Reactive Electrospinning of Hydrogel Nanofibers

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Abstract:

Electrospinning has been used to produce networks of hydrogel nanofibers. These fibers were spun from a mixture of monomer, cross-linker and photoinitiator, pre-polymerized to achieve the necessary viscosity. UV irradiation of the fibers in flight allows polymerization and cross-linking of the nanofibers prior to collection.

Using this technique, fibers of sub-micron diameter have been produced. The fibers have been characterized by optical microscopy and SEM. Effects of applied voltage, flow rate and needle-substrate spacing have been investigated. In aqueous solution, the swollen fiber network allows efficient mass transport of ions and other dissolved species, as well as serving as a support structure; these properties make hydrogel nanofibers a good candidate for biomedical applications.

Introduction:

Hydrogels are hydrophilic polymer networks swollen with water; the polymer network may be held together via bonding or intermolecular forces. Hydrogels have found wide use with the biomedical field for use in drug delivery, cell and enzyme immobilization, tissue engineering, and optical lenses [1, 2]. One, particular hydrogel, poly(2-hydroxyethyl methacrylate), first proposed for biomedical used in 1960, has seen use in all of these areas [2].

Diffusion through the hydrogel matrix is of particular importance for biological applications [3]. Cells require a supply of nutrients, and a mechanism to remove waste products and enzymes cannot catalyze reactions without a supply of substrate. By increasing the surface area to volume ratio of the matrix, the rate of diffusion can be increased. One method to increase this ratio when working with fibers is to decrease the diameter; hence nanofibers have a higher surface area to volume ratio than a microfiber.

Nanofibers can be produced by several methods; drawing, template synthesis, self-assembly, or electro-spinning. Of these methods, only electrospinning offers a clear path to industrial scale up. Electrospinning uses a high potential, in the kilovolt range, to eject a jet of viscous fluid from a capillary. Traditionally this jet has been a polymer solution or melt which solidifies via solvent evaporation or cooling in flight, resulting in a continuous fiber non-woven mat on the collector [4].

Traditionally, hydrogel structures have been formed in templates or via machining of the polymer in the dry state. Neither of these methods are viable for the production of nanofibers. Electrospinning allows the production of continuous hydrogel nanofibers by spinning a jet of polymer precursor under UV irradiation. The jet consists of monomer, cross-linker and photoinitiator which polymerizes and cross-links in flight. This process uses a chemical reaction during the electrospinning process, hence the term reactive electrospinning.

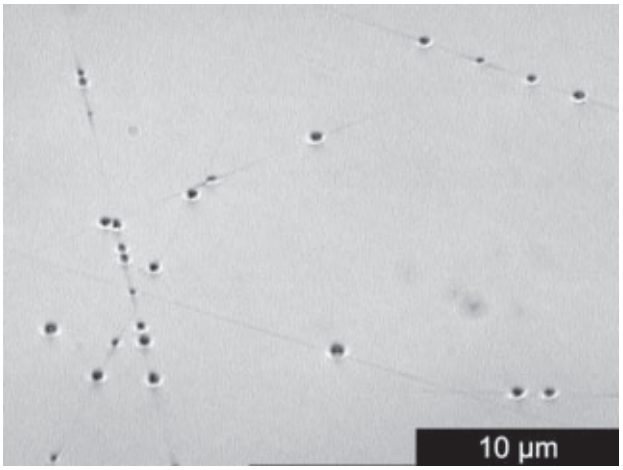
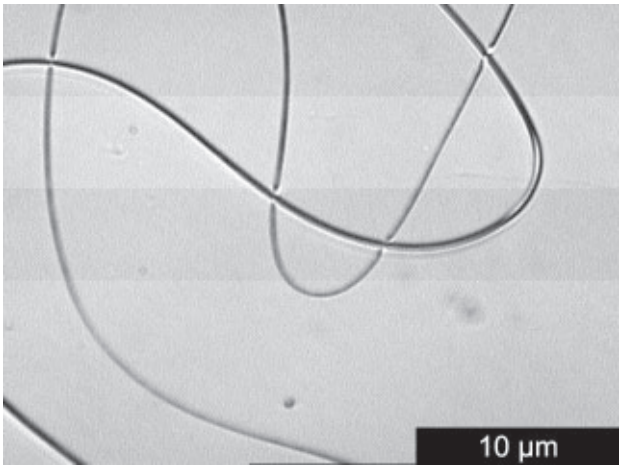


Figure 1, above: 2000x optical image of low viscosity 0% MAA sample (7 kV, 18 cm, 0.0005 mL/min).

Figure 2, below: 2000x optical image of high viscosity 0% MAA sample (7 kV, 18 cm, 0.0010 mL/min).



Experimental Procedure:

2-hydroxyethyl methacrylate (HEMA) and methacrylic acid (MAA) were used as monomers, cross-linked by ethylene glycol dimethacrylate. 2,2'-azobisisobutyronitrile (AIBN) was used for thermal initiated radical polymerization. HEMA, MAA, EGDMA and AIBN were obtained from Aldrich. Final polymerization used Dorocur-1173, a commercial photoinitiator from Ciba Chemical.

Two mixtures were used: HEMA, MAA 0 mol% or 8 mol%; EGDMA 0.3 mol%; AIBN 0.25 mol%; and Dorocur-1173, 4 mol%. These precursor mixtures were heated in a water bath at 78-82°C for four to six minutes. Following removal from the water bath, polymerization was quenched in cold water for approximately two minutes.

A three mL slip tip syringe (Becton-Dickson) with a 30 gauge 1/2 inch needle (Becton-Dickson) was filled to 1.5-2 mL using the previously pre-polymerized mixture. The syringe was placed into a syringe pump (Harvard, PHD 2000) and infused at a rate of 0.0003-0.0007 mL/min. A positive high voltage of ~6-10 kV was applied to the needle tip; the grounded collector was placed 10-25 cm from the needle. UV irradiated during electrospinning and for the 5 minute post-spin cure was supplied by a 200 W UV lamp (Oriel).

Discussion:

A range of fiber diameters are produced ranging from sub-micron to several microns. The large fibers are easily visible under optical microscopy, as shown in Figures 1 and 2.

Electrospinning has a large parameter space. Within this space, some parameters can be easily controlled and their effects qualified, such as applied potential, others such as humidity are more difficult.

In investigating this parameter space, three parameters were varied systematically: applied potential (6-10 kV), tip-to-collector distance (10, 18, 25 cm), and infuse rate (0.0003, 0.0005, 0.0007 mL/min). Unlike infuse rate and applied potential, tip-to-collector distance was always optimized to a single value, 18 cm. 10 cm does not allow sufficient time for polymerization during flight, and 25 cm is too far away to easily attract the fibers. Observed trends where similar to those reported in the literature [5].

Of all of the parameters effecting fiber morphology, the most crucial, yet difficult to control parameter, is viscosity. Viscosity control, using the water bath, is coarse and has poor reproducibility, due to the rapidly changing viscosity as the degree of polymerization increases. Considering two samples, one of low viscosity and one of high viscosity, can demonstrate the importance of this parameter. Figures 1 and 2 show optical micrographs of low and high viscosity samples, respectively. Lower viscosity produces finer beaded fibers, while higher viscosity produces thicker, smoother fibers.

SEM characterization of the produced fibers reveals that fibers were produced with a minimum diameter of 193 nm, shown in Figure 4. This demonstrates that true nanofibers can be produced using reactive electrospinning.

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References:

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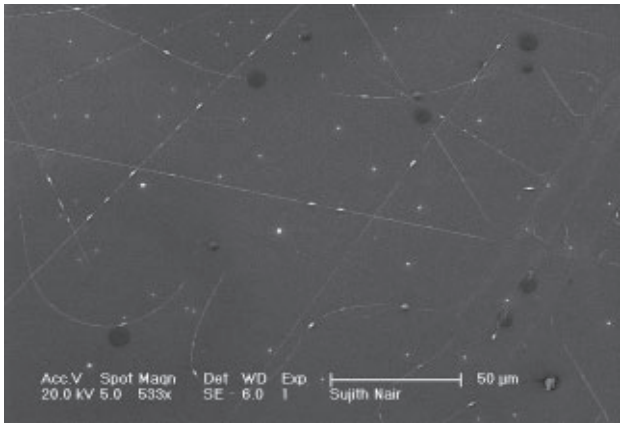

Figure 3, above: SEM of wide view of produced fibers.

Figure 4, below: SEM of smallest produced fiber, 193 nm.