One-pot depolymerization-repolymerization of PET waste into sustainable photocurable liquid copolyesters for high-performance additive manufacturing

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SUPPORTING INFORMATION

Catalyst	Concentration	Reaction Temperature	Reaction Time	Reaction outcome
		ONE-STEP		
$Co(OAc)_2$	5 mol.%	190°C	2 h @ P_{atm} 2 h vacuum	Soluble oligomers
$Zn(C_{18}H_{35}O_2)_2$	5 mol.%	190°C	2 h @ P_{atm} 2 h vacuum	Soluble oligomers
DBTO	2 mol.%	170°C	2 h @ P_{atm} 2 h vacuum	Crosslinked polyester
DBTDL	2 mol.%	140°C	2 h @ P_{atm} 2 h vacuum	Crosslinked polyester
		TWO-STEPS		
DBTO	2 mol.%	170°C	STEP 1: 2 h STEP 2: 1 h @ P_{atm} 1 h vacuum	Viscous liquid polyester
DBTDL	2 mol.%	140°C	STEP 1: 2 h STEP 2: 1 h @ P_{atm} 1 h vacuum	Viscous liquid polyester

Table S1. Screening of depolymerization-repolymerization catalysts and reaction conditions. For all tests, the PET:DMI:BDO molar ratio was 0.2:1:1.2. Catalyst content is expressed as mol.% with respect to the diol.

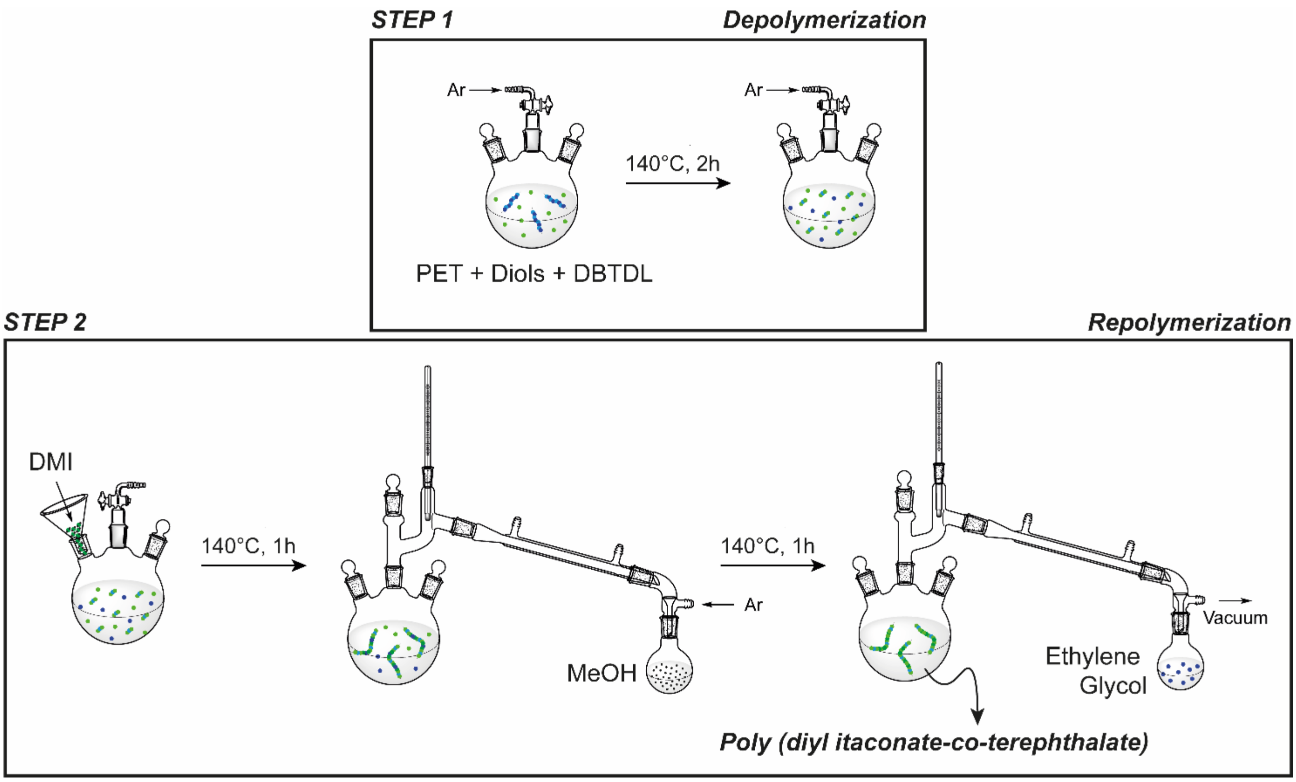

Figure S1. Schematic representation of the experimental setup employed for PET depolymerization-repolymerization into photocurable itaconic acid-based polyesters.

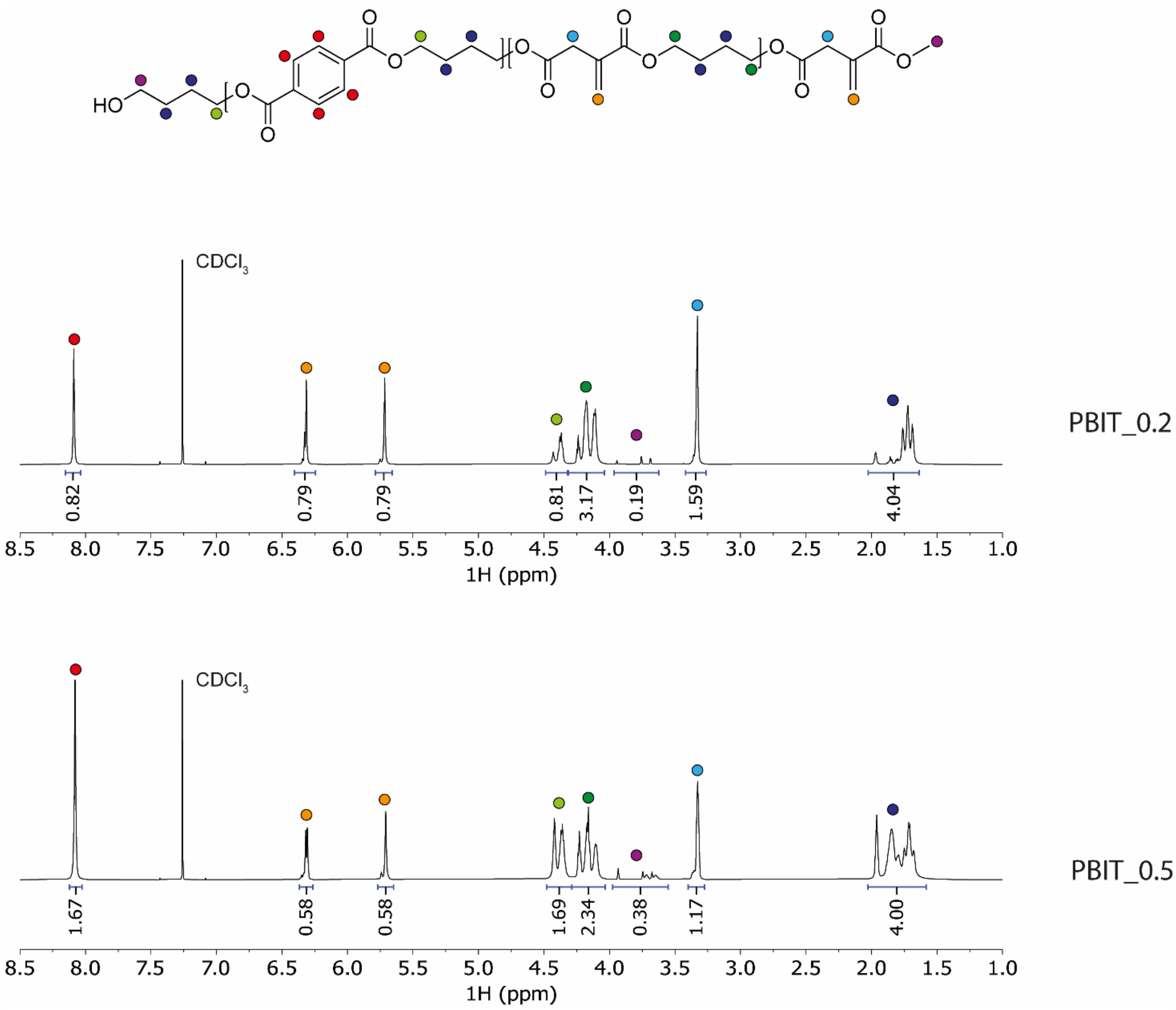

Figure S2. ^{1}H-NMR (600 MHz, $CDCl_3$) of poly(butanediyl itaconate-*co*-terephthalate)s PBIT_0.2 and PBIT_0.5 with the corresponding spectral assignments.

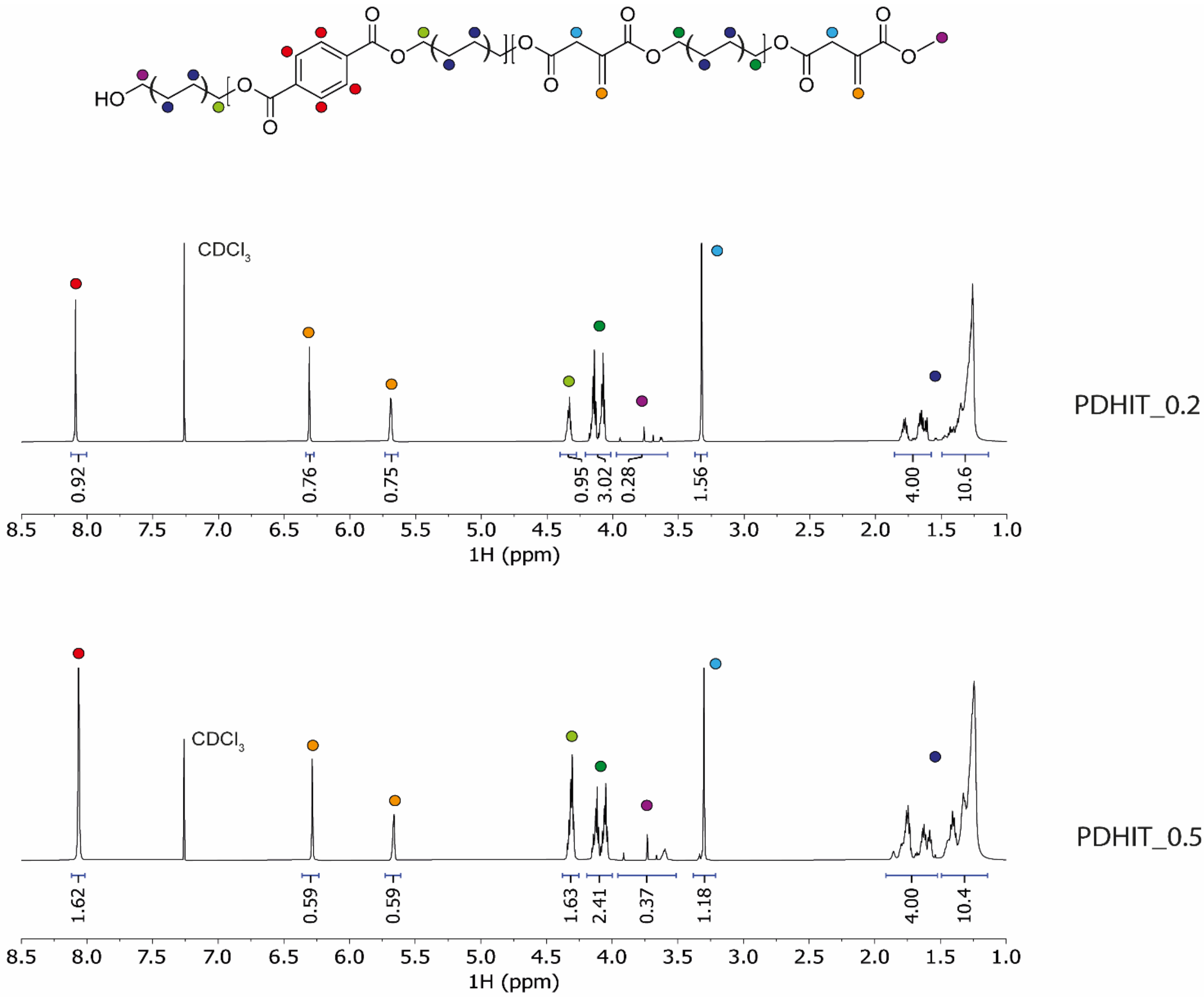

Figure S3. [1]H-NMR (600 MHz, $CDCl_3$) of poly(dodecanediyl-*co*-hexanediyl itaconate-*co*-terephthalate)s PDHIT_0.2 and PDHIT_0.5 with the corresponding spectral assignments.

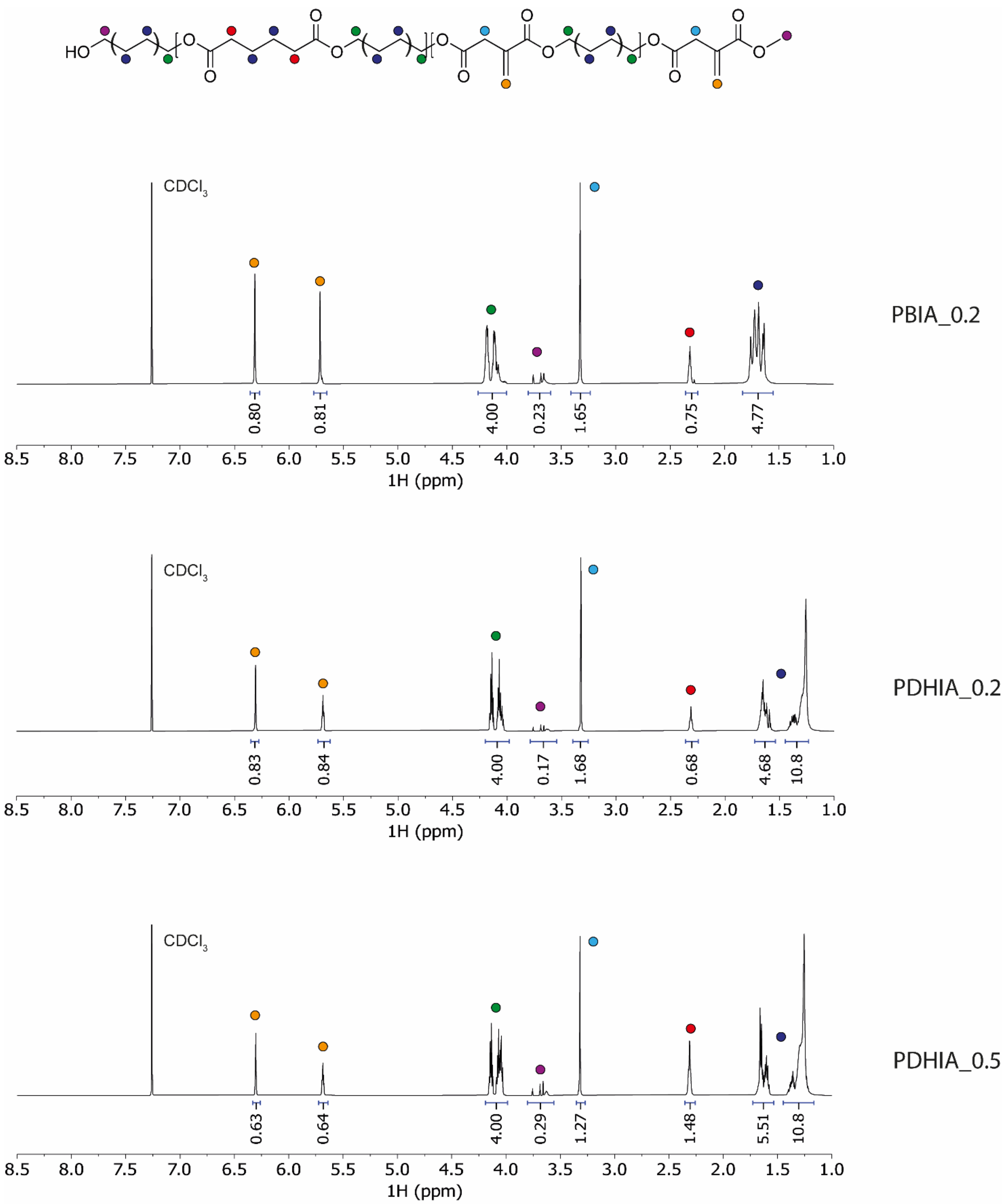

Figure S4. ^{1}H-NMR (600 MHz, $CDCl_3$) of poly(butanediyl itaconate-*co*-adipate)s PBIA_0.2, and poly(dodecanediyl-*co*-hexanediyl itaconate-*co*-adipate)s PDHIA_0.2 and PDHIA_0.5 with the corresponding spectral assignments.

Sample	**TA**	**BDO**	**DDO + HDO**	**IA**	**AA**	$\boldsymbol{TA}$ **(wt.%)**	**Terminal units peak area**
PBIT_0.2	0.27	1.26	-	1.0	-	15.7	0.19
PBIT_0.5	0.72	1.72	-	1.0	-	30.2	0.38
PDHIT_0.2	0.32	-	1.32	1.0	-	13.7	0.28
PDHIT_0.5	0.69	-	1.69	1.0	-	22.6	0.37
PBIA_0.2	-	1.23	-	1.0	0.23	-	0.23
PDHIA_0.2	-	-	1.20	1.0	0.20	-	0.17
PDHIA_0.5	-	-	1.58	1.0	0.58	-	0.29

Table S2. NMR characterization of the synthetized photocurable polyesters, including the molar ratios between the different monomers calculated from NMR integrals (TA = terephthalic acid, BDO = 1,4-butanediol, DDO+HDO = 1,12-dodecanediol + 1,6-hexanediol, IA = itaconic acid, and AA = adipic acid), the terephthalic acid mass content (TA) and the area of the peaks related to terminal monomers.

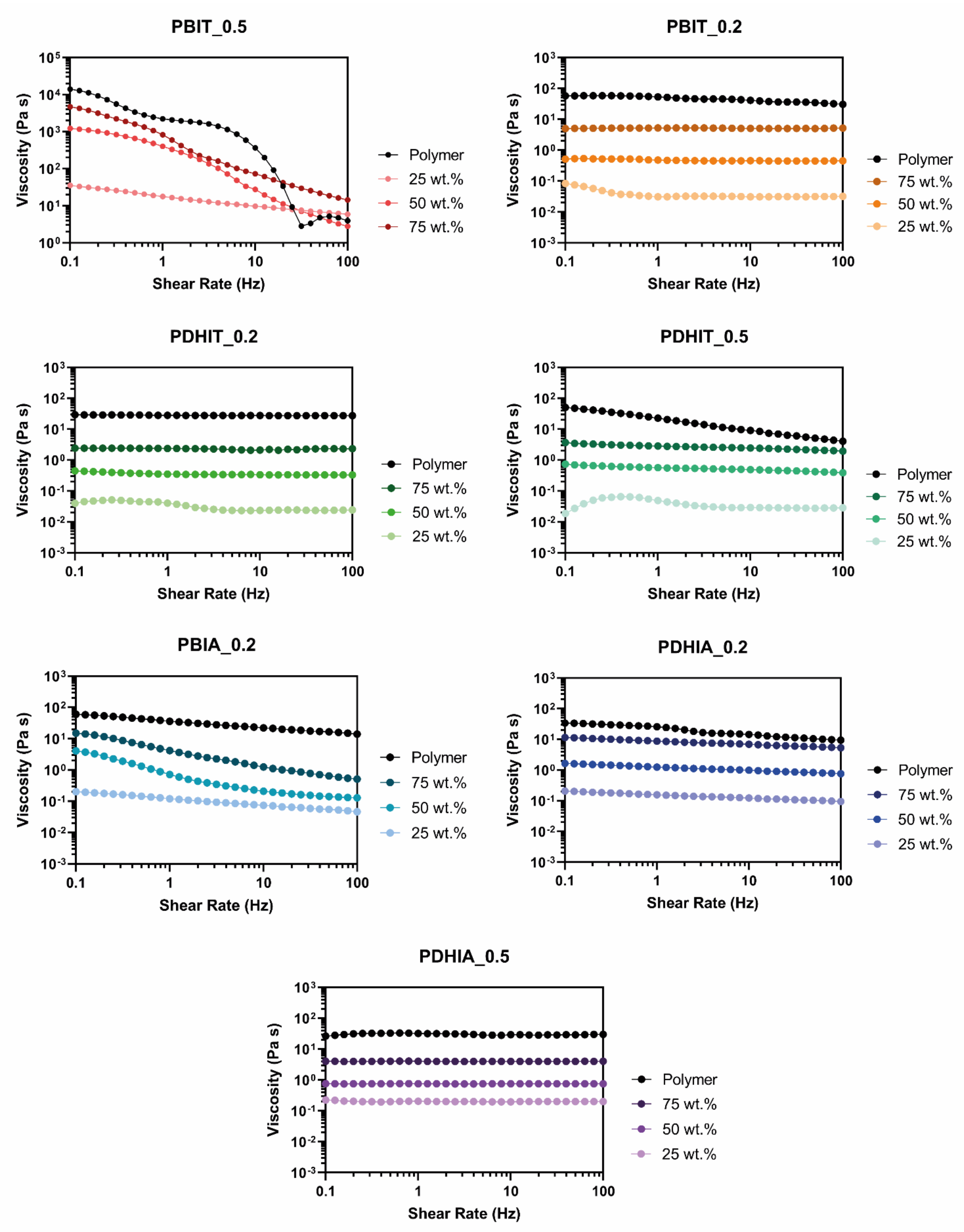

Figure S5. Rotational viscosity measurements of photocurable polyesters and their formulations for VP 3D printing.

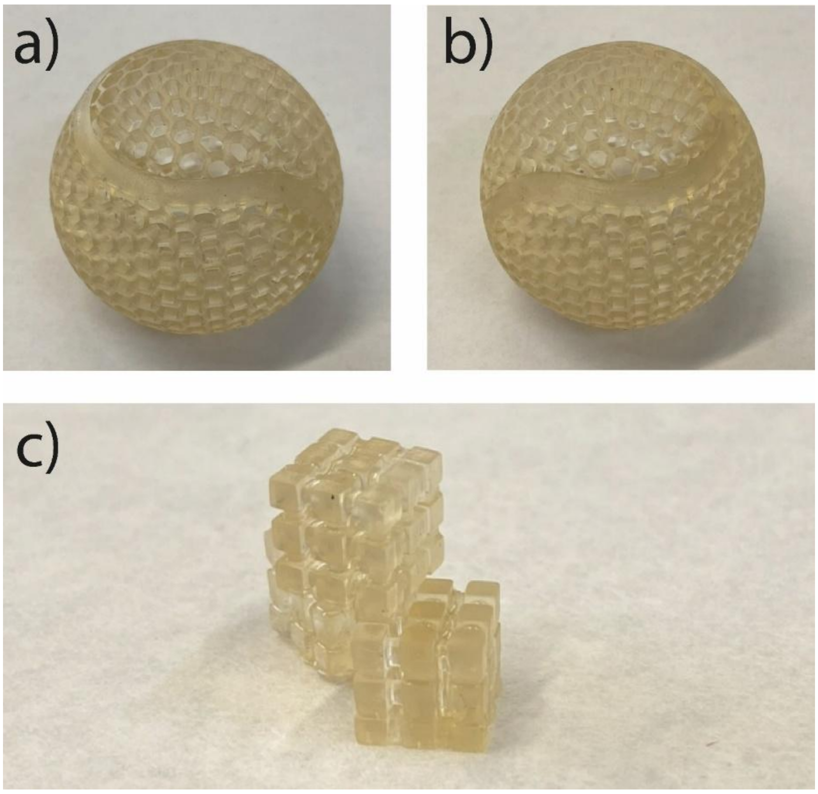

Figure S6. Examples of 3D printed objects using resins with the highest recycled PET contents. Honeycomb-patterned hollow tennis ball printed with 75 wt.% PDHIT_0.5 (a) and with 75 wt.% PBIT_0.2 (b). Object diameter is 40 mm. (c) Small hollow cubes printed with 75 wt.% PBIT_0.2. Cube lateral size is 10 mm.

Component	$BCC_{i,\%}$	f_{haz}	f_{solv}	f_T	f_t	f_{T+t}	AE	F_{syn}	F_{EoL}	Synthesis conditions
HEMA	33%	0.7	1.2	0.8	1	0.8	0.73	0.49	0.8	Methacrylic acid 1 eq, Ethylene oxide 1.5 eq 100°C 2 h
EGPEA	18%	0.7	1.2	0.8	1	0.8	0.69	0.46	0.8	Acrylic acid 1 eq, 2-phenoxyethanol 1 .5 eq 100°C 5 h
HDDA	50%	0.7	1.2	0.8	1	0.8	0.68	0.46	0.8	Acrylic acid 1 eq, 1,6-hexanediol 0.75 eq 100°C 5 h
PBIT_0.2	100%	0.9	1.2	0.8	1	0.8	0.84	0.73	0.8	PET, BDO, DMI, 140°C 2 h
PDHIT_0.2	100%	0.9	1.2	0.8	1	0.8	0.80	0.69	0.8	PET, HDO, DDO, DMI, 140°C 2 h
PDHIT_0.5	100%	0.9	1.2	0.8	1	0.8	0.83	0.71	0.8	PET, HDO, DDO, DMI, 140°C 2 h
PBIA_0.2	100%	0.9	1.2	0.8	1	0.8	0.87	0.75	0.8	DMA, BDO, DMI, 140°C 2 h
PDHIA_0.2	100%	0.9	1.2	0.8	1	0.8	0.85	0.74	0.8	DMA, HDO, DDO, DMI, 140°C 2 h
PDHIA_0.5	100%	0.9	1.2	0.8	1	0.8	0.86	0.75	0.8	DMA, HDO, DDO, DMI, 140°C 2 h

Table S3. Synthetic factors assigned to each component of the photocurable formulations for the calculation of the Sustainable Formulation Score (SFS). Such values were determined according to their original definition (see ref. 27).

		TENSILE TESTING			FLEXURAL TESTING		
		Young's Modulus (GPa)	**Elongation at Break (%)**	**Tensile Strength (MPa)**	**Flexural Modulus (MPa)**	**Deformation at Break (%)**	**Flexural Strength (MPa)**
Blank		0.068 ± 0.016	43.3 ± 1.1	7.2 ± 0.9	0.083 ± 0.015	> 20	2.7 ± 0.4
PBIT_0.2	25%	0.159 ± 0.015	9.7 ± 0.5	8.3 ± 0.5	0.196 ± 0.017	10.3 ± 0.6	8.9 ± 0.8
	50%	0.659 ± 0.042	7.5 ± 2.0	21.5 ± 1.6	0.782 ± 0.027	7.4 ± 0.2	32.9 ± 0.7
	75%	1.48 ± 0.05	2.7 ± 0.5	33.0 ± 6.6	1.40 ± 0.02	5.1 ± 0.8	54.2 ± 4.5
PDHIT_0.2	25%	0.042 ± 0.005	13.4 ± 1.3	4.2 ± 0.5	0.040 ± 0.003	14.0 ± 0.8	3.4 ± 0.3
	50%	0.418 ± 0.052	11.1 ± 1.8	15.4 ± 1.4	0.285 ± 0.019	8.0 ± 3.9	12.7 ± 4.3
	75%	0.507 ± 0.005	7.4 ± 0.5	19.4 ± 0.9	0.452 ± 0.011	8.3 ± 2.4	25.1 ± 2.7
PDHIT_0.5	25%	0.026 ± 0.002	19.3 ± 1.4	4.3 ± 0.2	0.026 ± 0.001	> 20	3.5 ± 0.1
	50%	0.074 ± 0.006	12.8 ± 0.5	7.1 ± 0.1	0.122 ± 0.004	13.1 ± 2.9	9.8 ± 1.0
	75%	0.174 ± 0.007	6.9 ± 0.9	9.8 ± 1.0	0.210 ± 0.012	13.2 ± 1.5	17.2 ± 0.5
PBIT_0.2	25%	0.226 ± 0.010	5.6 ± 0.6	7.8 ± 0.7	0.243 ± 0.016	6.7 ± 0.8	11.8 ± 1.0
	50%	0.971 ± 0.018	1.8 ± 0.3	16.1 ± 2.4	0.942 ± 0.026	1.5 ± 0.4	13.9 ± 3.6
	75%	0.987 ± 0.041	2.0 ± 0.6	16.9 ± 4.1	1.02 ± 0.02	3.5 ± 0.6	31.7 ± 4.5
PDHIA_0.2	25%	0.071 ± 0.005	15.0 ± 1.9	7.8 ± 1.0	0.074 ± 0.002	13.8 ± 1.4	7.5 ± 0.4
	50%	0.434 ± 0.023	7.2 ± 3.8	16.3 ± 4.1	0.430 ± 0.017	6.2 ± 3.3	18.4 ± 5.9
	75%	0.482 ± 0.035	4.3 ± 0.8	15.8 ± 2.4	0.464 ± 0.015	7.8 ± 0.9	26.0 ± 0.8
PDHIA_0.5	25%	0.024 ± 0.002	9.9 ± 4.4	2.4 ± 1.2	0.022 ± 0.001	19.1 ± 1.6	3.0 ± 0.1
	50%	0.117 ±\ 0.010	7.9 ± 2.3	6.8 ± 1.8	0.054 ± 0.001	9.9 ± 0.6	4.7 ± 0.3
	75%	0.200 ± 0.011	3.9 ± 0.9	6.9 ± 1.1	0.138 ± 0.010	7.1 ± 1.2	8.8 ± 1.2

Table S4. Tensile and flexural properties of 3D printed materials. Data are expressed as mean ± SD of a set of n = 5 replicates. Samples Blank and DHT5_25 did not break under flexural stress up to the limit of the universal testing machine (20%).

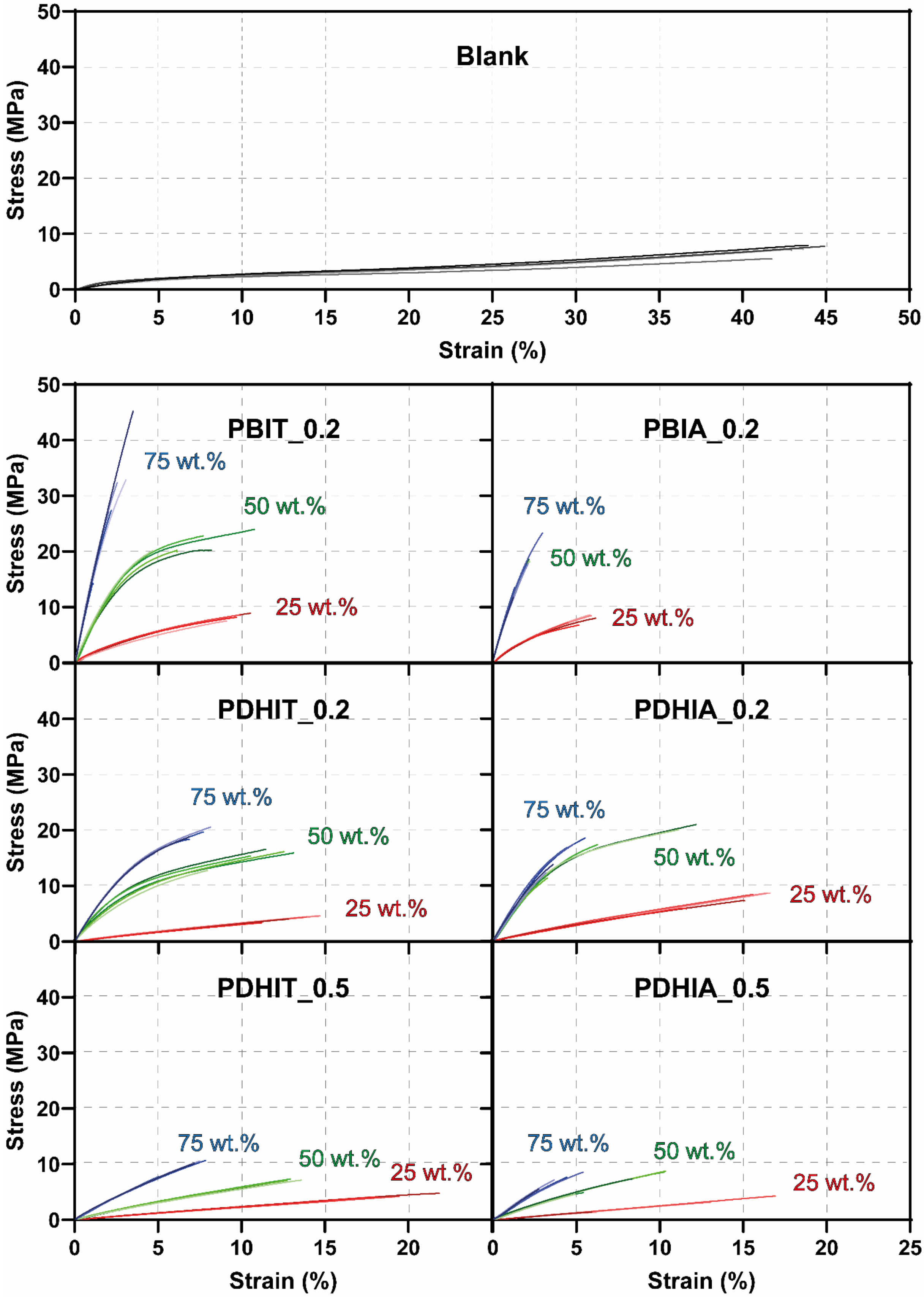

Figure S7. Individual tensile stress-strain curves obtained by testing 3D printed materials.

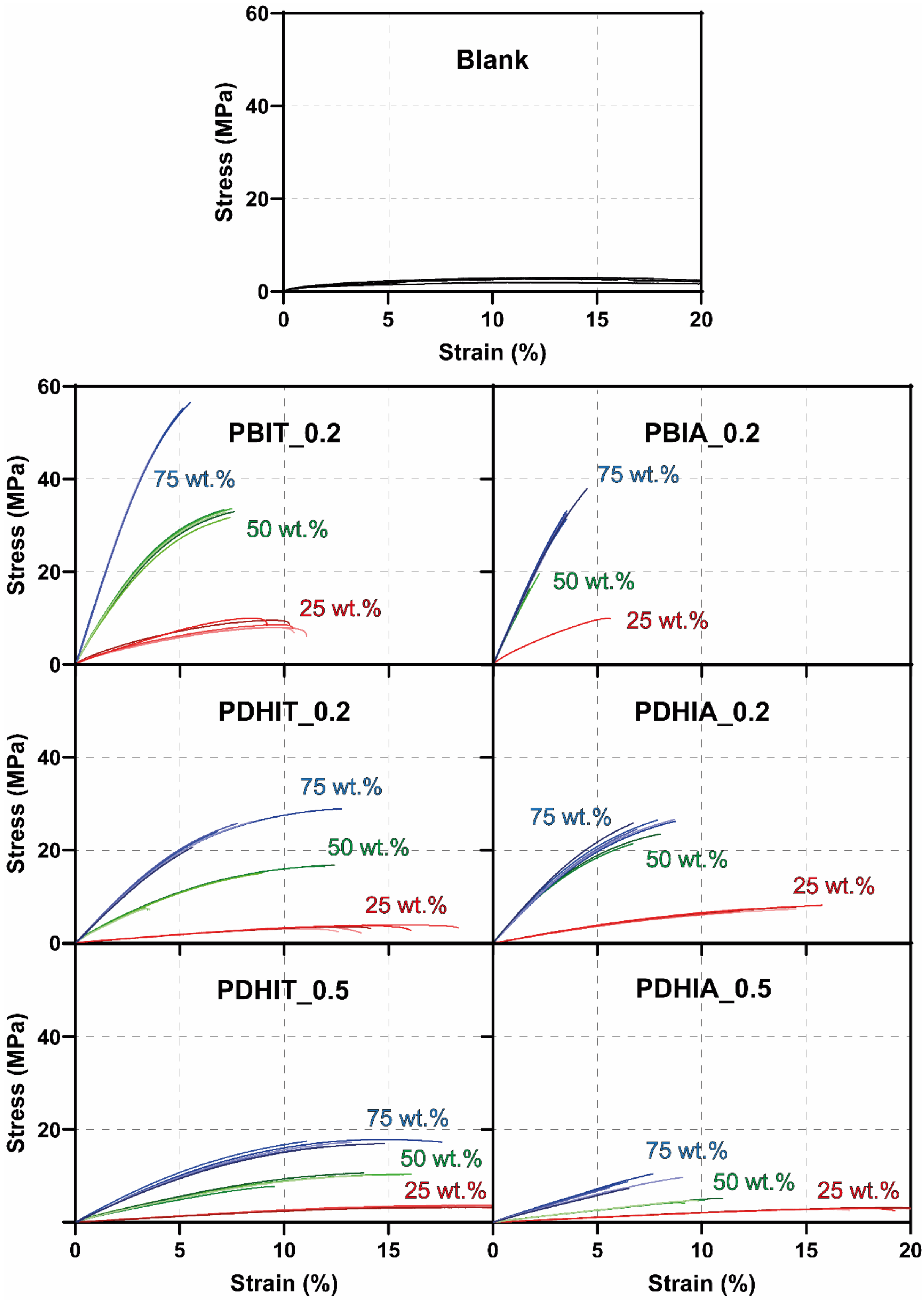

Figure S8. Individual flexural stress-strain curves obtained by testing 3D printed materials.

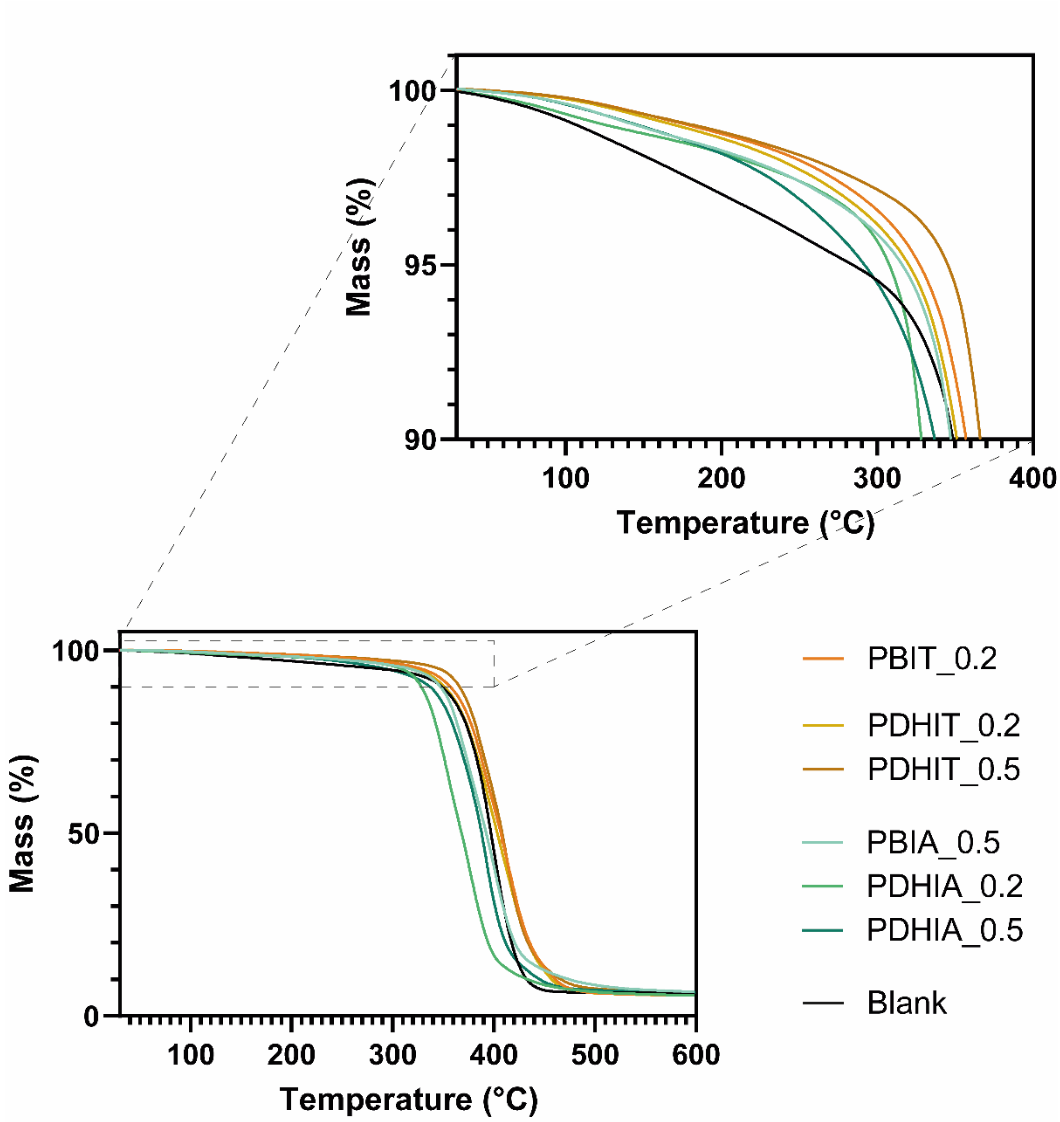

Figure S9. Thermogravimetric analysis (TGA) of 3D printed materials.