,300,000, T_g, equal to 160°C) in DCM. The polymer solution jet is ejected from the nozzle directly into a bath of CO_2 so that the ES-PCA process can be considered as a type of wet-spinning process. In many instances researchers will add salts to the polymer-solvent solutions to increase the ability of the solution jet to hold a charge. In the case described here, the PVP-DCM solution is not completely insulating and weak or local charges are expected to exist on the C, H, and Cl atoms in DCM and the N and O atoms in PVP due to the weak acidity of DCM and to PVP-DCM interactions. The local negative charges will be drawn by the electric field to the target, which results in a polymer jet ejecting from the nozzle and traveling to the target.

Figure 1 shows the morphology of the electrospun PVP fibers obtained when spinning directly into a bath of subcritical CO_2 at 22°C. At a CO_2 pressure of 14 bar the PVP fibers have a solid-core structure similar to the fibers formed at ambient conditions [9]. The CO_2 has enough solvent power, even at this very low pressure, to extract DCM as the jet flies to the target, so that a dry fiber is produced. As the CO_2 bath pressure is increased to 35 and ~50 bar, the fibers now have a porous internal structure. The fiber diameters in Figure 1 are quite large, on the order of 20 to 30 μm, likely due to the short nozzle to target distance used in these experiments. A newly designed ES cell will be described in the talk that allows for longer nozzle to target distances which results in much thinner fibers on the order of 1 μm or less. When the CO_2 pressure is increased above ~55 bar, the CO_2 extracts the DCM very effectively and the nozzle dries out and clogs with dried PVP polymer. So, in this instance, there is a very small operating range of pressures where fibers are produced.

When the polymer solution jet is ejected into the CO_2 bath, the CO_2 rapidly dissolves into the PVP-DCM mixture and induces a spinodal decomposition phase separation that sets up the initial polymer-rich, liquid network structure [10]. It is possible to estimate roughly the time it takes for CO_2 to diffuse into the liquid solution jet in the ES-PCA process. Consider the worst case scenario for a fiber with a radius of approximately 10 μm. It takes less than 0.06 seconds for the mass uptake of CO_2 to reach 50% of its final value in a cylindrical, PVP-DCM liquid-like jet assuming the diffusion coefficient (D_{CO_2}) for CO_2 is on the order of 10^{-6} cm^2/s, which is about an order of magnitude lower than that for a gas diffusing into a liquid. For a $D_{CO_2} = 10^{-7}$ cm^2/s, CO_2 reaches 50% of its final value in less than 0.6 seconds. At the same time it is important to recognize that the polymer solution jet rapidly develops a skin as DCM is extracted from the surface of the jet. At the jet surface the plasticizing effect of DCM is diminished and the effective T_g of PVP quickly surpasses the operating temperature so the polymer vitrifies into a skin. Although the CO_2 that replaces the DCM in the liquid jet also

lowers the effective T_g of PVP, the plasticizing effect of CO_2 is much less than that of DCM. A porous, open-cell structure is set up in the interior of the fiber as the bubbles of CO_2 begin to coalesce in the PVP-DCM solution. The coalesence and growth of the bubbles is countered by the polymer coating the outside of the bubbles. The CO_2 also has the effect of lowering the interfacial tension of the PVP-DCM-CO_2 phase relative to the CO_2-DCM phase which means that the CO_2 bubbles can more easily coalesce when they contact one another. As CO_2 extracts more and more DCM, the open-cell structure is locked into place since the operating temperature is now well below the T_g of PVP, which is 160 °C. It is shown with this example that very modest pressures are needed to tailor a specific fiber internal morphology when using a near-critical fluid, such as CO_2. The effective removal of the solvent from the polymer solution depends on the partitioning of the liquid solvent between the PVP-rich phase and the CO_2-rich phase. Solubility levels will be fixed by the type of intermolecular interactions between the components in each phase. All of these issues will be discussed in more detail in the presentation.

REFERENCES :

[1] Huang, Z.-M.; Zhang, Y.-Z.; Kotaki, M.; Ramakrishna, S. Composites Science and Technology, 63, **2003,** 2223.
[2] Li, D.; Xia, Y. Advanced Materials, 16, **2004,** 1151.
[3] Kendall, J. L.; Canelas, D. A.; Young, J. L.; DeSimone, J. M. Chemical Reviews, 99, **1999,** 543.
[4] Mandel, F. S.; Green, C. D.; Scheibelhoffer, A. S. Method of preparing coating materials. 5,399,597, March 21, 1995.
[5] McHugh, M. A.; Krukonis, V. J., Supercritical Fluid Extraction: Principles and Practice. 2nd ed.; Butterworth-Heinemann: Boston, 1994.
[6] Kazarian, S. G. Polymer Science, Series C, 42, **2000**, 78.
[7] Kikic, I.; Vecchione, F. Current Opinion in Solid State & Materials Science, 7, **2003,** 399.
[8] Kirby, C. F.; McHugh, M. A. Chemical Reviews, 99, **1999,** 565.
[9] Shen, Z., Thompson, B. E., and M. A. McHugh, Macromolecules, 39, **2006**, 8553.
[10] Bognitzki, M.; Czado, W.; Frese, T.; Schaper, A.; Hellwig, M.; Steinhart, M.; Greiner, A.; Wendorff, J. H. Advanced Materials, 13, **2001,** 70.
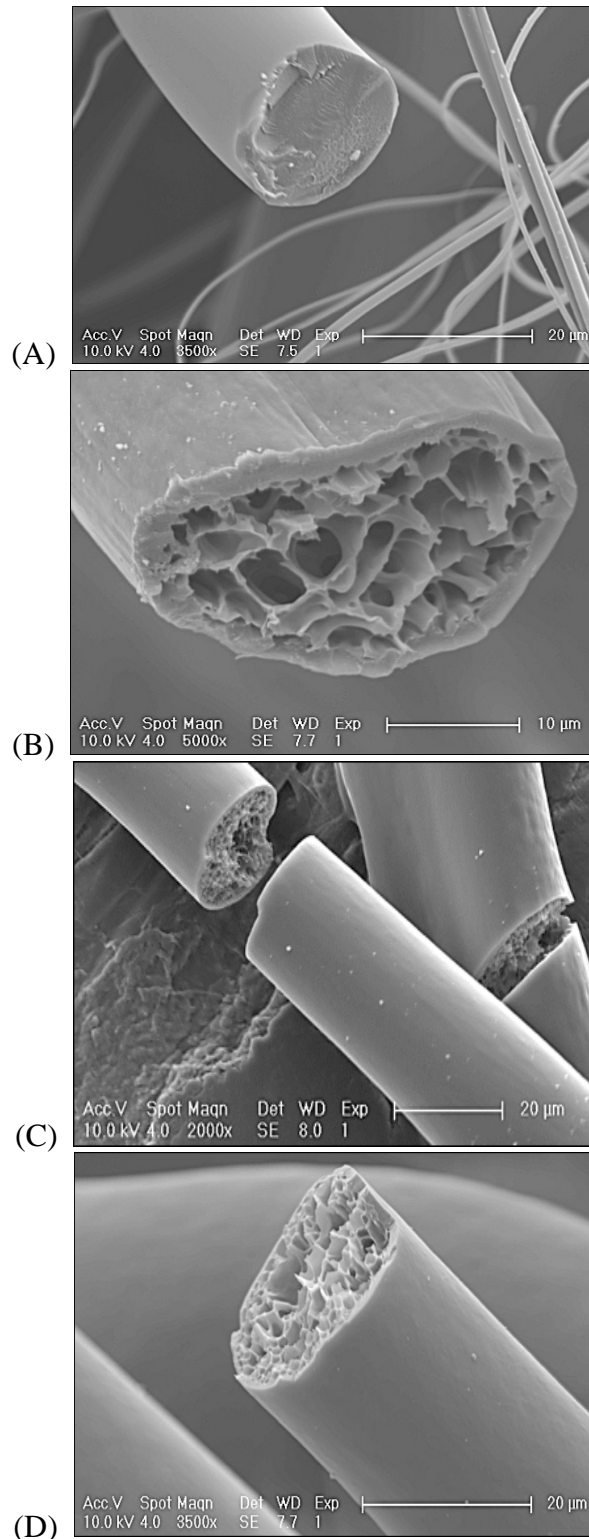
Figure 1 : SEM images of the PVP fiber morphologies obtained by spinning into a bath of pure CO_2 at 22°C and (A) 14, (B) 35, (C) 50, and (D) 52 bar [9]. The solution delivery rate is the same for all three cases.