3D Printing Thermosensitive Polymers:
The Development of Filament-Based Direct Writing Melt Electrospinning

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Statement of Purpose:
There are currently many advanced additive manufacturing technologies, but they all have limitations. While electrospinning can produce micron-scale fibers of sensitive polymers, there is little control over the orientation of the fibers. Direct writing melt electrospinning, a hybrid of electrospinning and fused deposition modelling (FDM), gives far greater control over the placement of micron-scale fibers, and has been one of the greatest advancements in biomedical additive manufacturing technology in recent years[1]. Currently, direct writing melt electrospinning systems use a molten polymer cartridge, which can have negative effects on thermosensitive degradable polymers. Our goal was to prototype a filament-based direct writing melt electrospinner to 3D print sensitive degradable polymers at micron-scale resolution.

Methods:
The prototype was based on a Type A Machines Series 1 FDM printer. The print plate was modified to incorporate a 100mm x 100mm copper plate connected to a high voltage generator and charged at +12 kV. A heating block was machined from solid poly(ether ether ketone) to electrically isolate the nozzle, which was directly grounded. Polycaprolactone (PCL) 1.75mm diameter filament was purchased from Monoprice, while tyrosine-derived polyesters, developed at the New Jersey Center for Biomaterials, were extruded into 1.75 mm filament using a modified melt indexer (Tinius Olsen, Horsham, PA).

Samples were printed in 20 mm x 20 mm orthogonal grids with ten superimposed alternating layers, defined by custom-written gcode. PCL was printed at 100˚C and 10 mm offset, while the tyrosine-derived polymer was printed at 120˚C and 5 mm offset.

Results:
With the prototype system, we have succeeded in printing PCL fibers with diameters less than 50 µm in controlled grid geometries (Fig 1A), with a considerable degree of alignment for subsequent layers (Fig 1B), and fusion of stacked fiber-fiber interfaces (Fig 1C) forming a mechanically cohesive unit.
The tyrosine-derived polyester investigated in this project had been developed for melt processing and printing. However, as with all degradable polyesters, the temperature and heating time must be tightly regulated, in this case below 160˚C and under 120 minutes. By processing with filament-based direct writing melt electrospinning, the polymer could be printed at 120˚C with only minutes at elevated temperatures, resulting in no discoloration or significant loss of molecular weight. The fibers produced from this polymer were highly consistent and approximately 10 µm in diameter (Figure 1D,E).

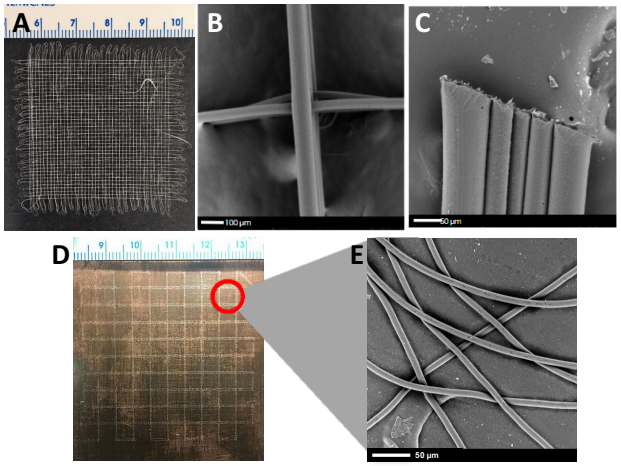

Figure 1. Filament-based direct writing melt electrospinning. ABC) 10-layer PCL grid showing macroscopic morphology (A), and the stacking precision and fusion of the microfibers from above a junction (B) and along an edge (C). DE) Grid of tyrosine-derived polymer fibers showing the macroscopic (D) and microscopic morphology (E).

Preliminary *in vitro* characterization using human dermal fibroblasts grown on the tyrosine-derived polymer microfibers show the adhesion of cells, and the formation of dense extracellular matrix networks within 14 days.

Conclusions:
This work is the first example of filament-based direct writing melt electrospinning. This modification expands the application of this new and exciting additive manufacturing technique to a broader range of biomedically-relevant degradable polymers. PCL and tyrosine-derived polymer microfibers were successfully printed up to 40˚C below their normal processing temperatures with minimal time at high temperatures. Controlled spatial precision permitted the printing of stacked fibers with controlled geometries. Considerable work remains on further reducing the fiber diameter of the existing polymer systems, building a second-generation platform, and exploring additional previously non-printable polymers.

References:
Brown TD. Adv Mater, 2011;23(47): 5651-5657.