Supporting information for:

Tunable Porosity in Fused Filament 3D-Printed Blends of Intrinsically Porous Polymer and Thermoplastic Aliphatic Polyesters Polycaprolactone and Polylactic Acid

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Full details on the synthesis of PIM-1 (continued from experimental in the main text)
5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane (5.14 g, 0.0159 mol) and tetrafluoroterephthalonitrile (3.02 g, 0.0151 mol) were added to an oven dried, Ar flushed, 500 mL vessel containing a magnetic stir bar. Anhydrous dimethylformamide (100 mL) was added via an Ar filled syringe followed by anhydrous K_2CO_3 (17.7 g, 0.128 mol). The solution was sparged with Ar for 30 min. At this point an Ar purge was then maintained throughout the remainder of the polymerization. The mixture was then heated to 65 °C and stirred at 300 rpm for 72 h. The mixture was removed from heat, let cool to room temperature, then added to H_2O (150 mL) to precipitate a yellow solid. The solid was captured by filtration on a coarse-fritted funnel and washed with H_2O (3 x 100 mL) and acetone (2 x 50 mL). Chloroform (225 mL, in portions) was then used to dissolve the solid through the frit into a clean flask. PIM-1 was re-precipitated from the chloroform solution by addition of methanol (200 mL). The mixture was stirred for 15 min and PIM-1 was isolated by filtration again on a coarse-fritted funnel. PIM-1 as a yellow solid was then ground in a mortar and pestle and was fully dried at 80 °C in a low-vacuum oven for 48 h. The polymer was stored at room temperature under Ar prior to use.

Table S1: Preparation quantities used in the production of pure thermoplastic and binary thermoplastic/PIM-1, extrusion barrel temperature used during the processing of each sample, and the resulting filament diameter obtained by extrusion through a 1.56 mm diameter nozzle.

Composition[a]	Thermoplastic mass (g)	Thermoplastic/ $CHCl_3$ volume (mL)	PIM-1 mass (g)	Addl. $CHCl_3$ (mL)	Extrusion temp. (°C)	Filament diameter[e] (mm)
PCL	1.5	15[b]	—	—	125	1.75 ± 0.06
(50:50)-PCL/PIM-1	0.75	7.5[b]	0.75	7.5	115	1.59 ± 0.01
PLA	1.5	15[c]	—	—	185	1.71 ± 0.03
(50:50)-PLA/PIM-1	0.75	15[d]	0.75	—	195	1.68 ± 0.03

[a]Preparation conditions listed for typical screening production on a 1.5 g scale.
[b]0.1 g PCL / mL $CHCl_3$.
[c]0.1 g PLA / mL $CHCl_3$.
[d]0.05 g PLA / mL $CHCl_3$.
[e]Average diameter (n = 12 measurements) measured by calipers along the length of the filament.

Table S2: Preparation quantities used in the production of ternary PCL/PLA/PIM-1 composites, extrusion barrel temperature used during the processing of each composite, and the resulting filament diameter obtained by extrusion through a 1.81 mm diameter nozzle.

Composition[a]	PCL mass (g)	PCL / $CHCl_3$ vol.[b] (mL)	PLA mass (g)	PLA / $CHCl_3$ vol.[c] (mL)	PIM-1 mass (g)	Addl. $CHCl_3$ (mL)	Extrusion temp. (°C)	Filament diameter[d] (mm)
(37.5:12.5:50)-PCL/PLA/PIM-1	0.563	5.63	0.187	1.87	0.75	7.5	185	1.82 ± 0.03
(25:25:50)-PCL/PLA/PIM-1	0.375	3.75	0.375	3.75	0.75	7.5	185	1.84 ± 0.05
(12.5:37.5:50)-PCL/PLA/PIM-1	0.187	1.87	0.563	5.63	0.75	7.5	185	1.85 ± 0.04

[a]Preparation conditions listed for typical screening production on a 1.5 g scale.
[b]0.1 g PCL / mL $CHCl_3$.
[c]0.1 g PLA / mL $CHCl_3$.
[d]Average diameter (n = 12 measurements) measured by calipers along the length of the filament.

Table S3: A summary of the FFF printed homopolymer and binary blends examined in this study: physical characteristics relevant to FFF and N_2 physisorption isotherm features.

Printed polymer sample (d = 400 μm)	Characteristics Related to Printability in FFF	N_2 physisorption isotherm characteristics of printed strands (plotted in Figure 2)
PIM-1 polymer (*not printed*)	non-melting, T_g = 442 ± 20 °C (lit., as film)[1]	(*not printed)* powder: high microporosity, moderate desorption hysteresis. Avg. SA_{BET} = 735 m^2 g^{-1}
PCL (Sigma-Aldrich, M_n = 80,000)	T_m = 58-63 °C (lit.)[2-4] T_g = [-58, -54] °C (lit.) [4,5]; good printability	non-porous
PLA (NatureWorks Ingeo Biopolymer 4043D)	peak T_m = 145-160 °C[6]; T_g = 55-60 °C[6]; excellent printability	non-porous
(50:50)-PCL/PIM-1	poor printability (soft, deformation by roller drive gear)	non-porous
(50:50)-PLA/PIM-1	poor printability (brittle, prone to fracture)	non-porous

Table S4: A summary of the FFF printed ternary blends examined in this study: physical characteristics relevant to FFF and N_2 physisorption isotherm features before and after post-processing treatments.

Printed polymer sample (800 μm)	**Characteristics Related to Printability in FFF**	**N_2 physisorption isotherm characteristics**	**Mass loss with 3-chloro-1-propanol (3C1P) treatment**	**N_2 physisorption isotherm characteristics after 3C1P treatment**
(37.5:12.5:50)-PCL/PLA/PIM-1	Good printability, most flexible ternary filament	High macroporosity	Avg = 38.6 %; N = 2, (38.5 %, 38.7%)	High microporosity/broad range of small pores, moderate desorption hysteresis, SA_{BET} = 397 m^2 g^{-1}
(25:25:50)-PCL/PLA/PIM-1	Good printability, moderate flexibility in ternary filaments	High macroporosity	Avg. = 33.9 %; N = 2, (33.0%, 34.7%)	High microporosity, moderate desorption hysteresis, SA_{BET} = 379 m^2 g^{-1}
(12.5:37.5:50)-PCL/PLA/PIM-1	Good printability, least flexible ternary filament	Moderate macroporosity	Avg. = 13.0 %; N = 2, (13.4%, 12.7%)	Low microporosity/sharp increase at high p/p_o, large desorption hysteresis, SA_{BET} = 43 m^2 g^{-1}
(37.5:12.5:50)-PCL/PLA/PIM-1 *inverse addition*	Good printability, most flexible filament	Low macroporosity	not determined	High microporosity, moderate desorption hysteresis, SA_{BET} = 460 m^2 g^{-1}

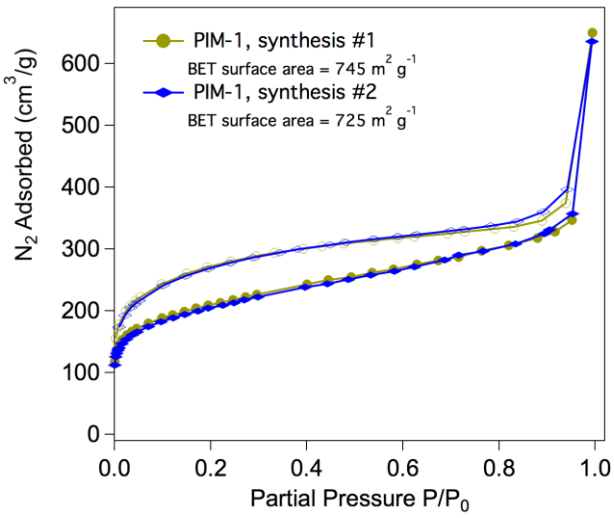

Figure S1: N_2 physisorption isotherms recorded at -196 °C of PIM-1 powders from two separate reactions.

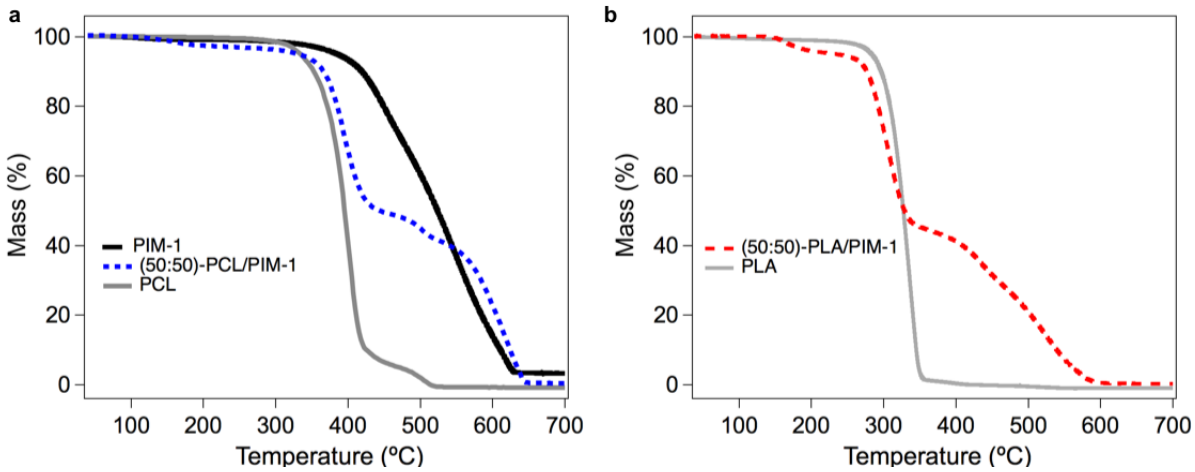

Figure S2: TGA analyses (air, heating rate of 5 °C min^{-1}) of (a) PIM-1 powder, (50:50)-PCL/PIM-1, PCL extruded filaments and (b) (50:50)-PLA/PIM-1, PLA extruded filaments. The primary decomposition feature of the thermoplastic component in each composite is clearly observed first as the temperature increased, followed by a second primary decomposition step from that of PIM-1. The exact ratio was not calculated from this data, as there may be residual trapped $CHCl_3$ present (below < 200 °C) from solution processing (see Figure S5) and/or shifting in the decomposition features due to interactions between the two components. However, each component appears to be approximately in equal proportion after processing the composites into filament, in correlation with the original input ratio.

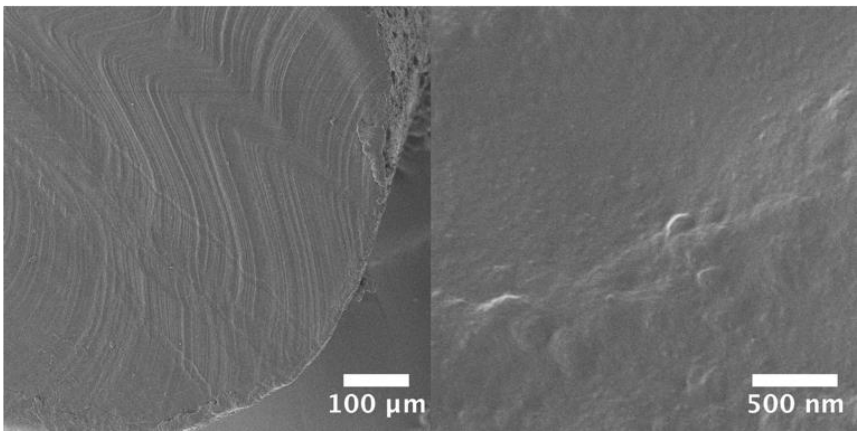

Figure S3: HeIM images of a FFF printed PCL (d = 800 µm) strand in cross-section at low magnification (left) and high magnification (right).

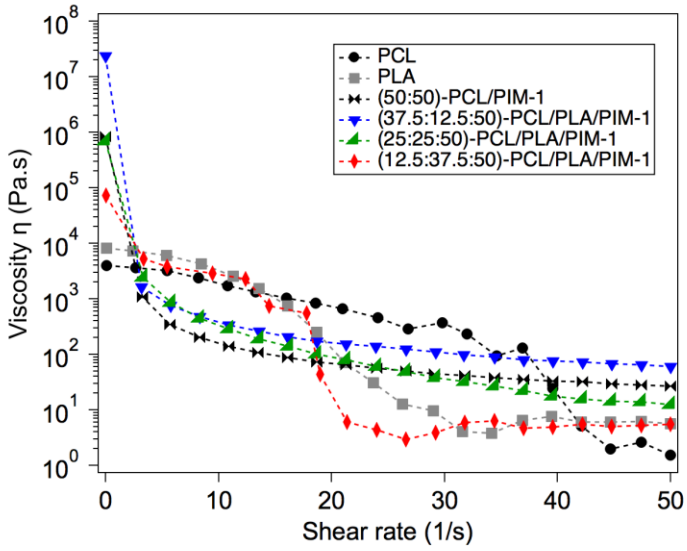

Figure S4: Viscosity (η) as a function of shear rate for homopolymer thermoplastics, binary (50:50)-PCL/PIM-1 blend, and ternary PCL/PLA/PIM-1 blends at 185 °C

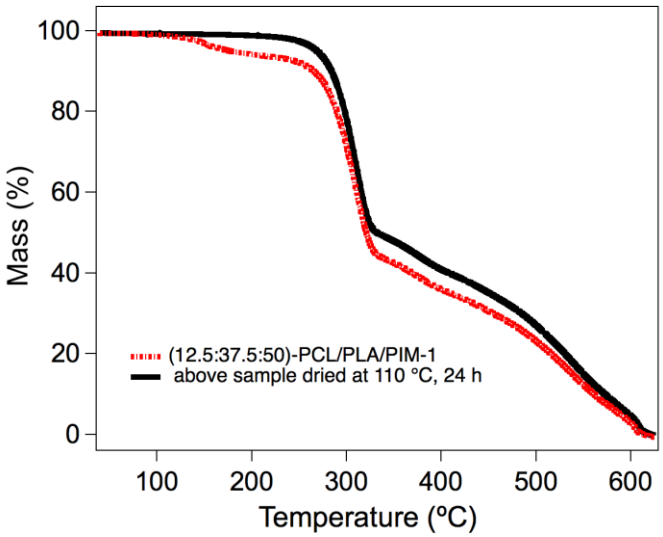

Figure S5: TGA analyses (air, heating rate of 5 °C min^{-1}) on FFF printed (12.5:37.5:50)-PCL/PLA/PIM-1 (d = 800 µm) strands after drying with the standard protocol (50 °C for 24 h, red-dashed trace) and with drying at 110 °C for 24 h (solid black trace).

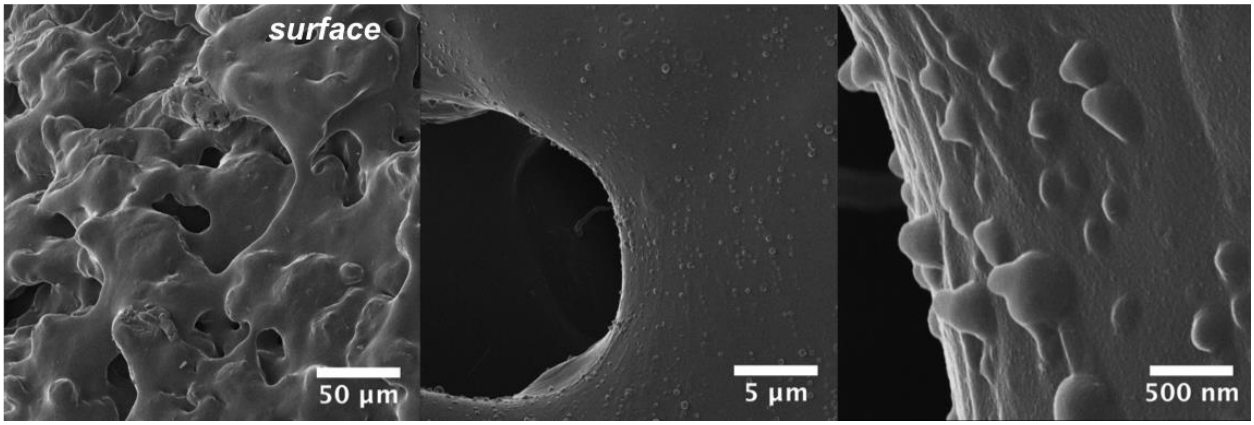

Figure S6: HeIM images of a FFF printed (37.5:12.5:50)-PCL/PLA/PIM-1 strand (d = 800 µm) in plane view (i.e. along the surface). Note: cross-section images of the same material provided in Figure 7c of the main text.

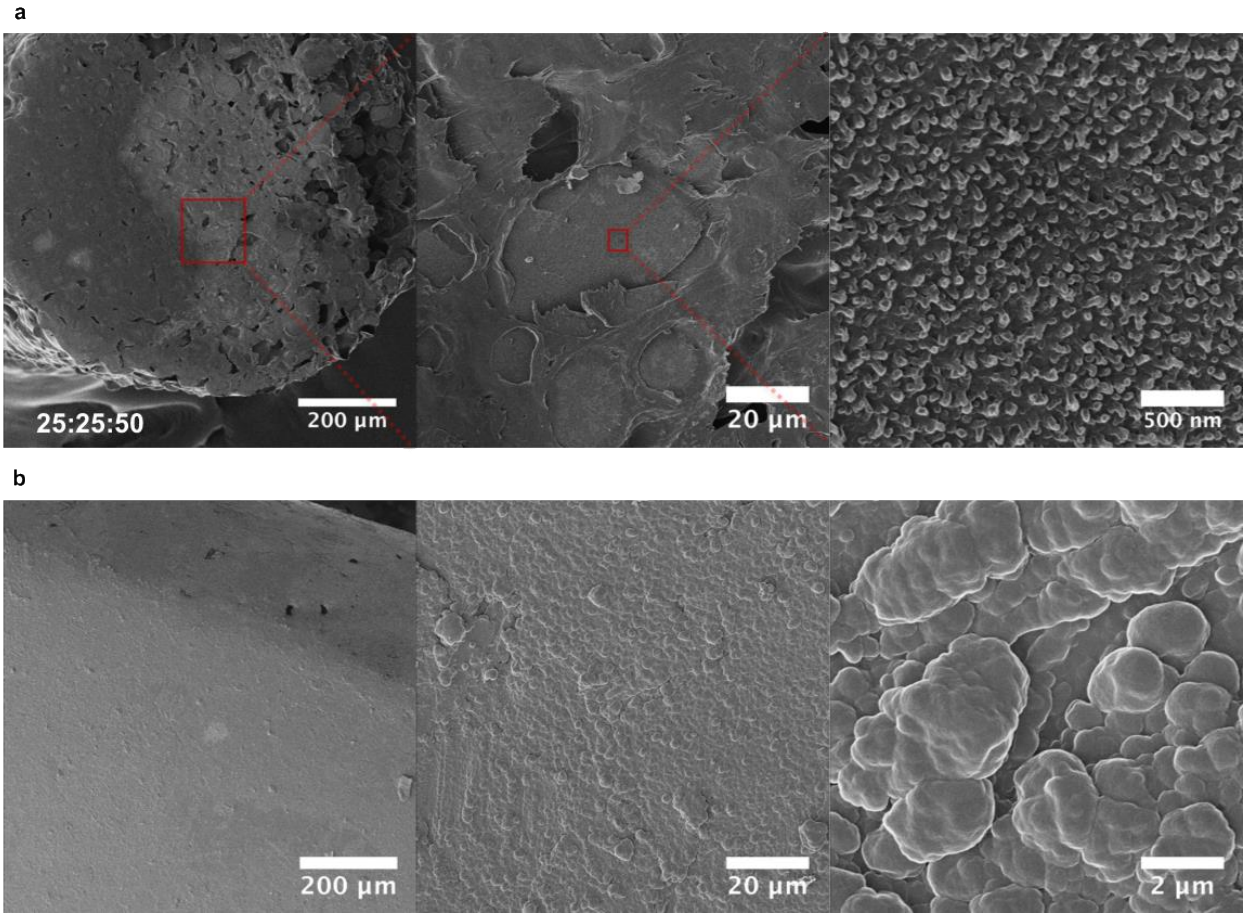

Figure S7: HeIM images of a FFF printed (25:25:50)- PCL/PLA/PIM-1 strand (d = 800 µm) in cross-section (a) as printed and (b) after 3-chloro-1-propanol (3C1P) treatment (22 h soak).

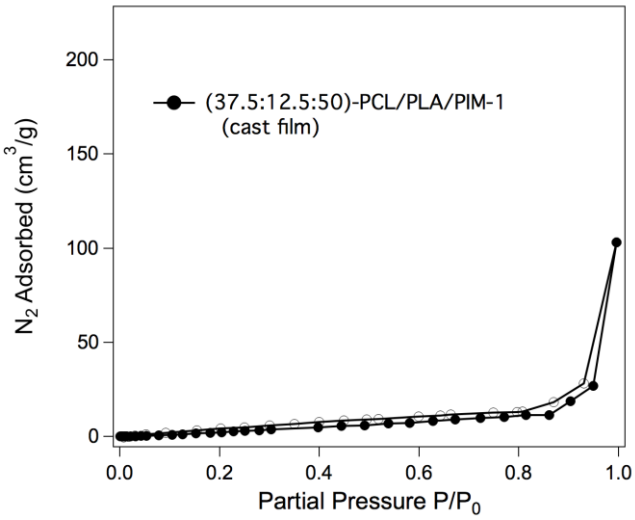

Figure S8: N_2 physisorption isotherm of solution cast (37.5:12.5:50)-PCL/PLA/PIM-1 film.

References

1. Yin, H.; Zen Chua, Y.; Yang, B.; Schick, C.; Harrison, W. J.; Budd, P. M.; Böhning, M.; Schönhals, A. "First Clear-Cut Experimental Evidence of a Glass Transition in a Polymer with Intrinsic Microporosity: PIM-1". *J. Phys. Chem. Lett.* **2018**, *9*, 2003-2008.
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