Towards additive manufacturing of semiconducting polymers : hot-melt extrusion of PCL:P3HT blends

SUPPORTING INFORMATION

Jiayi Chen, Nahel Blanc, Audrey Laventure*

Département de Chimie, Université de Montréal, 1375 Avenue Thérèse-Lavoie-Roux, Montréal, QC H2V 0B3, Canada.

*e-mail: audrey.laventure@umontreal.ca

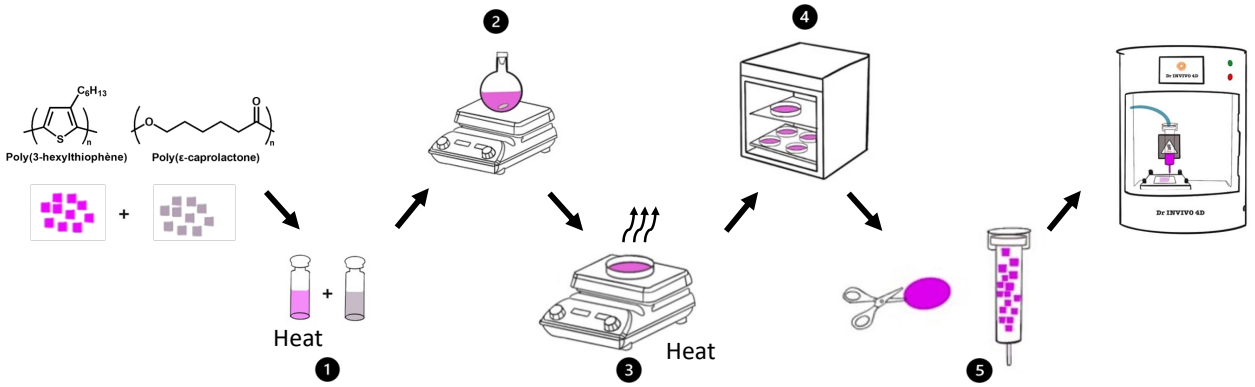

Figure S1. Formulation method of PCL-P3HT blend. (1) P3HT and PCL are separately solubilized in chloroform. (2) Both solutions are mixed with a stir bar. (3) Solvent evaporation with heat. (4) Residual solvent evacuation under vacuum. (5) Resulting films cut into pieces and ready to print using HME.

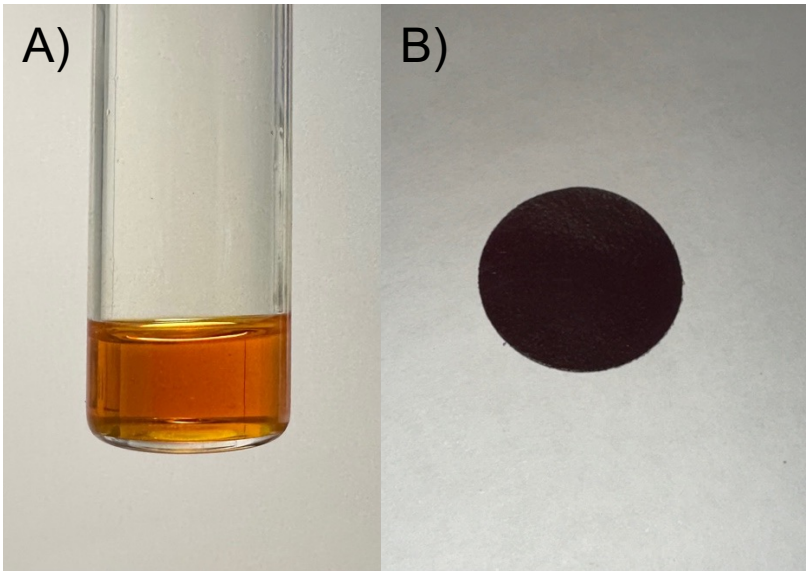

Figure S2. Optical image of P3HT solution and dry PCL-P3HT-1 film.

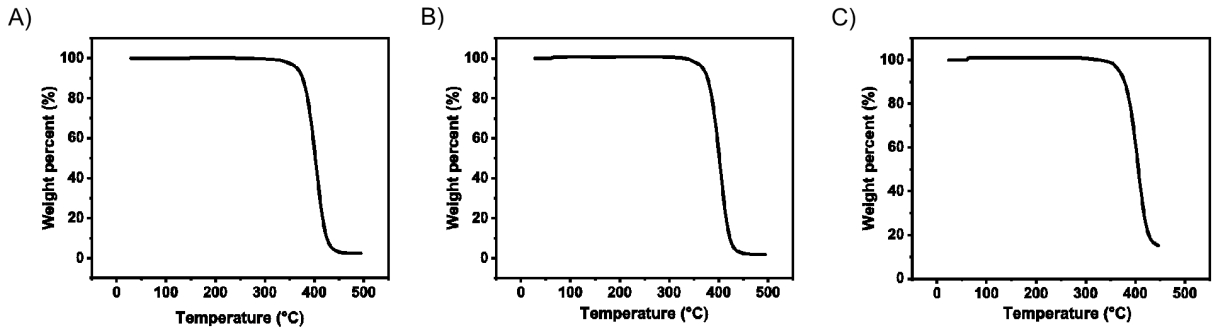

Figure S3. TGA under nitrogen atmosphere of (A) PCL-P3HT-1 (B) PCL-P3HT-4 (C) PCL-P3HT-10.

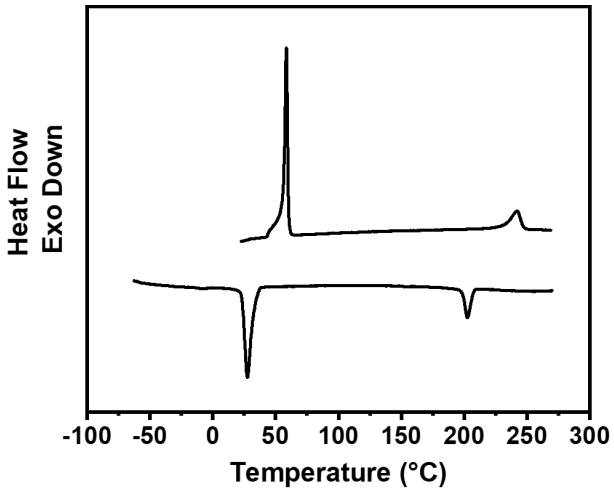

Figure S4. Differential scanning calorimetry analyses of PCL-P3HT-50.

Table S1. Profilometry results of PCL.

Nozzle size (µm)	Temperature (°C)	Pressure (kPa)	Print speed (mm/s)	Printing angle	Height average* (µm)	Width average* (µm)	Roundness	Uniformity parameter
200	80	700	4	0°	96 (± 1)	185 (± 4)	0.52	0.93
200	80	600	4	0°	82 (± 1)	155 (± 3)	0.53	0.77
200	80	500	4	0°	-	-	-	-
200	80	400	4	0°	-	-	-	-
200	100	700	4	0°	134 (± 4)	225 (± 8)	0.60	1.12
200	100	600	4	0°	122 (± 1)	212 (± 4)	0.57	1.06
200	100	500	4	0°	104 (± 1)	200 (± 5)	0.52	1.00
200	100	400	4	0°	84 (± 1)	179 (± 3)	0.47	0.89
200	120	700	4	0°	167 (± 1)	277 (± 3)	0.60	1.38
200	120	600	4	0°	153 (± 1)	255 (± 4)	0.60	1.28
200	120	500	4	0°	135 (± 1)	235 (± 3)	0.57	1.18
200	120	400	4	0°	116 (± 1)	213 (± 3)	0.55	1.06
200	140	700	4	0°	202 (± 1)	321 (± 4)	0.63	1.61
200	140	600	4	0°	186 (± 1)	302 (± 4)	0.62	1.51
200	140	500	4	0°	169 (± 1)	273 (± 4)	0.62	1.37
200	140	400	4	0°	148 (± 1)	246 (± 3)	0.60	1.23

Table S2. Profilometry results of PCL-P3HT-1.

Nozzle size (µm)	Temperature (°C)	Pressure (kPa)	Print speed (mm/s)	Printing angle	Height average* (µm)	Width average* (µm)	Roundness	Uniformity parameter
200	80	700	4	0°	88 (± 6)	186 (± 2)	0.47	0.93
200	80	600	4	0°	74 (± 4)	162 (± 1)	0.45	0.81
200	80	500	4	0°	-	-	-	-
200	80	400	4	0°	-	-	-	-
200	100	700	4	0°	121 (± 2)	223 (± 3)	0.54	1.12
200	100	600	4	0°	108 (± 2)	204 (± 1)	0.53	1.02
200	100	500	4	0°	101 (± 1)	190 (± 5)	0.53	0.95
200	100	400	4	0°	101 (± 1)	187 (± 1)	0.54	0.93
200	120	700	4	0°	159 (± 3)	288 (± 3)	0.55	1.44
200	120	600	4	0°	141 (± 1)	262 (± 1)	0.54	1.31
200	120	500	4	0°	127 (± 2)	241 (± 1)	0.53	1.21
200	120	400	4	0°	117 (± 1)	208 (± 3)	0.56	1.04
200	140	700	4	0°	187 (± 2)	338 (± 2)	0.55	1.69
200	140	600	4	0°	166 (± 2)	312 (± 1)	0.53	1.56
200	140	500	4	0°	162 (± 2)	286 (± 2)	0.57	1.43
200	140	400	4	0°	143 (± 2)	258 (± 3)	0.56	1.29

Table S3. Profilometry results of PCL-P3HT-4.

Nozzle size (µm)	Temperature (°C)	Pressure (kPa)	Print speed (mm/s)	Printing angle	Height average* (µm)	Width average* (µm)	Roundness	Uniformity parameter
200	80	700	4	0°	94 (± 2)	187 (± 1)	0.50	0.94
200	80	600	4	0°	85 (± 2)	168 (± 3)	0.51	0.84
200	80	500	4	0°	-	-	-	-
200	80	400	4	0°	-	-	-	-
200	100	700	4	0°	132 (± 1)	239 (± 7)	0.55	1.20
200	100	600	4	0°	114 (± 1)	209 (± 4)	0.55	1.04
200	100	500	4	0°	100 (± 3)	196 (± 4)	0.51	0.98
200	100	400	4	0°	87 (± 3)	183 (± 6)	0.48	0.91
200	120	700	4	0°	154 (± 3)	271 (± 4)	0.57	1.36
200	120	600	4	0°	137 (± 3)	252 (± 2)	0.54	1.26
200	120	500	4	0°	132 (± 2)	236 (± 2)	0.56	1.18
200	120	400	4	0°	114 (± 4)	220 (± 1)	0.52	1.10
200	140	700	4	0°	171 (± 3)	326 (± 4)	0.53	1.63
200	140	600	4	0°	171 (± 2)	302 (± 3)	0.57	1.51
200	140	500	4	0°	151 (± 3)	271 (± 2)	0.56	1.36
200	140	400	4	0°	141 (± 3)	246 (± 2)	0.57	1.23

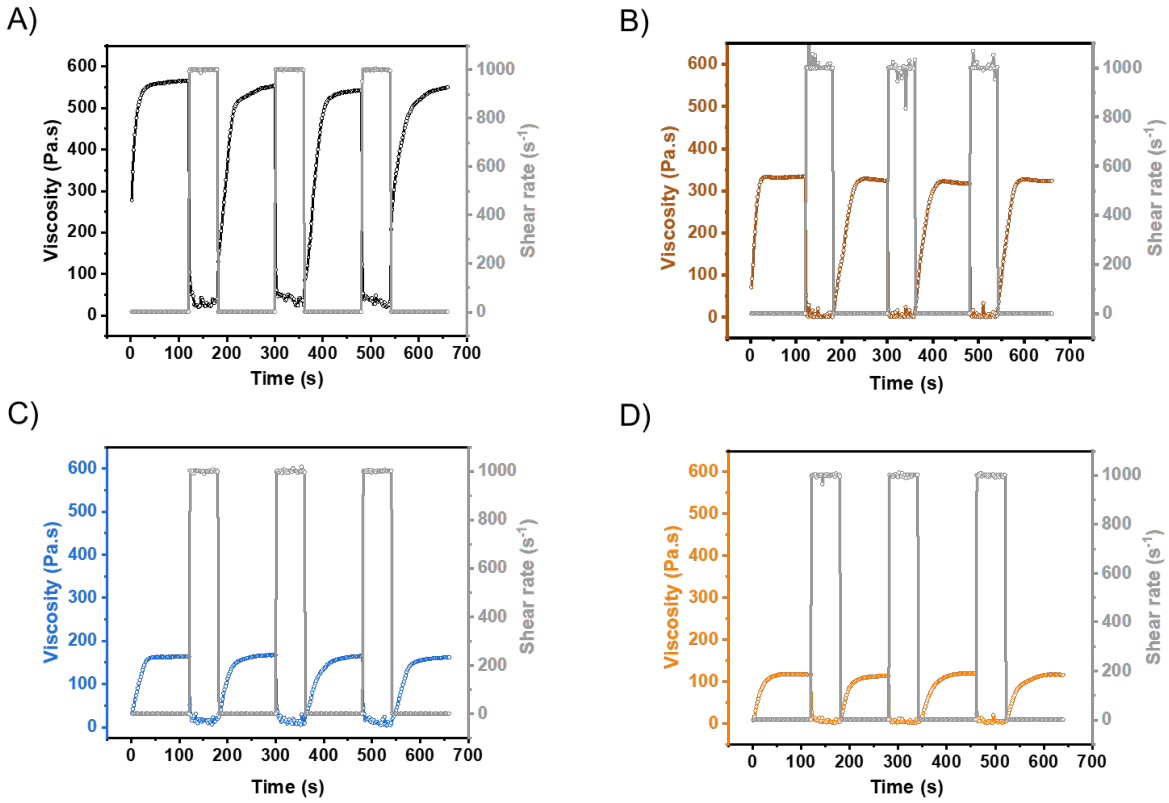

Figure S5. Thixotropy tests of PCL at A) 80°C, B) 100°C, C) 120°C, D) 140°C.

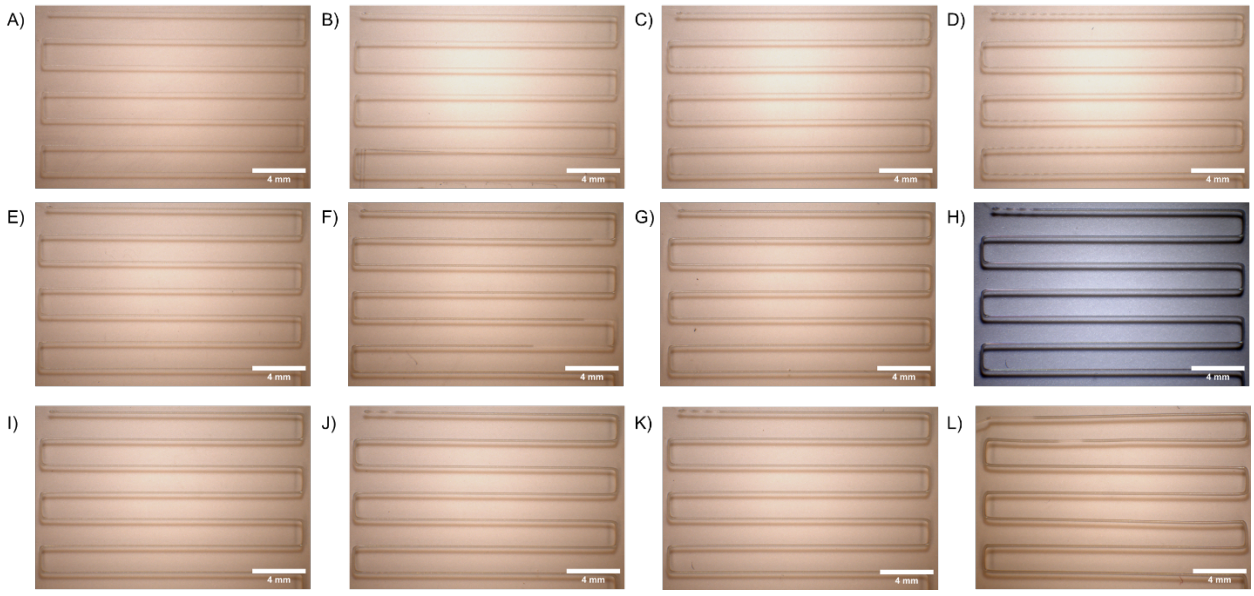

Figure S6. Stereomicroscopy images of PCL printed at 100 °C_4 mm.s^{-1}and A) 400 kPa B) 500 kPa C) 600 kPa D) 700 kPa. PCL printed at 120 °C_4 mm.s^{-1} and E) 400 kPa F) 500 kPa G) 600 kPa H) 700 kPa. PCL printed at 140 °C_4 mm.s^{-1} and I) 400 kPa J) 500 kPa K) 600 kPa L) 700 kPa.

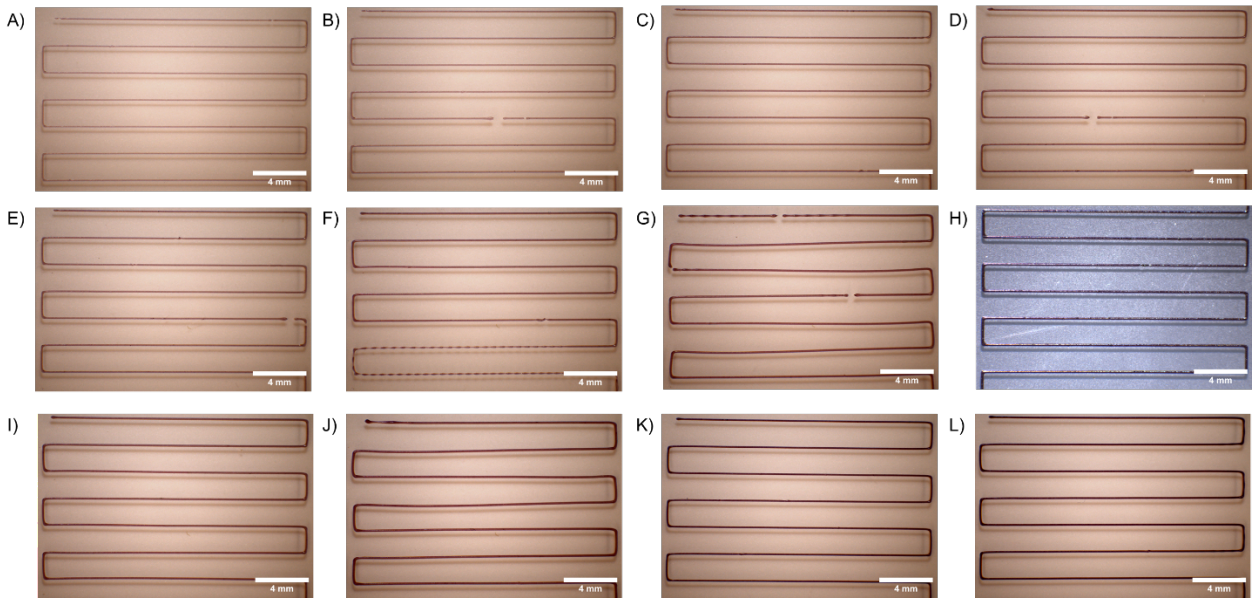

Figure S7. Stereomicroscopy images of PCL-P3HT-1 printed at 100 °C_4 mm.s^{-1} and A) 400 kPa B) 500 kPa C) 600 kPa D) 700 kPa. PCL-P3HT-1 printed at 120 °C_4 mm.s^{-1} and E) 400 kPa F) 500 kPa G) 600 kPa H) 700 kPa. PCL-P3HT-1 printed at 140 °C_4 mm.s^{-1} and I) 400 kPa J) 500 kPa K) 600 kPa L) 700 kPa.

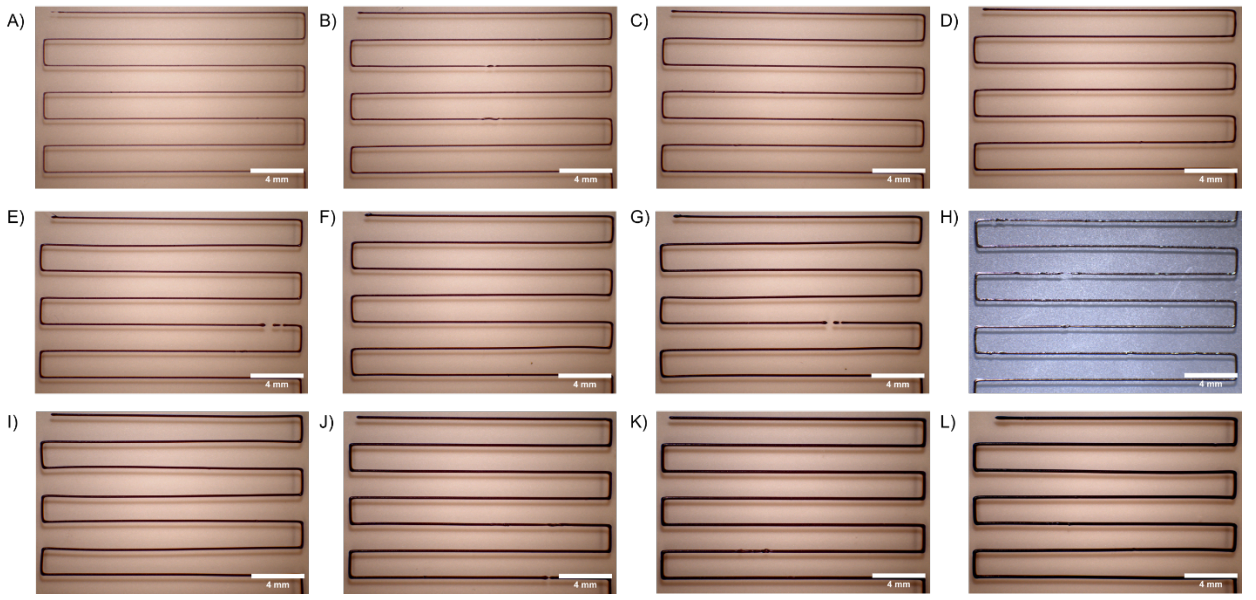

Figure S8. Stereomicroscopy images of PCL-P3HT-4 printed at 100 °C_4 mm.s^{-1} and A) 400 kPa B) 500 kPa C) 600 kPa D) 700 kPa. PCL-P3HT-4 printed at 120 °C_4 mm.s^{-1} and E) 400 kPa F) 500 kPa G) 600 kPa H) 700 kPa. PCL-P3HT-4 printed at 140 °C_4 mm.s^{-1} and I) 400 kPa J) 500 kPa K) 600 kPa L) 700 kPa.

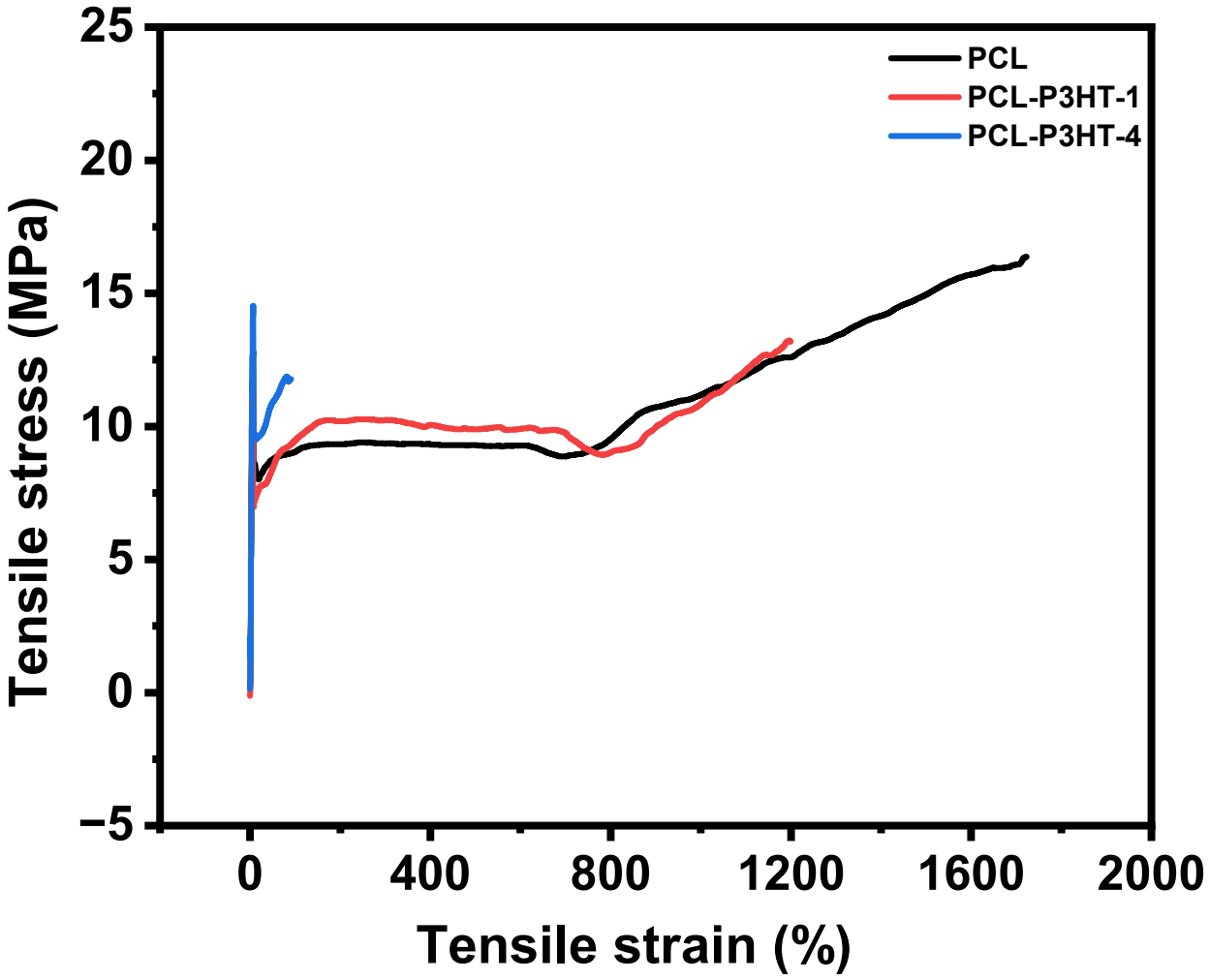

Figure S9. Representative stress-strain curve of PCL, PCL-P3HT-1 and PCL-P3HT-4. All samples are printed at 100 °C_500 kPa_4 $mm.s^{-1}$.

Table S4. Summary of elongation at break, ultimate tensile strength (UTS), and Young's modulus for PCL, PCL-P3HT-1 and PCL-P3HT-4. All samples are printed at 100 °C_500 kPa_4 $mm.s^{-1}$. Measurements are made in triplicate and the standard deviations are presented.

Samples	Elongation at break (%)	UTS (MPa)	Young's modulus (MPa)
PCL	1770 ± 310	18 ± 1	340 ± 50
PCL-P3HT-1	1440 ± 200	17 ± 4	340 ± 30
PCL-P3HT-4	140 ± 130	14 ± 2	340 ± 40

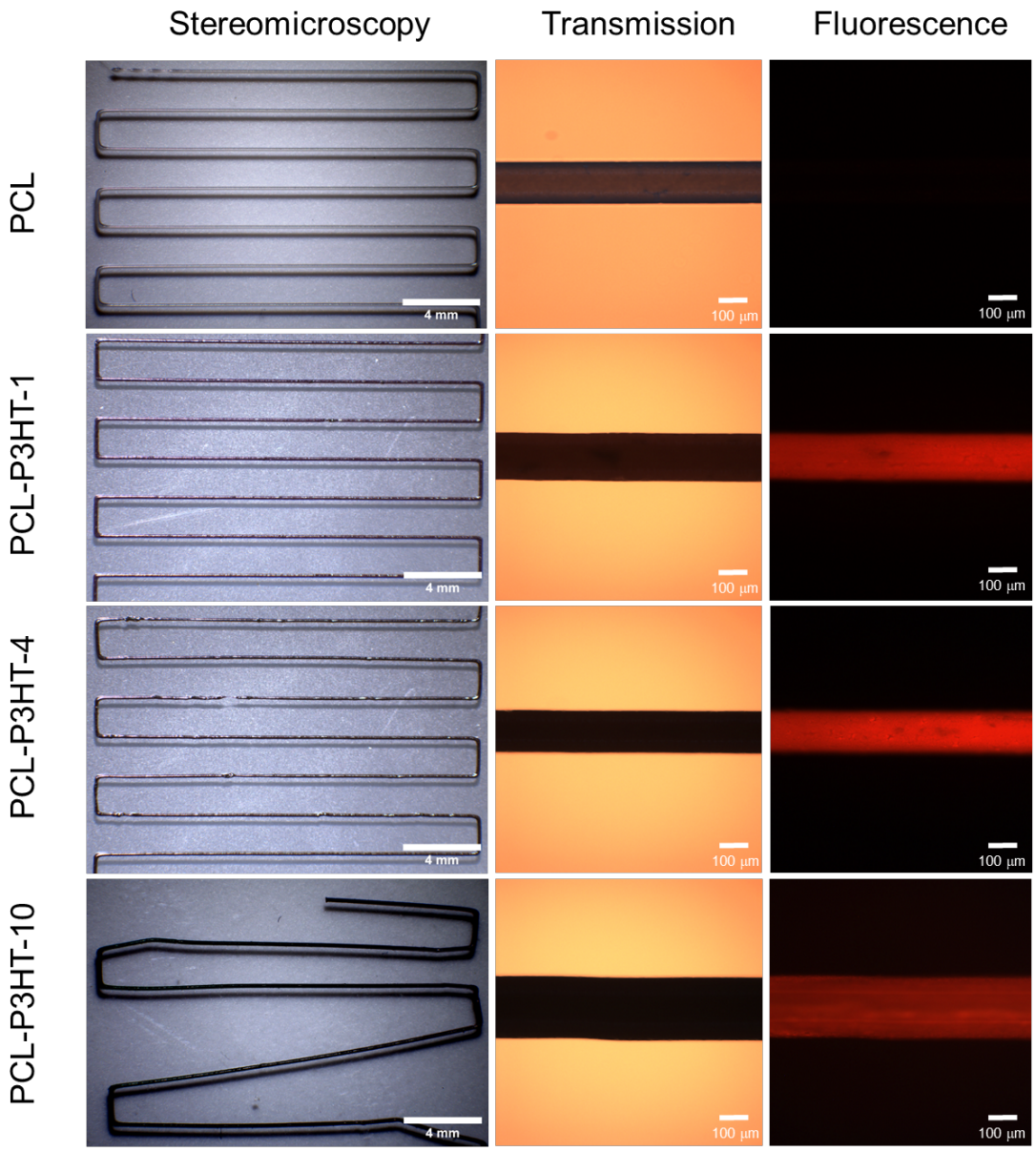

Figure S10. Characterization of the 3D printed PCL, PCL-P3HT-1, PCL-P3HT-4 and PCL-P3HT-10 digital snakes using stereomicroscopy and optical and fluorescence microscopy.

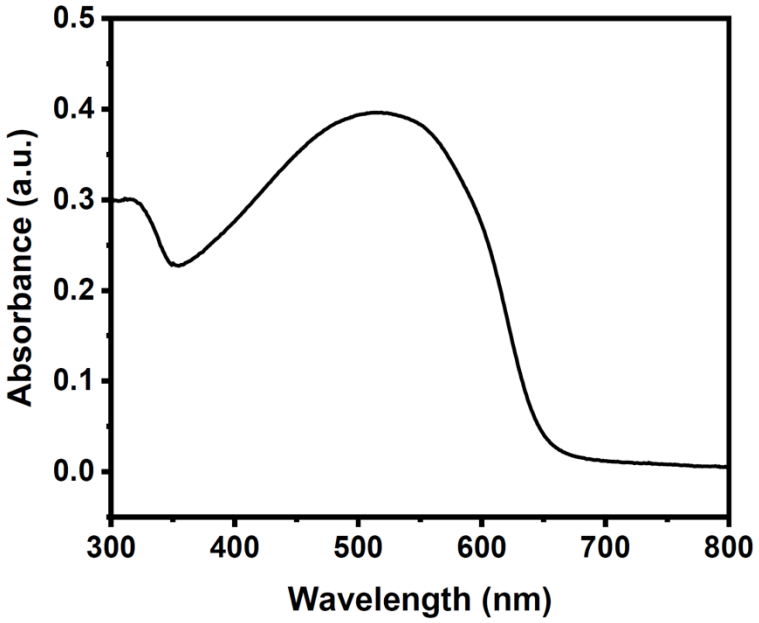

Figure S11. Diffuse reflectance UV-vis spectrum of printed PCL-P3HT-0.4 digital snakes printed at 250°C.

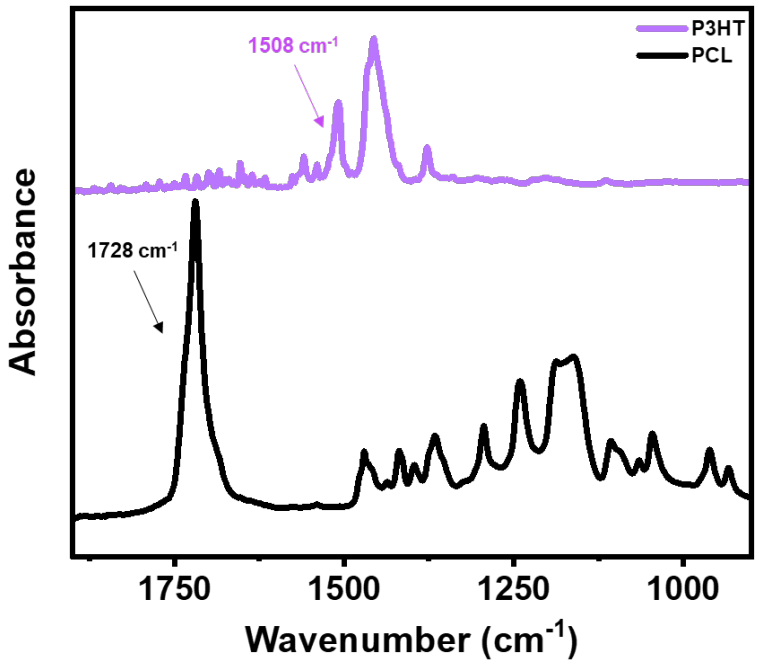

Figure S12. FTIR spectra of PCL and P3HT drop cast film from $CHCl_3$. The typical non-overlapping bands of both polymers are identified.

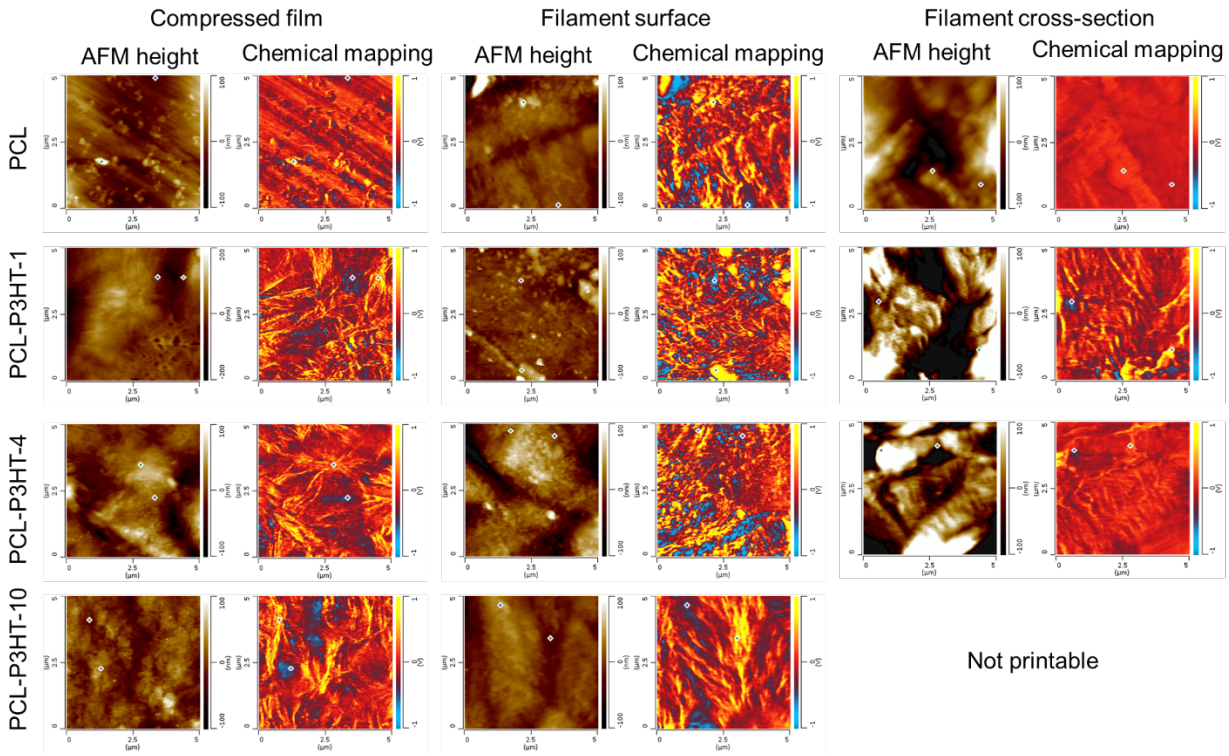

Figure S13. AFM height images and chemical mapping at 1732 cm^{-1} on compressed films, filament surface, and filament cross-section for pristine PCL and different blends. The blue and green dots on these images represent the location where the FTIR spectra are taken (cf. Figure S11).

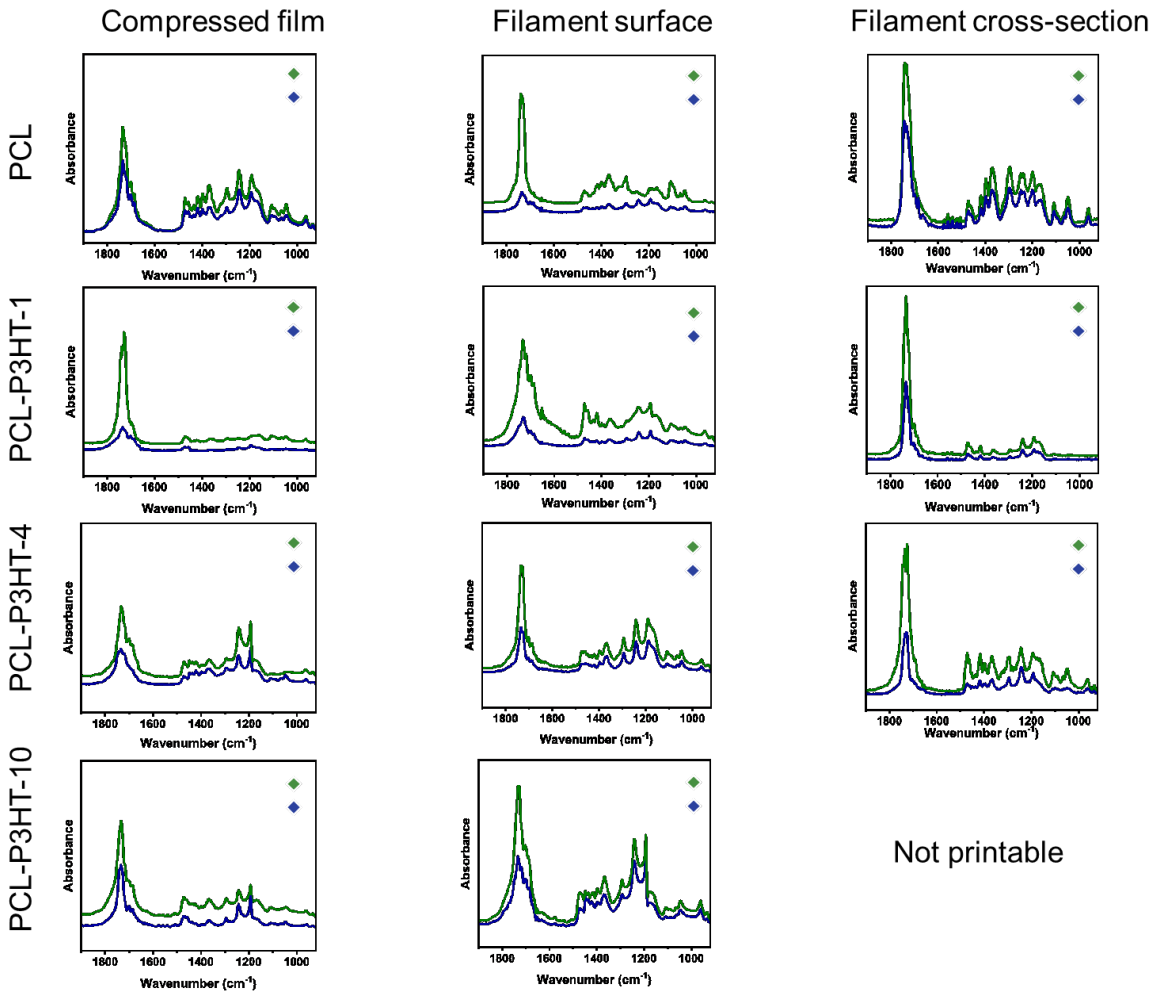

Figure S14. FTIR spectra taken on compressed films, filament surface, and filament cross-section of different blends. Blue and green curves correspond to the blue and green dots where the FTIR spectra are taken in Figure S10.

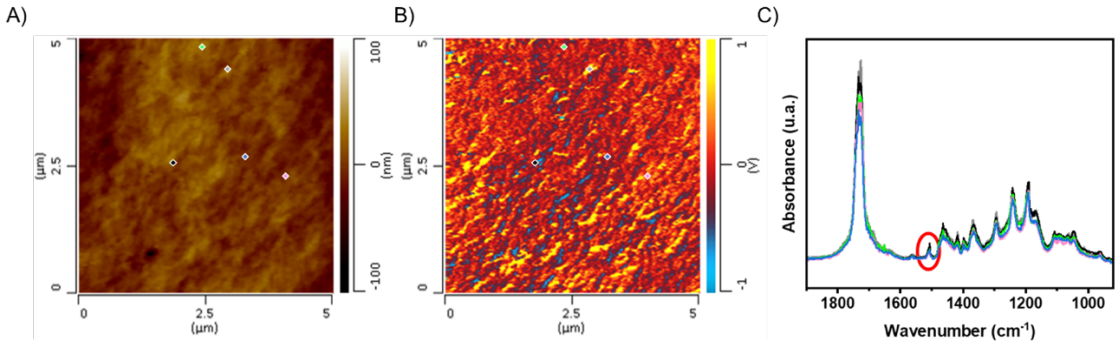

Figure S15. PCL-P3HT-50 drop cast film from $CHCl_3$. A) AFM height image. B) Chemical mapping at 1732 cm^{-1}. Dots on these images represent the place where the FTIR spectra are taken. Resulting spectra are shown in C) with the P3HT band at 1508 cm^{-1} highlighted in red.