Controlling Polymer Fiber Diameter in Electrospinning Process

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Statement of Purpose: Electrospinning (ES) is a method used to create micro or sub-micro sized polymer fibers. The fibers are spun from a polymer solution that is exposed to an electrostatic field. In the ES process, fiber diameters and properties are primarily influenced by the viscosity of the solution. In polymer systems this is achieved by either increasing the molecular weight of the polymer or copolymer concentration in solution. We recently reported a novel means of controlling fiber properties in ES process, which is independent of the above-mentioned variable by spinning relatively unstable w/o emulsions (Sy C. and Shastri VP, Proc. Natl. Acad. Sci, USA, 2006 (In Review)). We theorized from the results of this study, that by altering the viscosity of the aqueous phase, fiber diameter may be altered independently of aqueous volume fraction; thus allowing for control over fiber diameter that is completely independent of overall solution viscosity. Using the well-defined glycerol-water binary system, we studied the role of aqueous solution viscosity in the emulsion-based spinning of ethylene-co-vinyl acetate (EVA).

Methods: Poly(ethylene-co-vinyl acetate) (EVA, Elvax 40W, 250kDa) was a generous gift from DuPont (Wilmington, DE). Dichloromethane (99.9% HPLC grade), Triton X-100 (molecular biology grade), glycerol (99.5+%), were all purchased from Sigma-Aldrich (St. Louis, MO). A 7.5 wt% stock solution of EVA was prepared in dichloromethane at. Glycerol-water solution of varying weight fractions (0, 5, 10, 20, 30 and 50 %) glycerol were prepared and mixed with Triton X-100 (10 vol%). The aqueous volume fraction in emulsions was fixed at 15 v/v%. Emulsions of EVA was prepared by vortexing, followed by sonication (Sonic Systems, Danbury, CT) 40% duty cycle, 30 seconds, 30% amplitude). The emulsion was immediately loaded into 3 ml syringe and placed in a syringe pump (Cole-Palmer, Vernon Hills, IL) and fed at a delivery rate of 0.1 ml/min through a 20-gauge blunt tip needle. A grounded target was placed 15cm from the needle and a voltage bias of 15kV (Model RR-30, Gamma High Voltage Research, Ormond Beach FL) was applied. Prior to imaging using SEM (Hitachi S4200), samples were sputter coated with Au-Pd, and the fiber diameters measured using Scion Image (NIH Image) image analysis freeware.

Results/Discussion: The effect of increasing glycerol wt-fraction on EVA fiber diameter is shown in Figure 1. It is clear that electrospun fiber diameters can be influenced independently of aqueous volume fraction in the emulsions and polymer concentration. Example SEM images are shown in Figure 2. An increase in solution viscosity is known to improve stability of the Taylor Cone, thus favoring electrospinning over electrospraying. However, in this study, the change in overall solution viscosity is not expected to be dramatically altered, as increasing weight fraction of glycerol only results in a modest increase in viscosity from ~ 0.8 centipoise at 10 wt% to ~ 4 cps at 50 wt%. More importantly, the changes in the average fiber diameters were statistically significant at each glycerol wt fraction, with p values of ≤ 0.01. An important observation was that the reduction in fiber diameter comes at the expense of more coalescence of fibers due to probably diminished evaporation due to increased system viscosity.

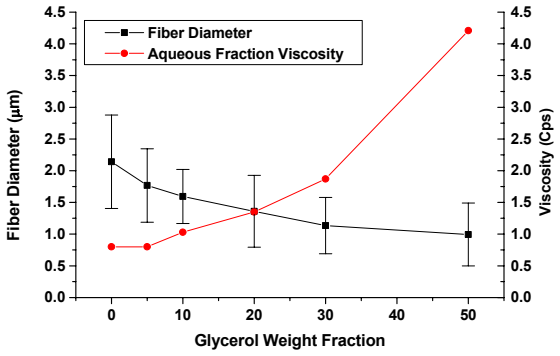

Figure 1: Relationship between diameter of electrospun EVA fibers, glycerol concentration in the aqueous phase, and glycerol solution viscosity.

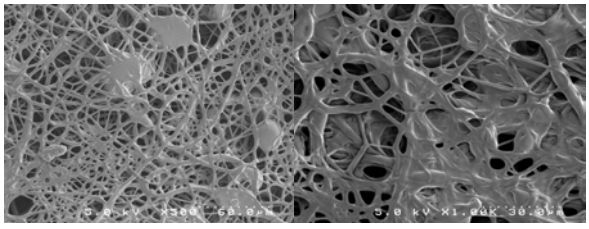

Figure 2: SEM images of EVA fibers. Left: 0% glycerol, Right: 50% Glycerol. (Scale bar: Left: 60 µm, Right: 30 µm)

Conclusions: The present findings open up interesting possibilities with regards to understanding and establishing causative relationships between the various components in an emulsion-based system for ES. More importantly, by using Boger fluids as the aqueous phase, the role of aqueous phase elasticity and deformation in extensional thinning of an evolving electrospinning jet can be elucidated. Such an understanding should pave the way for more predictability in fiber characteristics in the ES of polymers.

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