Supplementary Information

3D Printing of Poly(vinylidene fluoride-trifluoroethylene): a Poling-Free Technique to Manufacture Flexible and Transparent Piezoelectric Generators

Nick A. Shepelin,[1] Vanessa C. Lussini,[2] Phillip J. Fox,[2] Greg W. Dicinoski,[2] Alexey M. Glushenkov,[3,4] Joseph G. Shapter[5] and Amanda V. Ellis[1]*

[1] Department of Chemical Engineering, The University of Melbourne, Parkville, Victoria 3010, Australia
[2] Note Issue Department, Reserve Bank of Australia, Craigieburn, Victoria 3062, Australia
[3] Research School of Chemistry, The Australian National University, Canberra, ACT 2601, Australia
[4] Research School of Electrical, Energy and Materials Engineering, The Australian National University, Canberra, ACT 2601, Australia
[5] Australian Institute of Bioengineering and Nanotechnology, The University of Queensland, Brisbane, Queensland 4072, Australia
* Corresponding author: Professor Amanda V. Ellis, amanda.ellis@unimelb.edu.au

The solubility of poly(vinylidene fluoride) (PVDF) in a solvent mixture consisting of *N,N*-dimethylformamide (DMF) and acetone was modelled using Hansen[1] solubility parameters reported by Bottino *et al.*[2] as a function of solvent ratios. This was achieved through the use of the root means squared (RMS) error method of the variation in solubility parameters of each solvent and the polymer (shown in Table S1). The distance between the Hansen solubility parameters for PVDF and the solvent mixture with varying acetone volume fraction is shown in Figure S1a, whereby the dashed line at the origin represents the optimal value for the dissolution of PVDF. To the best knowledge of the authors, the solubility parameters of poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE) have not been determined, hence PVDF was used to determine the optimal solvent ratios.

Table S1: Solubility parameters of PVDF and solvents acetone and DMF, as well as the difference in total solubility parameters between PVDF and solvent using the RMS method.

Influence of parameter	δ_d Dispersion	δ_p Dipolar intermolecular	δ_h Hydrogen	δ difference (RMS) $\sqrt{\frac{\sum_{i=d}^{h}\left(\delta_{i,s}-\delta_{i,PVDF}\right)^2}{N_i}}$
PVDF	17.2	12.5	9.2	0.0
Acetone	15.5	10.4	7.0	2.01
DMF	17.4	13.7	11.3	1.4

The RMS variation in solubility parameter ($\delta_{difference}$) was then calculated by Equation S1 for ratios of acetone and DMF in the solvent mixture ranging from 100 vol% DMF to 100 vol% acetone.

$$\delta_{difference} = \sqrt{\frac{\sum_{i=d}^{h}\left([a\delta_{i,DMF}+(1-a)\delta_{i,acetone}]-\delta_{i,PVDF}\right)^2}{N_i}} \tag{S1}$$

Here, a was the relative volume fraction of DMF in the solution mixture and $\delta_{i,DMF}$ and $\delta_{i,acetone}$ were the parameters given in Table S1 for each solvent. The $\delta_{difference}$, the RMS distance of the three solubility parameters, was then plotted as a function of the relative volume fraction resulting in the plot shown in Figure S1b. The dashed line represents the total RMS variation in the solubility parameters between PVDF and the solvent mixture at the commonly used volume fractions of DMF (80 vol%) and acetone (20 vol%).[3] It was noted that the dashed line additionally intercepts the curve at 61 vol% acetone, therefore the range of solvent ratios between 20 vol% and 61 vol% acetone was determined to successfully dissolve the fluoropolymer. Acetone has a significantly higher volatility relative to DMF, hence the solvent ratio used for this work maximized the acetone volume fraction to 60 vol% to decrease the drying time of the polymer upon printing.[4]

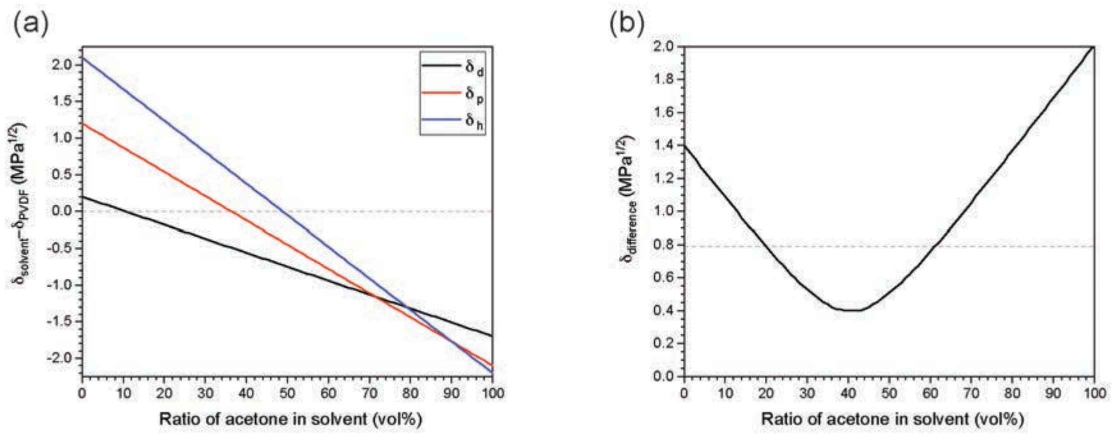

Figure S1: (a) Variation between the Hansen solubility parameters for PVDF and the solvent mixture and (b) RMS difference in solubility parameters for PVDF in a solution mixture consisting of acetone and DMF as a function of acetone volume fraction.

The viscosity of the PVDF-TrFE solutions at concentrations between 20 wt% and 40 wt% in a solvent mixture containing 60 vol% acetone and 40 vol% DMF was measured at shear rates between 0.01 s^{-1} and 1000 s^{-1}, shown in Figure S2.

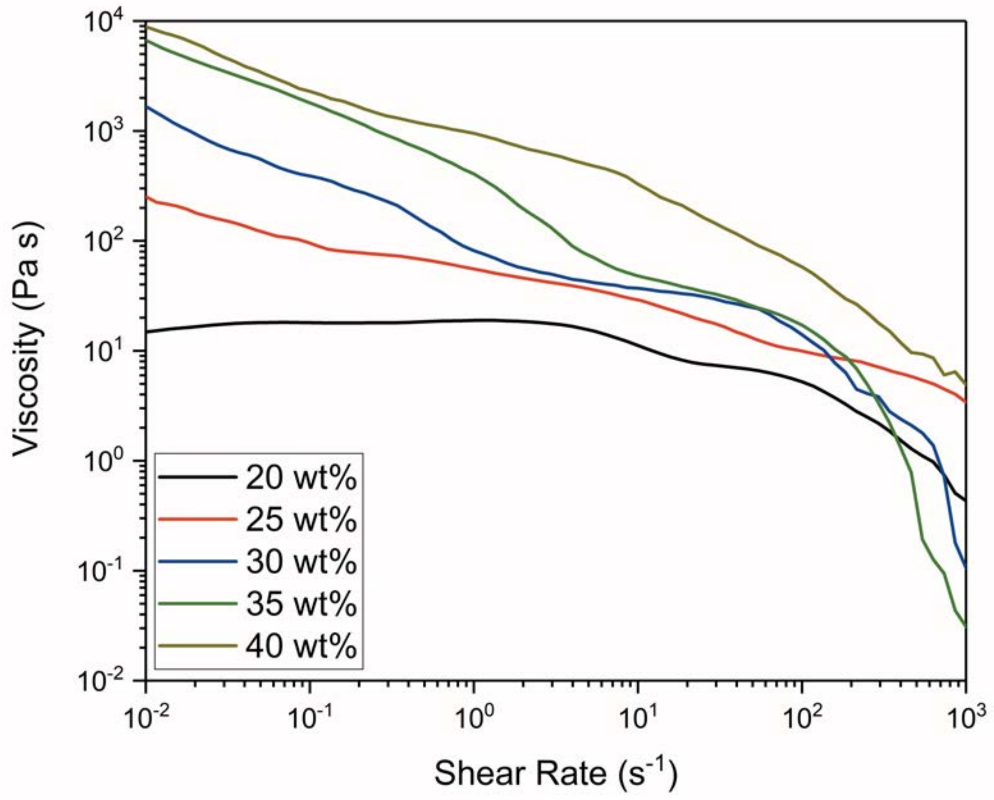

Figure S2: Viscosity of PVDF-TrFE solutions as a function of shear rate for PVDF-TrFE loadings between 20 wt% and 40 wt%.

The optimal printing parameters were investigated experimentally. Figure S3 shows an optical image of structures deposited onto a glass substrate at x-y robot head speeds between 5 mm s^{-1} and 45 mm s^{-1} using a raster pattern with a line spacing of 2 mm. Here, the lamps in the background were used to demonstrate the transparency of the printed structures after drying. Figure S4 shows the optical micrographs of the corner sections of the structures, highlighting the resolution of printing at various speeds.

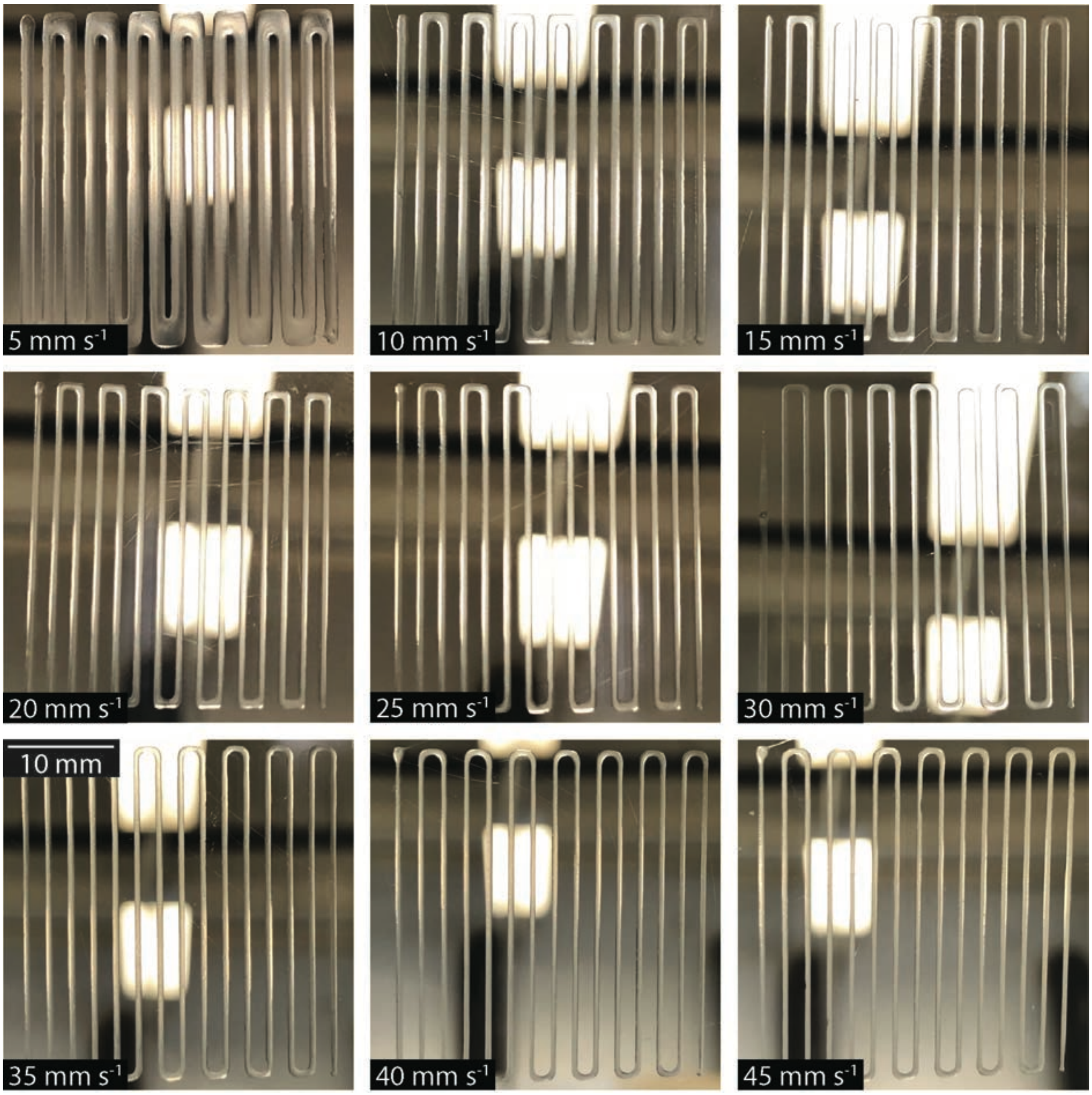

Figure S3: Optical images showing the structures during optimisation of x-y speed of the 3D Bioplotter for the printing of PVDF-TrFE at 30 wt% in solution. The lamps in the background are used to demonstrate the transparency of the printed structures.

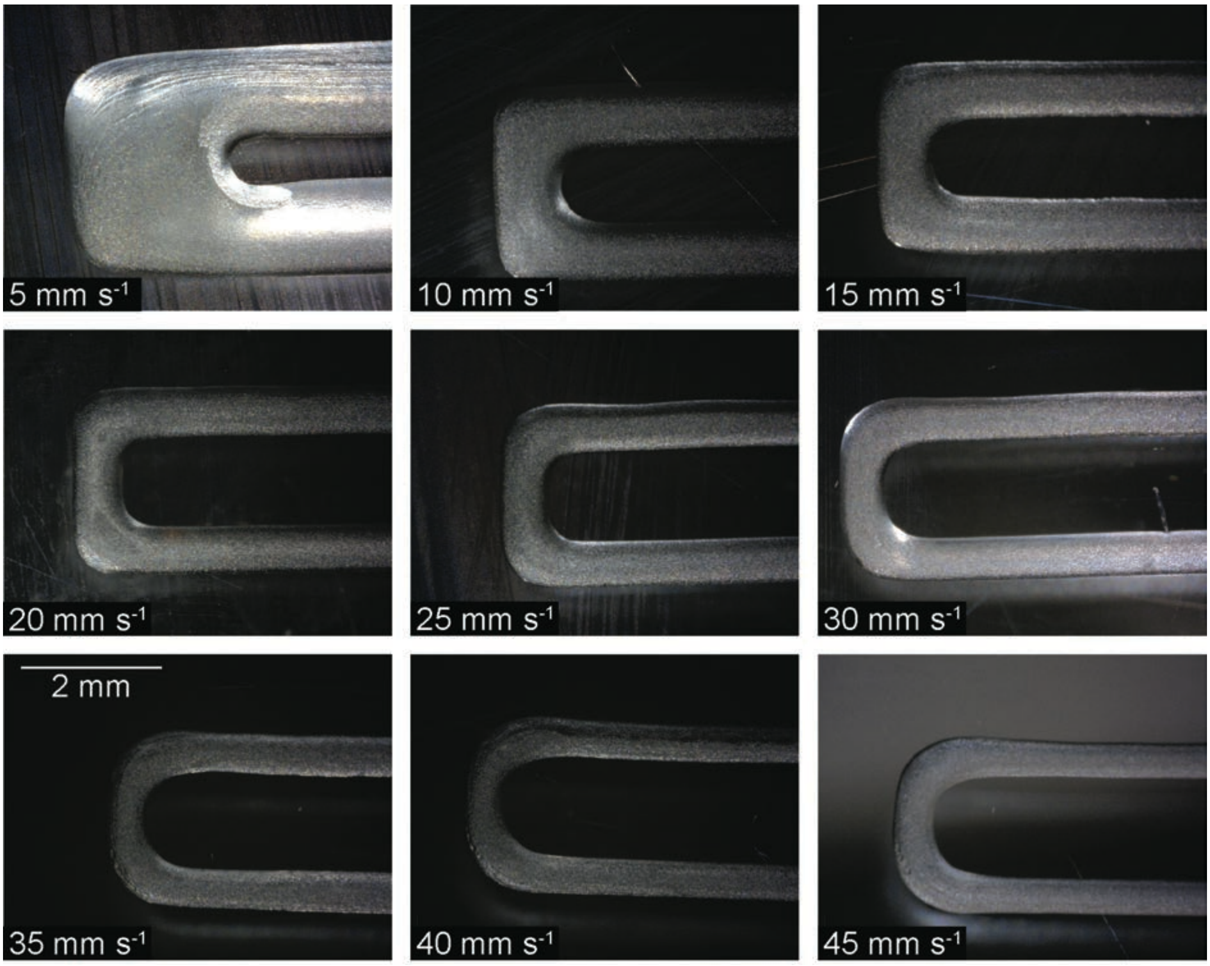

Figure S4: Optical microscope images of the edge of the raster pattern during optimisation of x-y speed of the 3D Bioplotter for the printing of PVDF-TrFE at 30 wt% in solution.

Figure S5 shows the results of the thin film optimization. In this study, the width between lines in the raster pattern was controlled between 1.2 mm (top left) and 0.4 mm (bottom right). The cross-sectional HIM micrograph is shown in Figure S6 for the thin film printed using a 0.4 mm line width for the raster pattern. Here, the thickness was found to be below 40 μm.

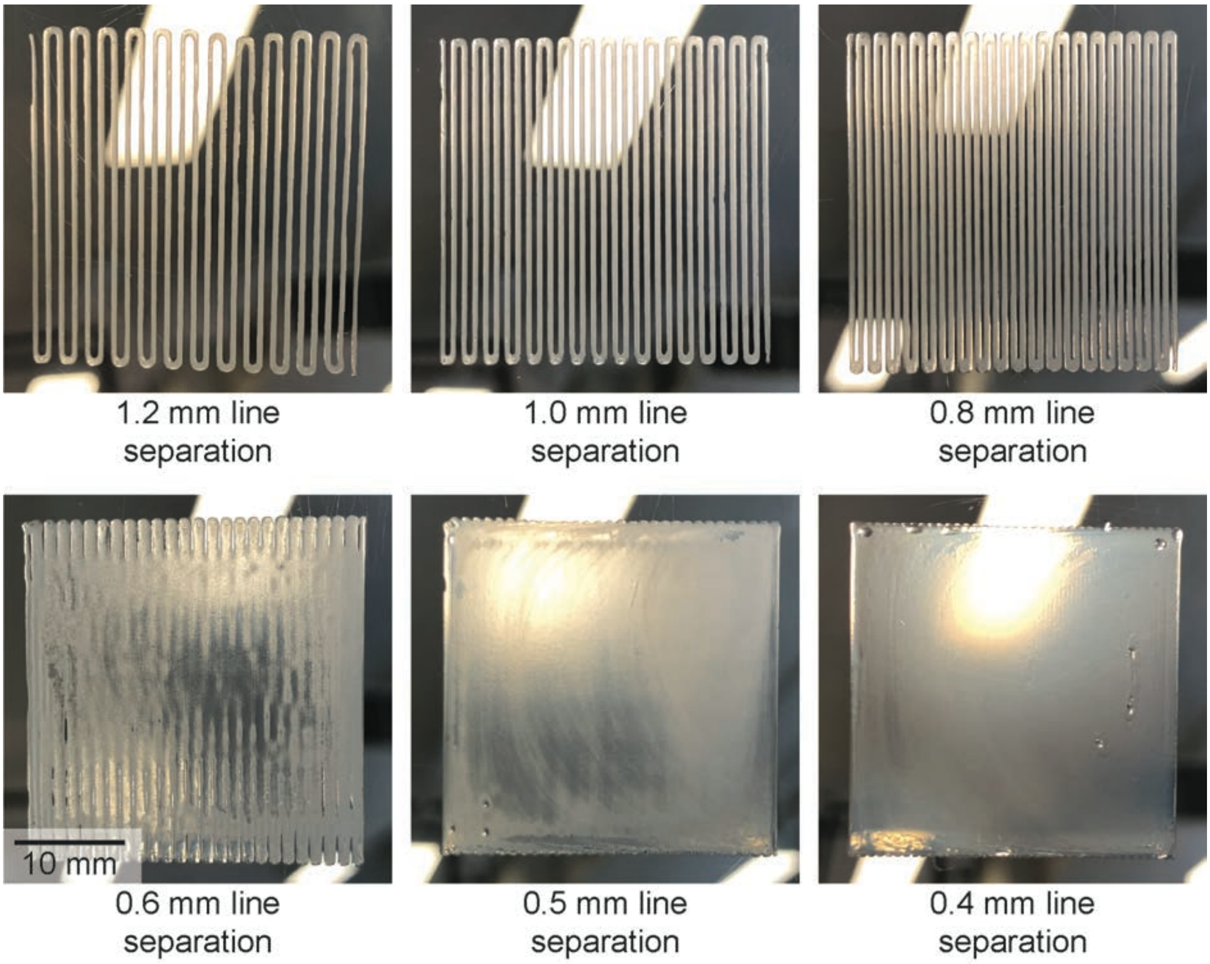

Figure S5: Optical images of PVDF-TrFE 3D printed onto a glass substrate, whereby the spacing of a raster pattern was investigated for the printing of a solid thin film. Printing conditions as follows: 178 kPa extrusion pressure, 30 mm/s x-y robot head speed, 5 °C cartridge temperature, 24 °C ambient temperature.

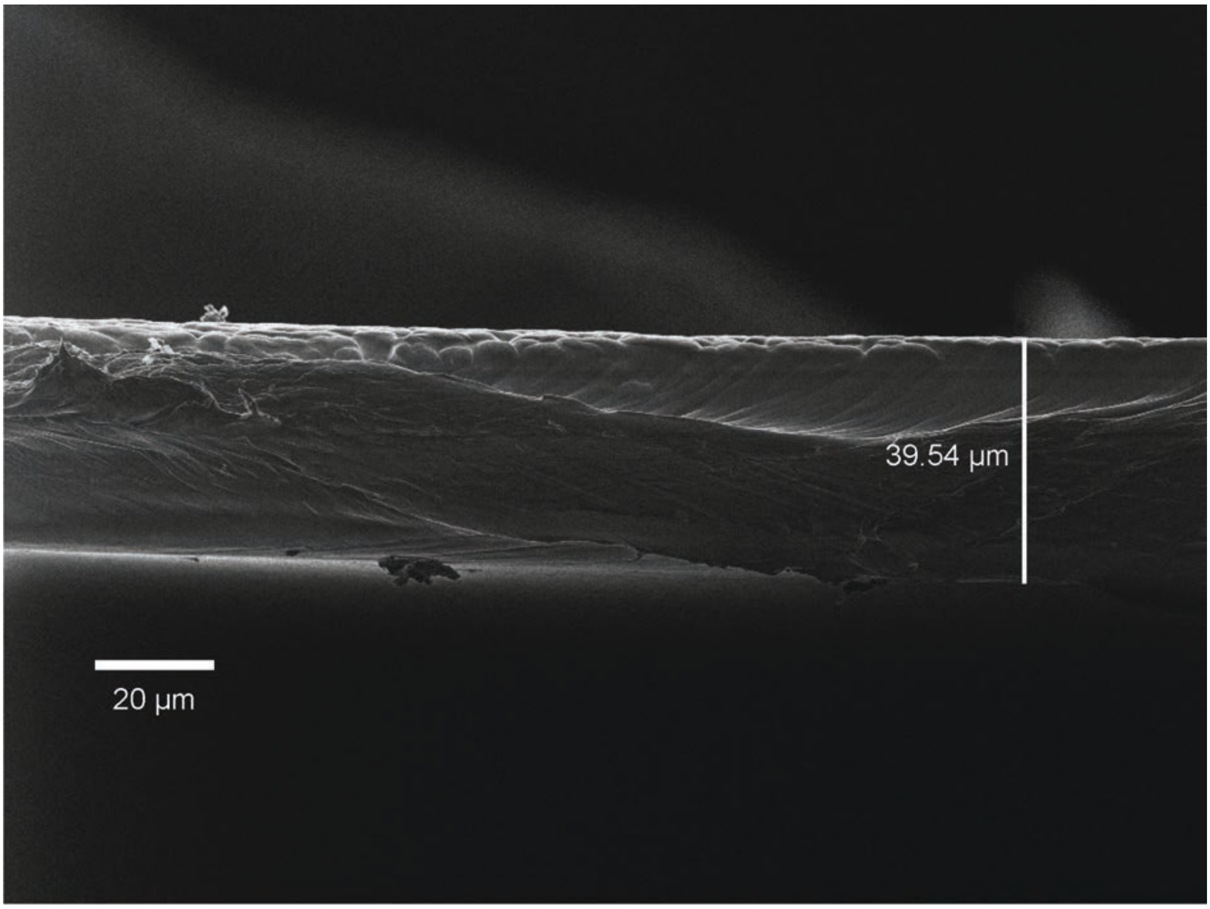

Figure S6: HIM image showing the cross section of an optimized SEA 3D printed PVDF-TrFE thin film with a 0.4 mm raster line width.

References

1. C. M. Hansen, *Hansen solubility parameters : a user's handbook*, 2007.
2. A. Bottino, G. Capannelli, S. Munari and A. Turturro, *J. Polym. Sci., Part B: Polym. Lett.*, 1988, **26**, 785-794.
3. L. Yu and P. Cebe, *Polymer*, 2009, **50**, 2133-2141.
4. M. Baqeri, M. M. Abolhasani, M. R. Mozdianfard, Q. P. Guo, A. Oroumei and M. Naebe, *J. Appl. Polym. Sci.*, 2015, **132**, 11.