Supplementary Information (SI) for Analyst.

Supporting Information for:

The effect of different plasticisers on the electrochemical performance of bespoke conductive additive manufacturing filament using recycled PLA

Robert D. Crapnell,[1] Iana V.S. Arantes,[1,2] Elena Bernalte,[1] Evelyn Sigley,[1] Graham C. Smith,[3] Thiago R.L.C. Paixão,[2] and Craig E. Banks[1*]

[1]*Faculty of Science and Engineering, Manchester Metropolitan University, Manchester, Chester Street, Dalton Building, M1 5GD, Great Britain.*

[2]*Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, São Paulo, SP, 05508-000, Brazil.*

[3]*School of Natural Sciences, Faculty of Science, Business and Enterprise, University of Chester, Parkgate Road, Chester CH1 4BJ, UK.*

[*]To whom correspondence should be addressed.

E-mail: c.banks@mmu.ac.uk; Tel: +44(0)1612471196

Experimental Details

Prior to any mixing or filament production, all rPLA was dried in an oven at 60 °C for a minimum of 2.5 h, which removed any residual water in the polymer. All bespoke compositions were prepared using 65 wt% rPLA and 25 wt% CB, along with 10 wt% of each individual plasticiser by placing in a chamber of 63 cm^3 and mixing at 170 °C with Banbury rotors at 70 rpm for 5 min using a Thermo Haake Poydrive dynameter fitted with a Thermo Haake Rheomix 600 (Thermo-Haake, Germany). The resulting polymer composites were allowed to cool to room temperature before being granulated to create a finer granule size using a Rapid Granulator 1528 (Rapid, Sweden). The granulated sample was collected and processed through the hopper of a EX6 extrusion line (Filabot, VA, United States). The EX6 was set up with a single screw and had four set heat zones of 60, 190, 195 and 195 °C respectively. The molten polymer was extruded from a 1.75 mm die head, pulled along an Airpath cooling line (Filabot, VA, United States), through an inline measure (Mitutoyo, Japan) and collected on a Filabot spooler (Filabot, VA, United States). The filament was then ready to use for additive manufacturing.

All computer designs and .3MF files seen throughout this manuscript were produced using Fusion 360® (Autodesk®, CA, United States). These files were sliced and converted to .GCODE files ready for printing by the printer specific software, PrusaSlicer (Prusa Research, Prague, Czech Republic). The additively manufactured electrodes were 3D-printed using fused filament fabrication (FFF) technology on a Prusa i3 MK3S+ (Prusa Research, Prague, Czech Republic). All additive manufactured electrodes were printed using a 0.6 mm nozzle with a nozzle temperature of 215 °C, 100% rectilinear infill, 0.15 mm layer height, and print speed of 70 mm s^{-1}.

X-ray Photoelectron Spectroscopy (XPS) data were acquired using an AXIS Supra (Kratos, UK), equipped with a monochromated Al X-ray source (1486.6 eV) operating at 225 W and a hemispherical sector analyser. It was operated in fixed transmission mode with a pass energy of 160 eV for survey scans and 20 eV for region scans with the collimator operating in slot mode for an analysis area of approximately 700 x 300 μm, the FWHM of the Ag 3d5/2 peak using a pass energy of 20 eV was 0.613 eV. Before analysis, each sample was ultrasonicated for 15 min in propan-2-ol and then dried for 2.5 hours at 65 °C to remove excess contamination and minimise the risk of misleading data, as shown in our unpublished data. The binding energy scale was calibrated by setting the graphitic sp^2 C 1s peak to 284.5 eV; this calibration is acknowledged to be flawed [44], but was nonetheless used in the absence of reasonable alternatives, and because only limited information was to be inferred from absolute peak positions.

Scanning Electron Microscopy (SEM) measurements were recorded on a Supra 40VP Field Emission (Carl Zeiss Ltd., Cambridge, UK) with an average chamber and gun vacuum of 1.3×10^{-5} and 1×10^{-9} mbar, respectively. Samples were mounted on the aluminium SEM pin stubs (12 mm diameter, Agar Scientific, Essex, UK). To enhance the contrast of these images, a thin layer of Au/Pd (8 V, 30 s) was sputtered onto the electrodes with the SCP7640 from Polaron (Hertfordshire, UK) before being placed in the chamber.

Raman spectroscopy was performed on a Renishaw PLC in Via Raman Microscope controlled by WiRE 2 software at a laser wavelength of 514 nm.

All electrochemical measurements were performed on an Autolab 100N potentiostat controlled by NOVA 2.1.6 (Utrecht, the Netherlands). The electrochemical characterisation of the bespoke filament and comparison to the benchmarks were performed using a lollipop design (Ø 5 mm, 18 mm connection length, 1 mm thickness) electrodes alongside an external commercial Ag|AgCl (3M KCl) reference electrode and a nichrome wire counter electrode. All solutions were prepared using deionised water of resistivity not less than 18.2 MΩ cm from a Milli-Q system (Merck, Gillingham, UK). All solutions of $[Ru(NH_3)_6]^{3+}$ were purged of O_2 thoroughly using N_2 before any electrochemical experiments.

When applicable, activation of the additive manufactured electrodes was achieved through chronoamperometry as is commonplace in the literature. In brief, this involved placing the electrode head within an aqueous sodium hydroxide solution (0.5 M) and applying +1.4 V for 200 s, followed immediately by applying -1.0 V for 200 s. After this, the additive manufactured electrodes were removed from the solution, rinsed with deionised water and dried under a stream of nitrogen.

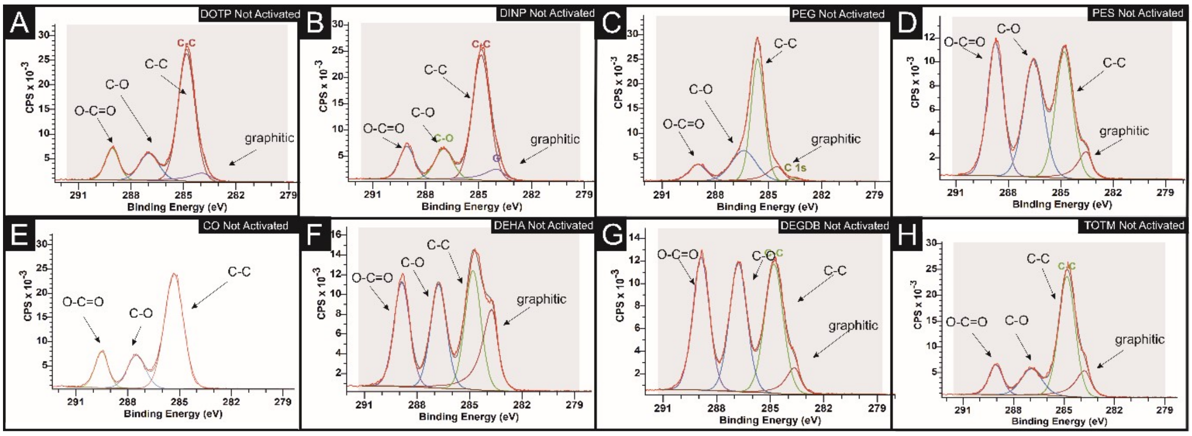

Figure S1. XPS C 1s spectra for as-printed electrodes with different plasticisers **A)** dioctyl terephthalate; **B)** diisononyl phthalate; **C)** poly(ethylene glycol); **D)** poly(ethylene succinate); **E)** castor oil; **F)** bis (2-ethylhexyl) adipate; **G)** diethylene glycol dibenzoate; and **H)** tris (2-ethylhexyl) trimellitate.

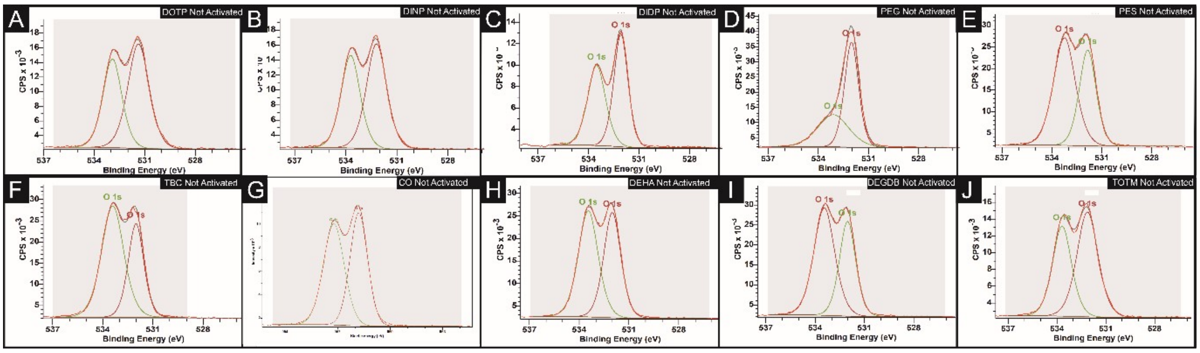

Figure S2. XPS O 1s spectra for as-printed electrodes with different plasticisers **A)** dioctyl terephthalate; **B)** diisononyl phthalate; **C)** diisodecyl phthalate; **D)** poly(ethylene glycol); **E)** poly(ethylene succinate); **F)** tributyl citrate; **G)** castor oil; **H)** bis (2-ethylhexyl) adipate; **I)** diethylene glycol dibenzoate; and **J)** tris (2-ethylhexyl) trimellitate.

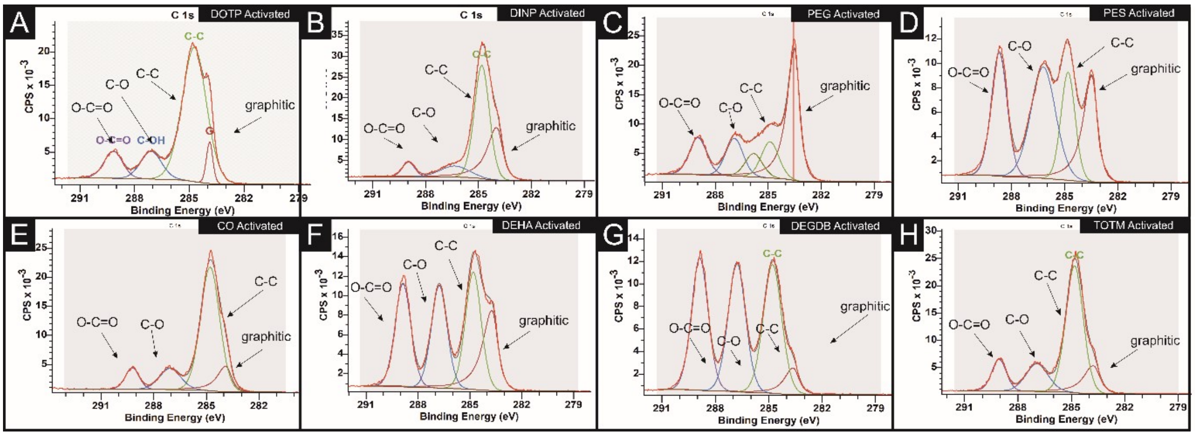

Figure S3. XPS C 1s spectra for electrochemically activated electrodes with different plasticisers **A)** dioctyl terephthalate; **B)** diisononyl phthalate; **C)** poly(ethylene glycol); **D)** poly(ethylene succinate); **E)** castor oil; **F)** bis (2-ethylhexyl) adipate; **G)** diethylene glycol dibenzoate; and **H)** tris (2-ethylhexyl) trimellitate.

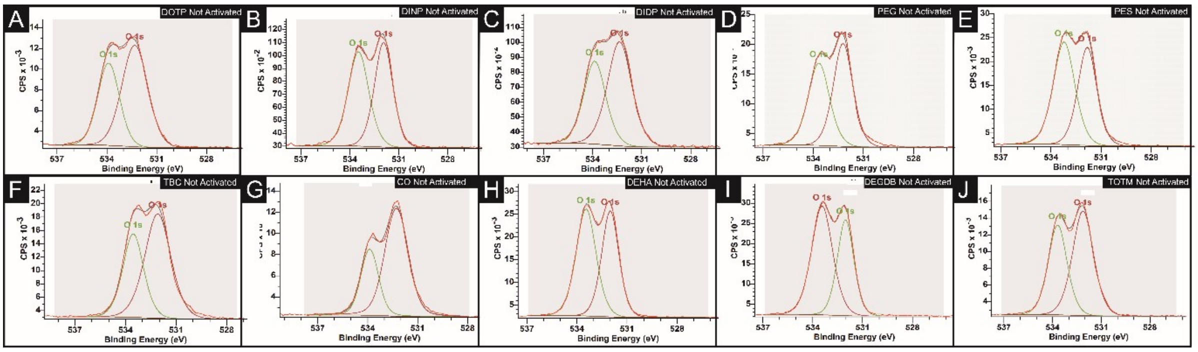

Figure S4. XPS O 1s spectra for electrochemically activated electrodes with different plasticisers **A)** dioctyl terephthalate; **B)** diisononyl phthalate; **C)** diisodecyl phthalate; **D)** poly(ethylene glycol); **E)** poly(ethylene succinate); **F)** tributyl citrate; **G)** castor oil; **H)** bis (2-ethylhexyl) adipate; **I)** diethylene glycol dibenzoate; and **J)** tris (2-ethylhexyl) trimellitate.

Table S1. A summary of the at% found by fitting the C 1s XPS spectrum for the additive manufactured electrodes printed from different filaments before and after electrochemical activation.

Filament	**Graphitic**	**C-C**	**C-OH**	**O-C=O**
NA – DOTP	2.91	66.9	13.14	17.05
A – DOTP	23.01	52.20	14.53	10.26
NA – DINP	4.05	65.15	17.05	13.75
A – DINP	23.77	59.23	11.11	5.89
NA – DIDP	-	85.89	8.68	5.43
A – DIDP	52.42	31.37	8.57	7.63
NA – PEG	14.24	47.03	29.63	9.11
A – PEG	33.29	41.55	10.64	14.53
NA – PES	5.08	32.07	32.74	30.12
A – PES	22.92	18.71	34.32	24.06
NA – TBC	4.99	34.35	30.91	29.75
A – TBC	42.42	22.10	18.87	16.61
NA – CO	-	68.74	17.31	13.95
A – CO	8.93	68.82	14.08	8.17
NA – DEHA	22.27	28.33	24.28	25.11
A – DEHA	44.80	32.79	8.14	14.26
NA – DEGDB	4.31	34.26	31.17	30.25
A – DEGDB	48.06	32.20	9.93	9.81
NA – TOTM	9.05	61.80	17.33	11.82
A – TOTM	23.77	54.19	11.56	10.48

Key: **NA** - not activated; **A** - activated; **DOTP** - dioctyl terephthalate; **DINP** - diisononyl phthalate; **DIDP** - diisodecyl phthalate; **PEG** - poly(ethylene glycol); **PES** - poly(ethylene succinate); **TBC** - tributyl citrate; **CO** - castor oil; **DEHA** - bis (2-ethylhexyl) adipate; **DEGDB** - diethylene glycol dibenzoate; **TOTM** - tris (2-ethylhexyl) trimellitate.

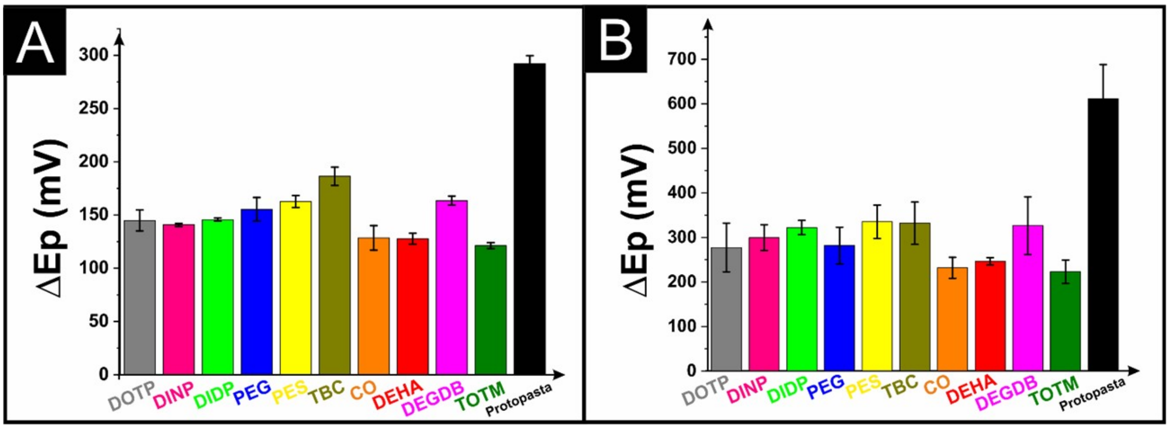

Figure S5. Peak-to-peak separation (ΔEp) values extracted from **(A)** $[Ru(NH_3)_6]^{3+}$ and **(B)** ferri/ferrocyanide cyclic voltammograms both at 50 mV s^{-1} (1 mM in 0.1 M KCl) for the bespoke CB/PLA filaments made with different plasticisers and the commercial CB/PLA filament (Protopasta).

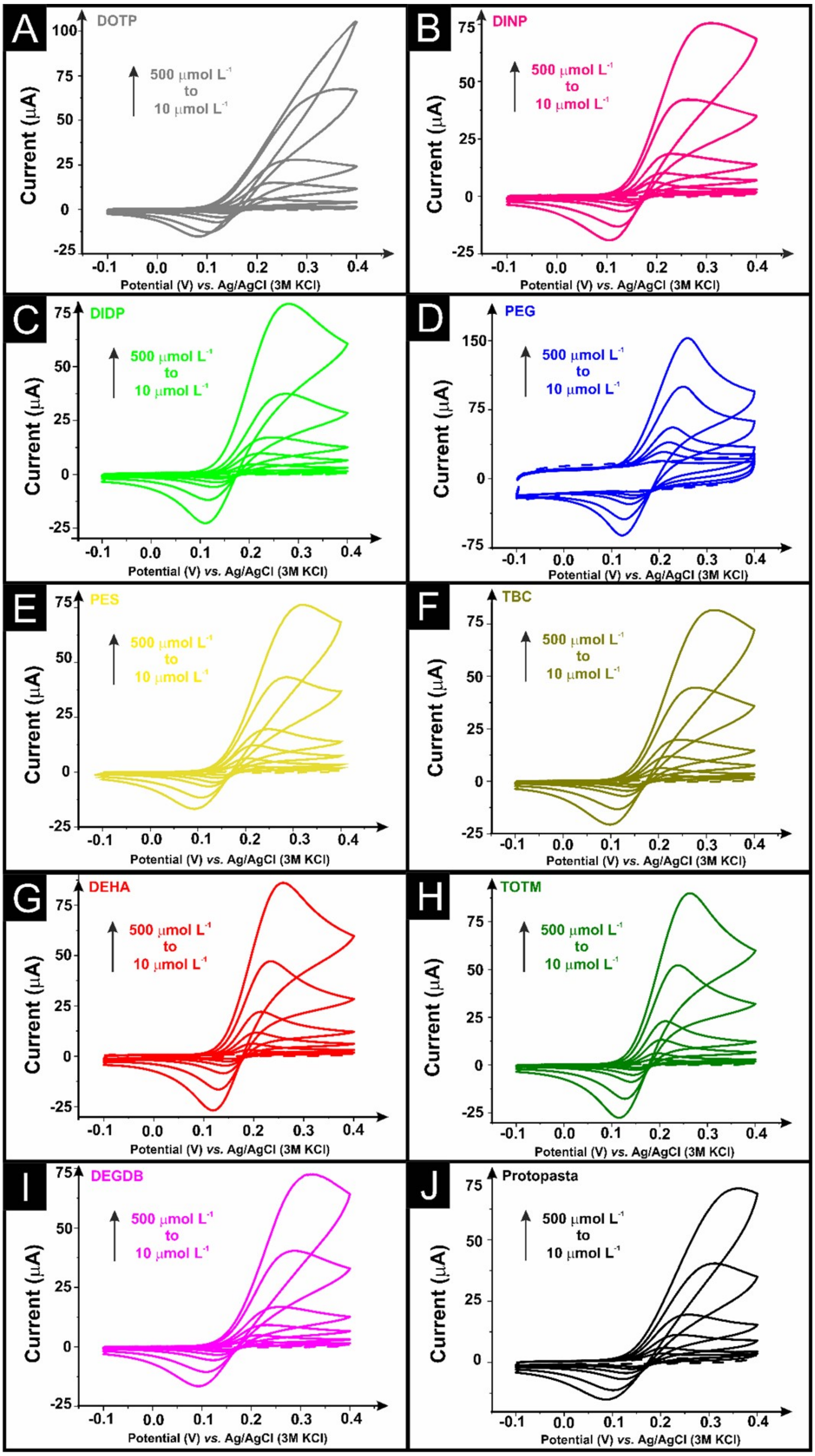

Figure S6. Cyclic voltammograms of dopamine in different concentrations (10, 25, 50, 100, 250, and 500 μM) in 0.1 M PBS pH 7.4 for the **(A – I)** bespoke CB/PLA filaments made with different plasticisers and the **(J)** commercial CB/PLA filament (Protopasta).