Supporting Information

Exploring the Limits of Toughness Enhancers for 3D Printed Photopolymers as Bone Replacement Materials.

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Materials and General Methods.

5-norbornene-2-carboxylic acid (endo/exo mixture; TCI Chemicals), oxalyl chloride (>98.0%; Sigma Aldrich), vinyl chloroformate (Merck), triethylamine (Et_3N; Bartelt) were purchased from respective companies and used as received unless otherwise noted.

3-point bending tests:

These experiments were done with rectangular shaped specimens (2x5x40 mm^3) on a Zwick Z050 testing machine with a span length of 32 mm and a fin of 2.5 mm radius. The crosshead speed was set to 1 $mm \cdot min^{-1}$ and the standard strain σ_{fC} was set to 7%. Analysis was done with the testXpert II testing software.

Synthesis Procedures.

Three different end group modifications of PCL (vinyl carbonate (VC), norbornene (NB) and allyl carbonate (AC)) were considered. The commercially available PCL diol (xkPCL) in two different molecular weights (10kDa and 45kDa) were end-capped. The systematic names YxkPCL, where Y indicates the end modification and x the molecular weight (MW) in kDa are henceforth used in the text. For example, PCL with allyl carbonate (AC) groups is named **AC10kPCL** or **AC45kPCL**, respectively.

Synthesis of norbornene modified PCL (NBxkPCL)

Synthesis of 5-norbornene-2-carbonyl chloride (NBCl)

A three-neck round bottom flask was equipped with a dropping funnel, evacuated, and flushed with argon three times. The flask was charged with oxalyl chloride (99.3 mL, 4 eq., 1158 mmol), DCM (40 mL) and DMF (0.4 mL). A solution of 5-norbornene-2-carboxylic acid (40.0 g, 1 eq. 290 mmol) and DCM (120 mL) was filled into the dropping funnel and was added dropwise to the precooled oxalyl chloride solution. The ice bath was removed after complete addition and the reaction mixture was stirred for 24 h at room temperature. The residual oxalyl chloride and DCM was removed under reduced pressure. The was distilled at 6 mbar and 47 °C to afford 35.4 g (78% of theory) 5-norbornene-2-carbonyl chloride (NBCl) as colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 6.32-6.17 (m, 1H, CH=CH endo/exo), 6.17-5.99 (m, 1H, CH=CH exo/endo), 3.49-2.71 (m, 3H, CH), 2.07-1.87 (m, 1H, CH_2, CH_2 bridge), 1.57-1.38 (m, 2H, CH_2, CH_2 bridge), 1.37-1.28 (m, 1H, CH_2, CH_2 bridge) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 175.19 (s, C=O), 139.17 (s, CH=CH exo), 138.83 (s, CH=CH endo), 135.02 (s, CH=CH exo), 131.75 (s, CH=CH endo), 56.56 (s, CHC=O endo), 56.45 (s, CHC=O exo), 49.36 (s, CH_2 bridge), 47.29 (s, CH endo), 47.03 (s, CH exo), 46.43 (s, CH_2 bridge), 43.00 (s, CH endo), 42.00 (s, CH exo), 31.29 (s, CH_2 exo), 30.21 (s, CH_2 endo) ppm.

Synthesis of norbornene modified PCL (NBxkPCL)

The hydroxyl terminated PCL diol in respective molecular weight (50.0 g, 1 eq., 5 mmol for 10 kDa| 50.0 g, 1 eq., 1 mmol for 45 kDa) was added to a three-neck round bottom flask, was evacuated and flushed with argon. Then, dry DCM (200| 400 mL) to dissolve the PCL diol and Et_3N (6.9 mL, 10 eq., 50 mmol| 1.5 mL, 10 eq., 11 mmol) as acid scavenger were added. The reaction mixture was cooled with an ice bath and NBCl (6.4 mL, 10 eq., 50 mmol| 1.4 mL, 10 eq., 11 mmol) was added dropwise *via* a syringe. After complete addition, the ice bath was removed, and the reaction mixture was stirred for 24 h at room temperature. The solution was extracted with 1N HCl (3x500 mL), then sat. NaHCO3 (2x500 mL) and last with 500 mL deion. water. The organic phase was precipitated twice in cold MeOH, filtered, and dried under reduced pressure at 50 °C to obtain the purified products in quantitative yields. After functionalization with norbornene, a conversion of 90% for **NB10kPCL** and for **NB45kPCL** 95% could be reached. ^{1}H NMR (600 MHz, $CDCl_3$,δ): 6.17-5.90 (ddd, , *J* = 163.7, 3.4, 2.7 Hz, 2H, CH=CH endo/exo), 6.13-6.12 (m, 2H, CH=CH endo/exo), 4.22 (t, *J* = 6.7 Hz, 4H, -O-C$\underline{H}_2$-CH_2-O-), 4.05 (t, *J* = 6.7 Hz, ~300 or 1800H, -CO-O-C$\underline{H}_2$-CH_2-CH_2-CH_2-CH_2-CO-O-), 3.68 (m, 4H, -O-CH_2-C$\underline{H}_2$-O-), 2.28 (t, *J* = 7.5 Hz, ~300 or 1800H, -CO-O-CH_2-CH_2-CH_2-CH_2-C$\underline{H}_2$-CO-O-), 1.92-1.86 (m, 1H, CH_2, CH_2 bridge)1.63 (ddt, *J* = 13.8, 11.6, 7.2 Hz, ~600 or 3600H, -CO-O-CH_2-C$\underline{H}_2$-CH_2-C$\underline{H}_2$-CH_2-CO-O-), 1.41 – 1.33 (m, ~300 or 1800H, -CO-O-CH_2-CH_2-C$\underline{H}_2$-CH_2-CH_2-CO-O-) ppm; GPC (THF): $\overline{M_w}$ = 14 or 44 kDa. DS calculated from ^{31}P(IG)-NMR = 90% or 95%.

Synthesis of vinyl carbonate modified PCL (VCxkPCL)

The hydroxyl terminated PCL diol (50.0 g, 1 eq., 5 mmol for 10 kDa| 50 g, 1 eq., 1 mmol for 45 kDa) and dry pyridine (4.8 mL, 12 eq, 60 mmol| 1.1 mL, 12 eq., 13 mmol) were dissolved in 200│400 mL of dry DCM under argon atmosphere. After cooling to -5 °C, vinyl chloroformate (5.6 mL, 12 eq, 60 mmol| 1.3 mL, 12 eq., 13 mmol) was added dropwise *via* syringe to the stirred solution within 10 min and the temperature was kept at 0 °C for 30 min. The solution was stirred for 24 h at room temperature and was quenched afterwards with 5 mL deionized water. The reaction mixture was extracted with 3 x 500 mL 1N HCl, then two times with 500 mL sat. $NaHCO_3$ solution and once with 500 mL water. For purification of the product, the solution was precipitated twice in cold MeOH (1200 mL). The purified product was filtered and dried *in vacuum* at 40 °C. The vinyl carbonate modified products could be synthesized with a conversion of 98% (**VC10kPCL**) and 93% (**VC45kPCL**). ^{1}H NMR (600 MHz, $CDCl_3$, δ) 7.08 (dd, J = 6.05, 13.74 Hz, 2 H, CH_2=C$\underline{H}$), 5.07 (dd, J = 2.70, 13.74 Hz, 2 H, trans-CH_2=), 4.77 (dd, J = 2.70, 6.05 Hz, 2 H, cis-CH_2=)., 4.22 (t, *J* = 6.7 Hz, 4H, -O-C<u>H</u>$_2$-CH_2-O-), 4.05 (t, *J* = 6.7 Hz, ~300 or 1800H, -CO-O-C<u>H</u>$_2$-CH_2-CH_2-CH_2-CH_2-CO-O-), 3.68 (m, 4H, -O-CH_2-C<u>H</u>$_2$-O-), 2.28 (t, *J* = 7.5 Hz, ~300 or 1800H, -CO-O-CH_2-CH_2-CH_2-CH_2-C<u>H</u>$_2$-CO-O-), 1.92-1.86 (m, 1H, CH_2, CH_2 bridge)1.63 (ddt, *J* = 13.8, 11.6, 7.2 Hz, ~600 or 3600H, -CO-O-CH_2-C<u>H</u>$_2$-CH_2-C<u>H</u>$_2$-CH_2-CO-O-), 1.41 – 1.33 (m, ~300 or 1800H, -CO-O-CH_2-CH_2-C<u>H</u>$_2$-CH_2-CH_2-CO-O-) ppm; GPC (THF): $\overline{M_w}$ = 14 or 44 kDa. DS calculated from ^{31}P(IG)-NMR = 98% or 93%.

Formulation preparation of functionalized PCLs.

Three different end group modifications of PCL (vinyl carbonate (VC), norbornene (NB) and allyl carbonate (AC)) were considered. Furthermore, two varying molecular weights (10kDa and 45kDa) and their influence on the mechanical properties were investigated. Moreover, two different thiols (commercially available 1,1,1-trimethylolpropane-tris(3-mercaptopropionate) (Thiol 1) and the synthesized rigid 1,3,5-tris(3-mercaptopropyl)-1,3,5-triazine-2,4,6-trione (Thiol 2)) and their impact on the final material properties were investigated. All compounds are listed in Figure S. 1.

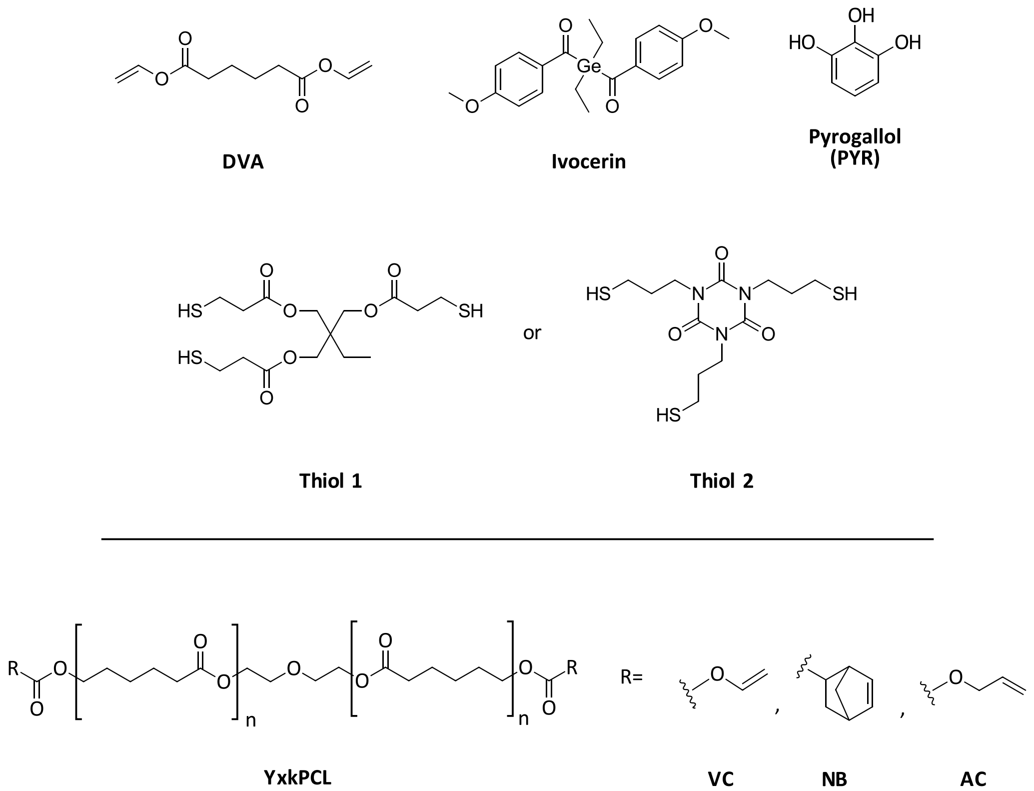

Figure S. 1. Structures of the components used in the references (top, Ref. Thiol 1 and Ref. Thiol 2) and the investigated additives (bottom); DVA as vinyl ester monomer, Thiol 1 and Thiol 2 as network regulator, Ivocerin as photoinitiator, pyrogallol (PYR) as stabilizer and YxkPCL as additives.

Viscosity measurements.

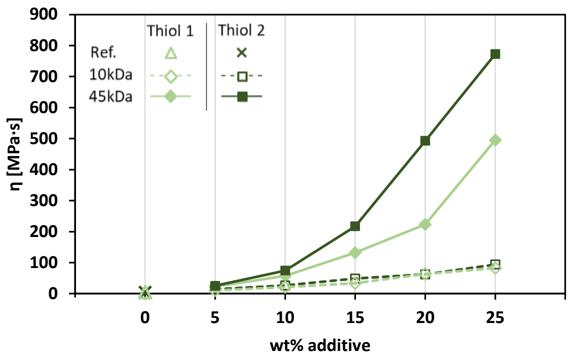

Figure S. 2. Rheological measurement results of formulations containing DVA, 15 db% thiol, 0.5 wt% Ivocerin and 0.02 wt% PYR. Ref. Thiol 1 (without additive): light green triangle; containing additional 5-25 wt% ACxkPCL (light green diamonds) or Ref. Thiol 2 (without additive): dark green cross; containing additional 5-25 wt% ACxkPCL (dark green squares). Empty symbols with dashed lines indicate AC10kPCL and full symbols with solid lines indicate AC45kPCL. The straight lines are only for a better visibility.

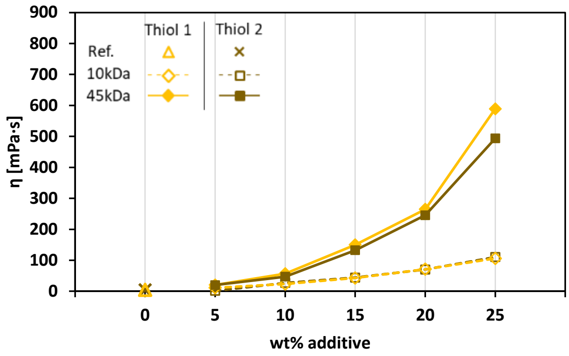

Figure S. 3. Rheological measurement results of formulations containing DVA, 15 db% thiol, 0.5 wt% Ivocerin and 0.02 wt% PYR. Ref. Thiol 1 (without additive): yellow triangle; containing additional 5-25 wt% NBxkPCL (yellow diamonds) or Ref. Thiol 2 (without additive): ochre cross; containing additional 5-25 wt% NBxkPCL (ochre squares). Empty symbols with dashed lines indicate NB10kPCL and full symbols with solid lines indicate NB45kPCL. The straight lines are only for a better visibility.

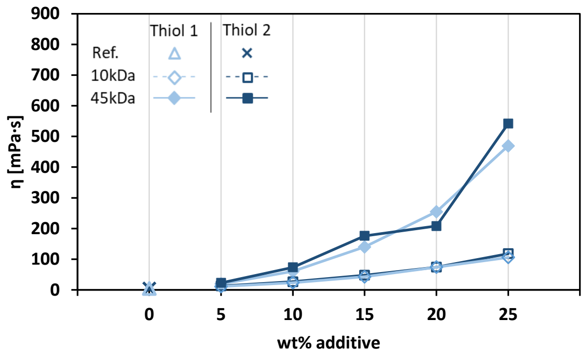

Figure S. 4. Rheological measurement results of formulations containing DVA, 15 db% thiol, 0.5 wt% Ivocerin and 0.02 wt% PYR. Ref. Thiol 1 (without additive): light blue triangle; containing additional 5-25 wt% VCxkPCL (light blue diamonds) or Ref. Thiol 2 (without additive): dark blue cross; containing additional 5-25 wt% VCxkPCL (dark blue squares). Empty symbols with dashed lines indicate VC10kPCL and full symbols with solid lines indicate VC45kPCL. The straight lines are only for a better visibility.

Table S. 1. Rheological measurement results of formulations containing DVA, 15 db% thiol, 0.5 wt% Ivocerin and 0.02 wt% PYR. Ref. Thiol 1 (without additive); containing additional 5-25 wt% YxkPCL.

Thiol	additive	wt% additive	η [mPa·s]
Thiol 1	Ref. Thiol 1	0	4.4
	AC10kPCL	5	10.5
		10	20.9
		15	33.6
		20	63.2
		25	82.7
	AC45kPCL	5	22.7
		10	57.4
		15	132.0
		20	223.4
		25	495.1
	NB10kPCL	5	11.4
		10	23.4
		15	42.7
		20	71.1
		25	106.0
	NB45kPCL	5	20.4
		10	56.9
		15	150.0
		20	264.8
		25	589.0
	VC10kPCL	5	11.1
		10	23.6
		15	42.7
		20	74.1
		25	106.0
	VC45kPCL	5	19.4
		10	60.4
		15	140.0
		20	254.6
		25	469.4

Table S. 2. Rheological measurement results of formulations containing DVA, 15 db% thiol, 0.5 wt% Ivocerin and 0.02 wt% PYR. Ref. Thiol 2 (without additive); containing additional 5-25 wt% YxkPCL.

Thiol	additive	wt% additive	η [mPa·s]
Thiol 2	Ref. Thiol 2	0	4.7
	AC10kPCL	5	14.0
		10	26.6
		15	48.8
		20	62.4
		25	93.8
	AC45kPCL	5	25.3
		10	74.3
		15	217.2
		20	492.7
		25	772.5
	NB10kPCL	5	1.3
		10	26.9
		15	44.1
		20	70.0
		25	110.2
	NB45kPCL	5	19.9
		10	47.1
		15	132.3
		20	245.6
		25	493.5
	VC10kPCL	5	12.7
		10	26.6
		15	47.8
		20	74.4
		25	118.0
	VC45kPCL	5	22.9
		10	73.4
		15	176.0
		20	208.0
		25	542.0

RT-FT-NIR-Photorheology.

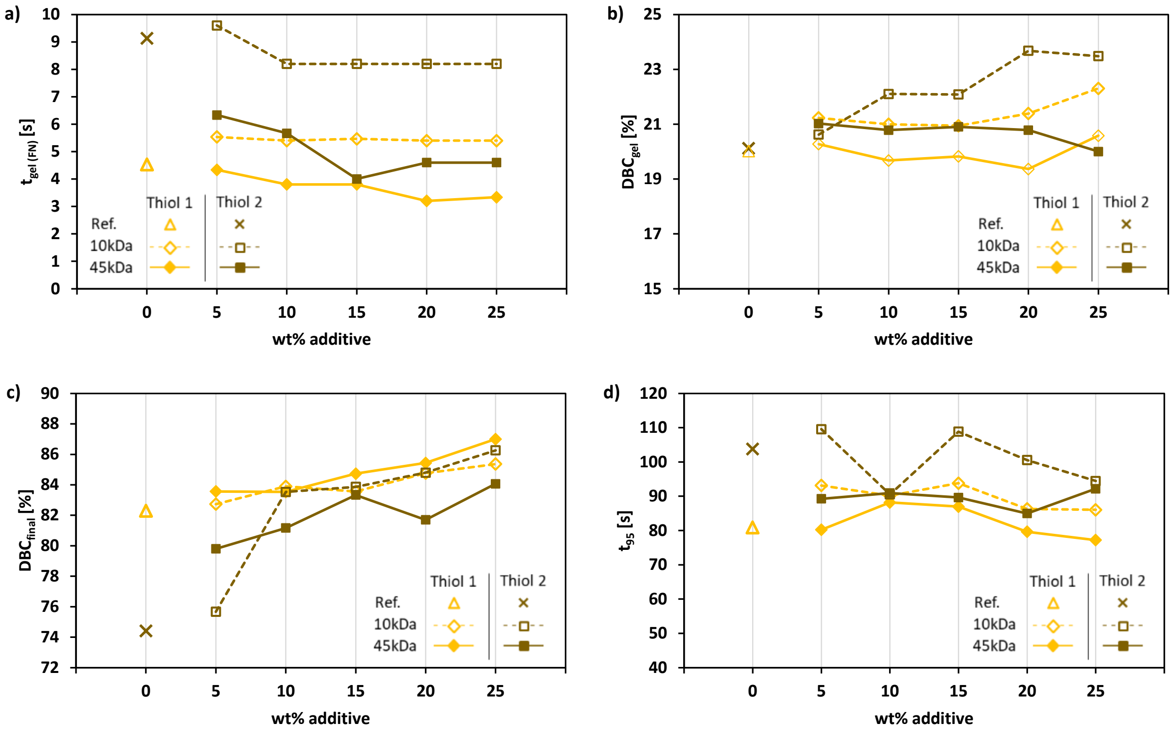

Figure S. 5. Photorheological measurement results of formulations containing DVA, 15 db% thiol, 0.5 wt% Ivocerin and 0.02 wt% PYR. Ref. Thiol 1 (without additive): yellow triangle; containing additional 5-25 wt% NBxkPCL (yellow diamonds) or Ref. Thiol 2 (without additive): ochre cross; containing additional 5-25 wt% NBxkPCL (ochre squares). Empty symbols with dashed lines indicate NB10kPCL and full symbols with solid lines indicate NB45kPCL. The straight lines are only for a better visibility. a) Obtained values for the gel point (t_{gel}); b) obtained values for the double bond conversion at t_{gel} (DBC_{gel}); c) obtained values for the final double bond conversion (DBC_{final}) and d) obtained values for the time to reach 95% of the final DBC (t_{95}).

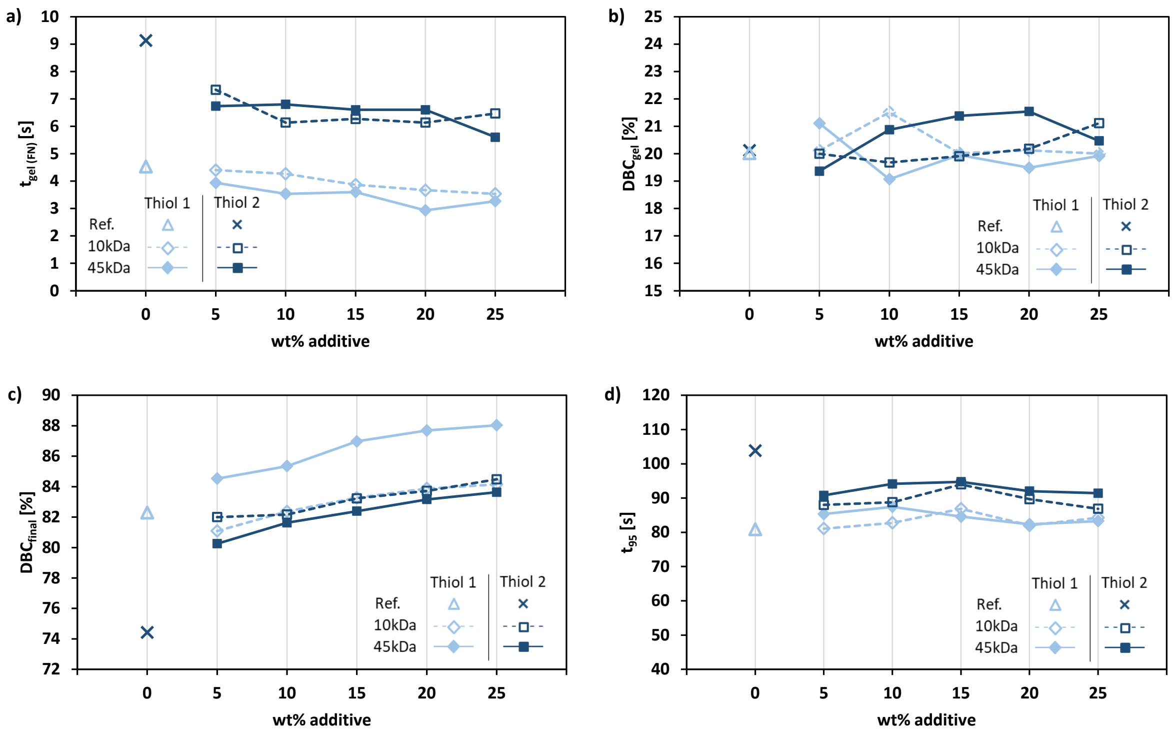

Figure S. 6. Photorheological measurement results of formulations containing DVA, 15 db% thiol, 0.5 wt% Ivocerin and 0.02 wt% PYR. Ref. Thiol 1 (without additive): light blue triangle; containing additional 5-25 wt% VCxkPCL (light blue diamonds) or Ref. Thiol 2 (without additive): dark blue cross; containing additional 5-25 wt% VCxkPCL (dark blue squares). Empty symbols with dashed lines indicate VC10kPCL and full symbols with solid lines indicate VC45kPCL. The straight lines are only for a better visibility. a) Obtained values for the gel point (t_{gel}); b) obtained values for the double bond conversion at t_{gel} (DBC_{gel}); c) obtained values for the final double bond conversion (DBC_{final}) and d) obtained values for the time to reach 95% of the final DBC (t_{95}).

Table S. 3. Photorheological measurement results of formulations containing DVA, 15 db% thiol, 0.5 wt% Ivocerin and 0.02 wt% PYR. Ref. Thiol 1 (without additive); containing additional 5-25 wt% YxkPCL.

Thiol	additive	wt% additive	t_{gel} [s]	DBC_{gel} [%]	t_{95} [s]	DBC_{final} [%]	G'_{max} [kPa]	F_{Nmax} [N]
Thiol 1	Ref. Thiol 1	0	4.5 ± 0.5	20 ± 1	81 ± 4	82 ± 0	143 ± 1	-10.9 ± 0.1
	AC10kPCL	5	4.0 ± 0.9	20 ± 1	87 ± 0	82 ± 0	128 ± 3	-11.6 ± 0.8
		10	4.1 ± 0.2	20 ± 1	85 ± 3	83 ± 0	124 ± 3	-12.7 ± 0.3
		15	3.5 ± 0.5	19 ± 2	85 ± 2	84 ± 0	121 ± 2	-11.8 ± 0.3
		20	3.0 ± 0.4	21 ± 1	81 ± 2	86 ± 0	151 ± 1	-8.9 ± 0.6
		25	2.7 ± 0.4	20 ± 1	81 ± 2	86 ± 0	150 ± 2	-8.5 ± 0.9
	AC45kPCL	5	3.7 ± 0.4	20 ± 1	89 ± 3	83 ± 0	137 ± 2	-10.1 ± 0.5
		10	3.7 ± 0.2	20 ± 1	89 ± 3	84 ± 1	134 ± 3	-10.4 ± 0.1
		15	3.2 ± 0.6	19 ± 1	90 ± 3	84 ± 0	163 ± 6	-11.1 ± 0.2
		20	2.6 ± 0.3	18 ± 1	83 ± 2	85 ± 0	129 ± 3	-0.4 ± 0.3
		25	2.9 ± 0.1	19 ± 1	84 ± 4	85 ± 0	130 ± 5	-10.9 ± 0.1
	NB10kPCL	5	5.5 ± 0.2	21 ± 1	93 ± 1	83 ± 0	143 ± 1	-10.9 ± 0.1
		10	5.4 ± 0.0	21 ± 0	90 ± 3	84 ± 0	142 ±1	-10.8 ± 0.3
		15	5.5 ± 0.1	21 ± 0	94 ± 3	84 ± 0	143 ± 6	-10.0 ± 0.6
		20	5.4 ± 0.0	21 ± 0	86 ± 4	84 ± 0	148 ± 6	-12.4 ± 1.6
		25	5.4 ± 0.0	22 ± 1	86 ± 2	85 ± 0	145 ± 4	-12.7 ± 0.6
	NB45kPCL	5	4.3 ± 0.1	20 ± 1	80 ± 1	84 ± 0	112 ± 2	-15.0 ± 0.6
		10	3.8 ± 0.3	20 ± 1	88 ± 2	84 ± 0	103 ± 2	-15.5 ± 0.1
		15	3.8 ± 0.2	20 ± 0	87 ± 1	85 ± 0	98 ± 7	-15.1 ± 0.0
		20	3.2 ± 0.0	19 ± 0	80 ± 3	85 ± 0	139 ± 3	-9.9 ± 0.7
		25	3.3 ± 0.1	21 ± 0	77 ± 2	87 ± 0	143 ± 2	-10.8 ± 0.7
	VC10kPCL	5	4.4 ± 0.4	20 ± 0	81 ± 3	81 ± 0	130 ± 2	-14.5 ± 1.3
		10	4.3 ± 0.8	22 ± 1	83 ± 3	82 ± 0	133 ± 7	-11.8 ± 1.8
		15	3.9 ± 0.4	20 ± 1	87 ± 0	83 ± 0	133 ± 2	-10.8 ± 0.3
		20	3.7 ± 0.8	20 ± 2	82 ± 3	84 ± 0	129 ± 4	-11.4 ± 0.6
		25	3.5 ± 0.2	20 ± 1	84 ± 3	84 ± 0	126 ± 1	-11.4 ± 0.5
	VC45kPCL	5	3.9 ± 0.1	21 ± 1	85 ± 2	85 ± 0	136 ± 2	-11.0 ± 1.4
		10	3.5 ± 0.8	19 ± 1	87 ± 2	85 ± 0	133 ± 0	-11.4 ± 0.5
		15	3.6 ± 0.4	20 ± 1	85 ± 3	87 ± 0	129 ± 4	-11.7 ± 0.5
		20	2.9 ± 0.4	19 ± 1	82 ± 1	88 ± 0	126 ± 0	-11.1 ± 0.2
		25	3.3 ± 0.3	20 ± 1	83 ± 1	88 ± 0	123 ± 2	-11.6 ± 0.5

Table S. 4. Photorheological measurement results of formulations containing DVA, 15 db% thiol, 0.5 wt% Ivocerin and 0.02 wt% PYR. Ref. Thiol 2 (without additive); containing additional 5-25 wt% YxkPCL.

Thiol	**additive**	**wt% additive**	t_{gel} **[s]**	**DBC**$_{gel}$ [%]	t_{95} [s]	**DBC**$_{final}$ [%]	**G'**$_{max}$ [kPa]	**F**$_{Nmax}$ [N]
Thiol 2	**Ref. Thiol 2**	0	9.1 ± 0.3	20 ± 0	104 ± 6	74 ± 0	148 ± 1	-11.3 ± 0.9
	AC10kPCL	5	4.8 ± 0.2	20 ± 1	77 ± 1	80 ± 0	118 ± 1	-11.6 ± 0.6
		10	4.6 ± 0.2	20 ± 1	79 ± 1	81 ± 0	113 ± 4	-120 ± 0.2
		15	4.6 ± 0.2	21 ± 1	85 ± 2	82 ± 0	109 ± 4	-11.9 ± 0.5
		20	5.9 ± 0.2	21 ± 0	88 ± 4	82 ± 0	144 ± 2	-10.0 ± 0.7
		25	4.6 ± 0.2	21 ± 1	72 ± 1	86 ± 0	145 ± 0	-9.0 ± 0.7
	AC45kPCL	5	5.6 ± 0.0	21 ± 0	88 ± 4	80 ± 0	132 ± 3	-10.9 ± 0.6
		10	4.8 ± 0.3	20 ± 0	84 ± 2	81 ± 0	128 ± 2	-12.2 ± 0.5
		15	4.7 ± 0.5	19 ± 1	83 ± 3	81 ± 0	121 ± 2	-11.8 ± 0.7
		20	4.5 ± 0.9	19 ± 1	92 ± 3	81 ± 0	124 ± 3	-10.9 ± 0.4
		25	4.3 ± 0.3	19 ± 0	90 ± 2	82 ± 0	120 ± 2	-10.5 ± 0.1
	NB10kPCL	5	9.6 ± 0.0	21 ± 0	110 ± 3	76 ± 0	146 ± 5	-11.6 ± 0.7
		10	8.2 ± 0.0	22 ± 1	91 ± 5	84 ± 0	145 ± 0	-12.1 ± 0.2
		15	8.2 ± 0.0	22 ± 0	109 ± 5	84 ± 0	141 ± 1	-11.2 ± 0.1
		20	8.2 ± 0.0	24 ± 1	101 ± 3	85 ± 0	139 ± 2	-10.3 ± 0.4
		25	8.2 ± 0.0	23 ± 1	94 ± 7	86 ± 1	140 ± 6	-7.7 ± 2.1
	NB45kPCL	5	6.3 ± 0.1	21 ± 0	89 ± 1	80 ± 0	119 ± 1	-10.8 ± 0.7
		10	5.7 ± 0.1	21 ± 1	91 ± 7	81 ± 0	119 ± 3	-10.5 ± 0.5
		15	4.0 ± 0.2	21 ± 1	90 ± 2	83 ± 0	110 ± 2	-9.6 ± 0.3
		20	4.6 ± 0.2	21 ± 0	85 ± 4	82 ± 1	110 ± 9	-9.2 ± 0.3
		25	4.6 ± 0.2	20 ± 1	92 ± 2	84 ± 0	125 ± 1	-11.4 ± 0.7
	VC10kPCL	5	7.3 ± 0.1	20 ± 1	88 ± 3	82 ± 1	146 ± 4	-13.8 ± 1.1
		10	6.1± 0.6	20 ± 2	89 ± 4	82 ± 0	142 ± 2	-13.6 ± 1.2
		15	6.3 ± 0.6	20 ± 1	94 ± 5	83 ± 0	139 ± 2	-13.7 ± 0.5
		20	6.1 ± 0.3	20 ± 0	90 ± 1	84 ± 0	136 ± 1	-12.9 ± 0.6
		25	6.5 ± 0.8	21 ± 2	87 ± 2	84 ± 0	133 ± 2	-13.4 ± 1.2
	VC45kPCL	5	6.7 ± 0.3	19 ± 1	91 ± 1	80 ± 0	154 ± 2	-12.0 ± 1.4
		10	6.8 ± 0.4	21 ± 0	94 ± 4	82 ± 0	151 ± 2	-11.7 ± 0.8
		15	6.6 ± 0.0	21 ± 1	95 ± 3	82 ± 0	146 ± 3	-10.4 ± 0.1
		20	6.6 ± 0.4	22 ± 1	92 ± 0	83 ± 0	144 ± 1	-9.9 ± 0.2
		25	5.6 ± 0.0	20 ± 1	91 ± 1	84 ±	140 ± 4	-9.6 ± 0.3

Thermomechanical Properties.

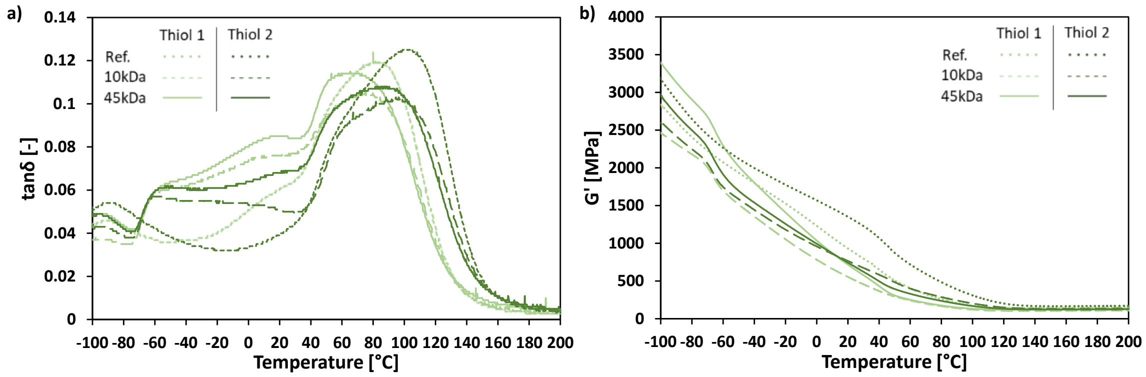

Figure S. 7. a) Loss factor (tanδ) and b) storage modulus (G') for formulations containing DVA, 15 db% thiol, 0.5 wt% Ivocerin and 0.02 wt% PYR. Ref. Thiol 1 (without additive): light green dotted line; containing additional 25 wt% ACxkPCL (light green) or Ref. Thiol 2 (without additive): dark green dotted line; containing additional 25 wt% ACxkPCL (dark green). Dashed lines indicate AC10kPCL and solid lines indicate AC45kPCL.

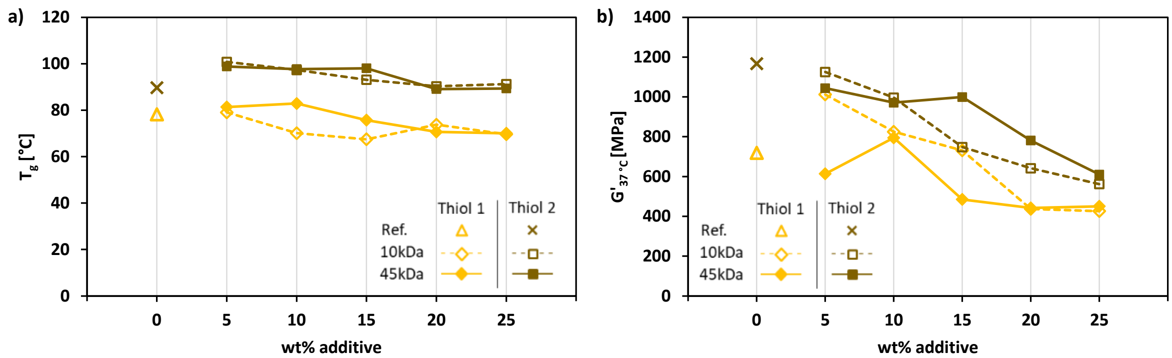

Figure S. 8. Results of DMTA measurements of formulations containing DVA, 15 db% thiol, 0.5 wt% Ivocerin and 0.02 wt% PYR. Ref. Thiol 1 (without additive): yellow triangle; containing additional 5-25 wt% NBxkPCL (yellow diamonds) or Ref. Thiol 2 (without additive): ochre cross; containing additional 5-25 wt% NBxkPCL (ochre squares). Empty symbols with dashed lines indicate NB10kPCL and full symbols with solid lines indicate NB45kPCL. The straight lines are only for a better visibility. a) Obtained values for the glass transition temperature (T_g); b) obtained values for the storage modulus at body temperature ($G'_{37\,°C}$).

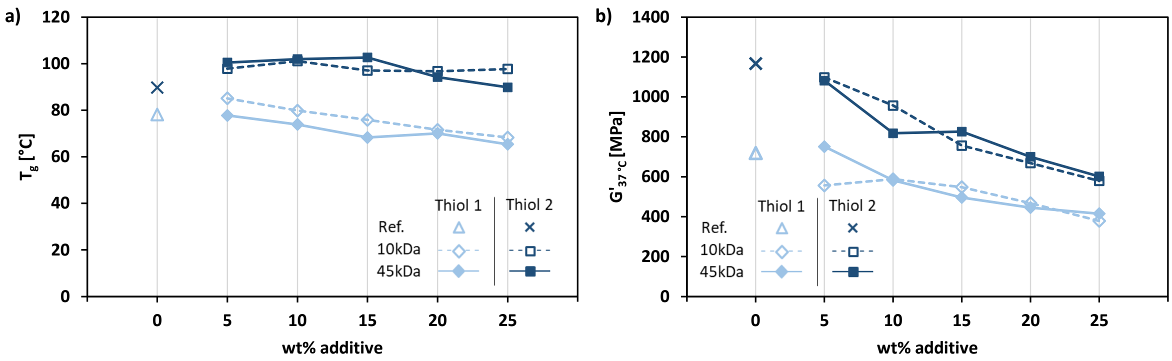

Figure S. 9. Results of DMTA measurements of formulations containing DVA, 15 db% thiol, 0.5 wt% Ivocerin and 0.02 wt% PYR. Ref. Thiol 1 (without additive): light blue triangle; containing additional 5-25 wt% VCxkPCL (light blue diamonds) or Ref. Thiol 2 (without additive): dark blue cross; containing additional 5-25 wt% VCxkPCL (dark blue squares). Empty symbols with dashed lines indicate VC10kPCL and full symbols with solid lines indicate VC45kPCL. The straight lines are only for a better visibility. a) Obtained values for the glass transition temperature (T_g); b) obtained values for the storage modulus at body temperature ($G'_{37\,°C}$).

Table S. 5. Results of DMTA measurements of formulations containing DVA, 15 db% thiol, 0.5 wt% Ivocerin and 0.02 wt% PYR. Ref. Thiol 1 (without additive); containing additional 5-25 wt% YxkPCL.

Thiol	additive	wt% additive	T_g [°C]	$G'_{25°C}$ [MPa]	$G'_{37°C}$ [MPa]	G'_R [MPa]
Thiol 1	Ref. Thiol 1	0	78	899	718	157
	AC10kPCL	5	70	1245	1048	254
		10	65	973	812	218
		15	63	882	717	184
		20	80	651	502	142
		25	75	507	391	111
	AC45kPCL	5	65	674	490	107
		10	80	679	534	127
		15	72	718	551	141
		20	67	569	427	109
		25	65	648	474	127
	NB10kPCL	5	79	1185	1012	236
		10	70	982	825	214
		15	67	892	731	191
		20	74	542	437	111
		25	70	536	426	117
	NB45kPCL	5	81	757	613	115
		10	83	954	795	139
		15	76	636	485	107
		20	71	573	442	120
		25	70	589	450	126
	VC10kPCL	5	85	674	556	106
		10	80	713	588	128
		15	76	686	548	131
		20	72	589	468	111
		25	68	488	379	101
	VC45kPCL	5	78	934	751	157
		10	74	747	582	134
		15	68	664	496	124
		20	70	598	445	114
		25	65	564	415	108

Table S. 6. Results of DMTA measurements of formulations containing DVA, 15 db% thiol, 0.5 wt% Ivocerin and 0.02 wt% PYR. Ref. Thiol 2 (without additive); containing additional 5-25 wt% YxkPCL.

Thiol	additive	wt% additive	T_g [°C]	$G'_{25°C}$ [MPa]	$G'_{37°C}$ [MPa]	G'_R [MPa]
Thiol 2	Ref. Thiol 2	0	90	1344	1167	234
	AC10kPCL	5	98	1178	1038	145
		10	94	1012	888	141
		15	91	864	737	125
		20	90	817	682	151
		25	89	722	610	134
	AC45kPCL	5	104	1137	975	171
		10	102	937	796	150
		15	98	862	708	148
		20	96	728	587	132
		25	81	685	538	127
	NB10kPCL	5	101	1275	1125	157
		10	97	1148	997	148
		15	93	877	748	129
		20	90	751	642	141
		25	91	673	562	128
	NB45kPCL	5	99	1211	1044	154
		10	98	1150	971	161
		15	98	1208	1000	177
		20	89	943	781	-
		25	89	752	610	135
	VC10kPCL	5	98	1258	1098	191
		10	101	1104	957	171
		15	97	891	756	152
		20	97	794	669	139
		25	98	692	579	129
	VC45kPCL	5	100	1242	1082	189
		10	102	968	818	147
		15	103	987	826	156
		20	94	860	700	155
		25	90	762	601	138

Mechanical Properties.

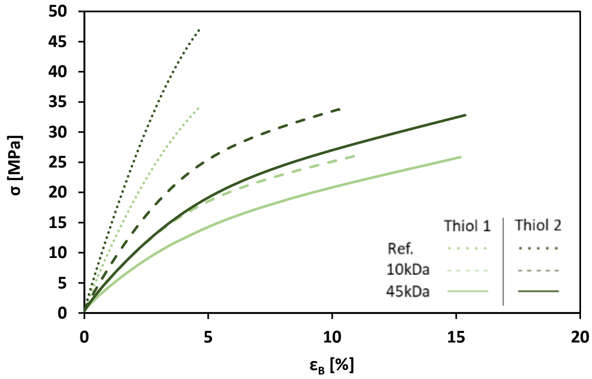

Figure S. 10. Tensile test curves for formulations containing DVA, 15 db% thiol, 0.5 wt% Ivocerin and 0.02 wt% PYR. Ref. Thiol 1 (without additive): light green dotted line; containing additional 25 wt% ACxkPCL (light green) or Ref. Thiol 2 (without additive): dark green dotted line; containing additional 25 wt% ACxkPCL (dark green). Dashed lines indicate AC10kPCL and solid lines indicate AC45kPCL.

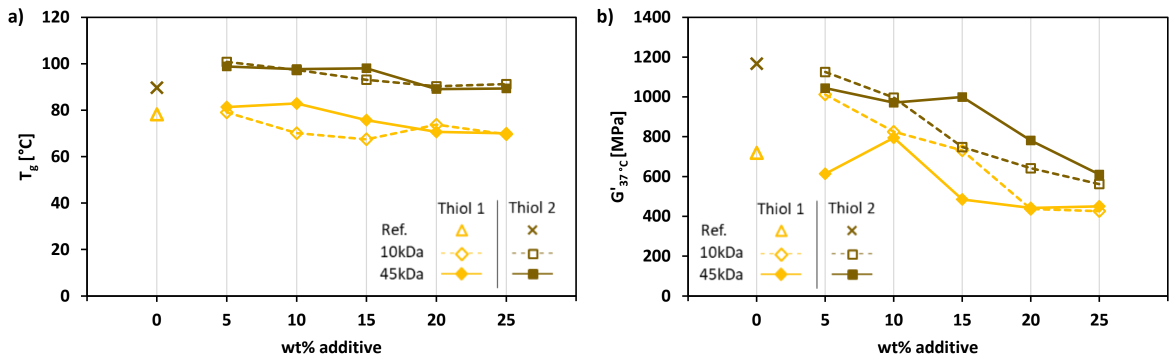

Figure S. 11. Results of tensile test measurements of formulations containing DVA, 15 db% thiol, 0.5 wt% Ivocerin and 0.02 wt% PYR. Ref. Thiol 1 (without additive): yellow triangle; containing additional 5-25 wt% NBxkPCL (yellow diamonds) or Ref. Thiol 2 (without additive): ochre cross; containing additional 5-25 wt% NBxkPCL (ochre squares). Empty symbols with dashed lines indicate NB10kPCL and full symbols with solid lines indicate NB45kPCL. The straight lines are only for a better visibility. a) Obtained values for the tensile strength σ; b) obtained values for the elongation at break ε_B.

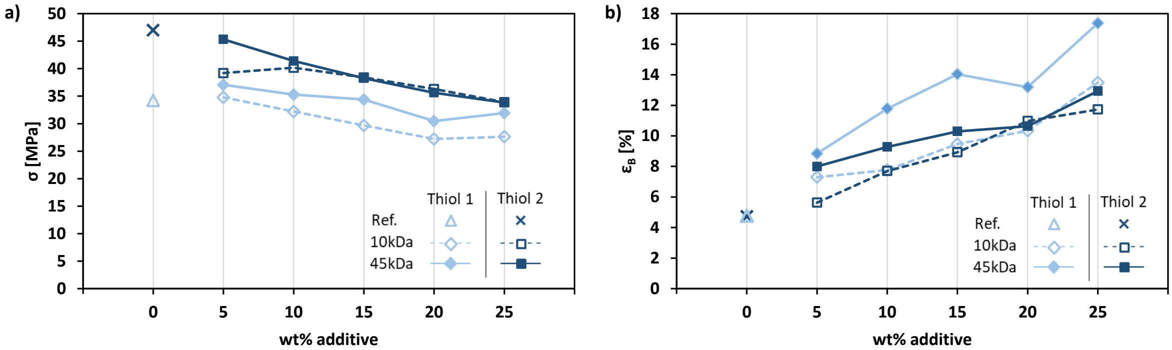

Figure S. 12. Results of tensile test measurements of formulations containing DVA, 15 db% thiol, 0.5 wt% Ivocerin and 0.02 wt% PYR. Ref. Thiol 1 (without additive): light blue triangle; containing additional 5-25 wt% VCxkPCL (light blue diamonds) or Ref. Thiol 2 (without additive): dark blue cross; containing additional 5-25 wt% VCxkPCL (dark blue squares). Empty symbols with dashed lines indicate VC10kPCL and full symbols with solid lines indicate VC45kPCL. The straight lines are only for a better visibility. a) Obtained values for the tensile strength σ; b) obtained values for the elongation at break ε_B.

Table S. 7. Results of tensile test measurements of formulations containing DVA, 15 db% thiol, 0.5 wt% Ivocerin and 0.02 wt% PYR. Ref. Thiol 1 (without additive); containing additional 5-25 wt% YxkPCL.

Thiol	additive	wt% additive	σ [MPa]	$ε_B$ [%]	U_T [MJ·m^{-3}]
Thiol 1	Ref. Thiol 1	0	34.2 ± 3.1	4.8 ± 0.8	0.9 ± 0.3
	AC10kPCL	5	32.6 ± 6.3	5.9 ± 2.9	1.3 ± 1.0
		10	32.1 ± 2.8	9.6 ± 2.0	2.1 ± 0.6
		15	33.4 ± 1.2	8.0 ± 0.8	1.7 ± 0.2
		20	26.2 ± 1.9	8.4 ± 1.6	1.5 ± 0.4
		25	25.9 ± 1.0	10.9 ± 0.9	1.9 ± 0.2
	AC45kPCL	5	27.7 ± 1.5	9.3 ± 1.5	1.7 ± 0.4
		10	31.6 ± 2.3	10.8 ± 1.5	2.3 ± 0.5
		15	30.0 ± 3.0	13.1 ± 2.5	2.6 ± 0.8
		20	28.4 ± 2.6	14.8 ± 2.9	2.8 ± 0.8
		25	25.5 ± 1.8	15.1 ± 1.5	2.5 ± 0.4
	NB10kPCL	5	27.8 ± 1.2	4.4 ± 0.8	0.7 ± 0.1
		10	33.4 ± 1.9	7.6 ± 1.0	1.6 ± 0.3
		15	27.3 ± 3.2	5.4 ± 1.5	1.0 ± 0.2
		20	26.4 ± 3.8	9.2 ± 3.1	1.7 ± 0.8
		25	25.0 ± 3.1	9.6 ± 2.4	1.6 ± 0.6
	NB45kPCL	5	32.6 ± 2.6	6.8 ± 1.1	1.5 ± 0.4
		10	32.4 ± 2.3	10.7 ± 2.1	2.4 ± 0.7
		15	31.3 ± 0.8	13.3 ± 0.8	2.8 ± 0.3
		20	29.4 ± 2.2	12.2 ± 2.0	2.4 ± 0.6
		25	28.7 ± 3.1	13.9 ± 2.6	2.7 ± 0.7
	VC10kPCL	5	34.8 ± 2.3	7.3 ± 1.5	1.7 ± 0.5
		10	32.2 ± 2.4	7.8 ± 1.7	1.7 ± 0.5
		15	29.7 ± 3.9	9.5 ± 2.7	1.9 ± 0.8
		20	27.2 ± 2.9	10.3 ± 2.4	1.9 ± 0.7
		25	27.6 ± 2.0	13.5 ± 2.0	2.5 ± 0.6
	VC45kPCL	5	37.1 ± 2.2	8.8 ± 1.5	2.2 ± 0.5
		10	35.3 ± 1.8	11.8 ± 2.2	2.9 ± 0.7
		15	34.4 ± 0.8	14.0 ± 0.8	3.3 ± 0.2
		20	30.5 ± 2.3	13.2 ± 2.4	2.7 ± 0.7
		25	31.9 ± 2.2	17.4 ± 2.1	3.7 ± 0.7

Table S. 8. Results of tensile test measurements of formulations containing DVA, 15 db% thiol, 0.5 wt% Ivocerin and 0.02 wt% PYR. Ref. Thiol 2 (without additive); containing additional 5-25 wt% YxkPCL.

Thiol	**additive**	**wt% additive**	**σ [MPa]**	**ε_B [%]**	**U_T [MJ·m^{-3}]**
Thiol 2	**Ref. Thiol 2**	0	47.0 ± 1.3	4.7 ± 0.2	1.3 ± 0.1
	AC10kPCL	5	40.6 ± 2.8	4.6 ± 0.7	1.1 ± 0.3
		10	42.8 ± 1.3	8.2 ± 0.9	2.4 ± 0.4
		15	37.3 ± 2.7	8.7 ± 1.7	2.2 ± 0.6
		20	33.6 ± 3.1	9.3 ± 2.3	2.1 ± 0.8
		25	32.9 ± 4.1	10.2 ± 3.1	2.3 ± 0.9
	AC45kPCL	5	36.6 ± 4.7	9.3 ± 1.1	2.1 ± 0.7
		10	41.7 ± 3.7	7.5 ± 1.7	2.1 ± 0.7
		15	37.5 ± 1.9	11.8 ± 1.3	2.9 ± 0.5
		20	35.8 ± 3.0	14.4 ± 2.5	3.5 ± 0.9
		25	32.8 ± 0.8	15.1 ± 0.7	3.3 ± 0.2
	NB10kPCL	5	42.7 ± 4.2	6.0 ± 2.0	1.7 ± 0.9
		10	40.9 ± 3.5	6.3 ± 1.3	1.7 ± 0.5
		15	39.0 ± 1.8	9.6 ± 1.3	2.6 ± 0.5
		20	31.5 ± 2.8	7.6 ± 1.7	1.6 ± 0.5
		25	31.9 ± 1.3	9.9 ± 1.1	2.2 ± 0.4
	NB45kPCL	5	40.6 ± 1.7	7.0 ± 1.6	1.9 ± 0.5
		10	39.6 ± 3.5	10.0 ± 2.6	2.8 ± 1.1
		15	36.2 ± 1.0	9.7 ± 1.0	2.4 ± 0.3
		20	31.2 ± 2.1	10.5 ± 1.8	2.2 ± 0.6
		25	32.7 ± 2.0	14.7 ± 1.5	3.2 ± 0.5
	VC10kPCL	5	39.2 ± 5.4	5.6 ± 1.8	1.6 ± 0.8
		10	40.2 ± 2.5	7.7 ± 1.3	2.1 ± 0.5
		15	38.4 ± 1.0	8.9 ± 0.7	2.3 ± 0.3
		20	36.3 ± 2.1	11.0 ± 1.9	2.8 ± 0.7
		25	33.9 ± 2.1	11.7 ± 1.8	2.7 ± 0.6
	VC45kPCL	5	45.3 ± 2.2	8.0 ± 1.4	2.6 ± 0.6
		10	41.4 ± 1.5	9.3 ± 0.9	2.6 ± 0.4
		15	38.3 ± 3.5	10.3 ± 2.4	2.7 ± 0.9
		20	35.6 ± 3.5	10.6 ± 2.3	2.6 ± 0.9
		25	33.8 ± 1.8	12.9 ± 1.3	2.9 ± 0.5

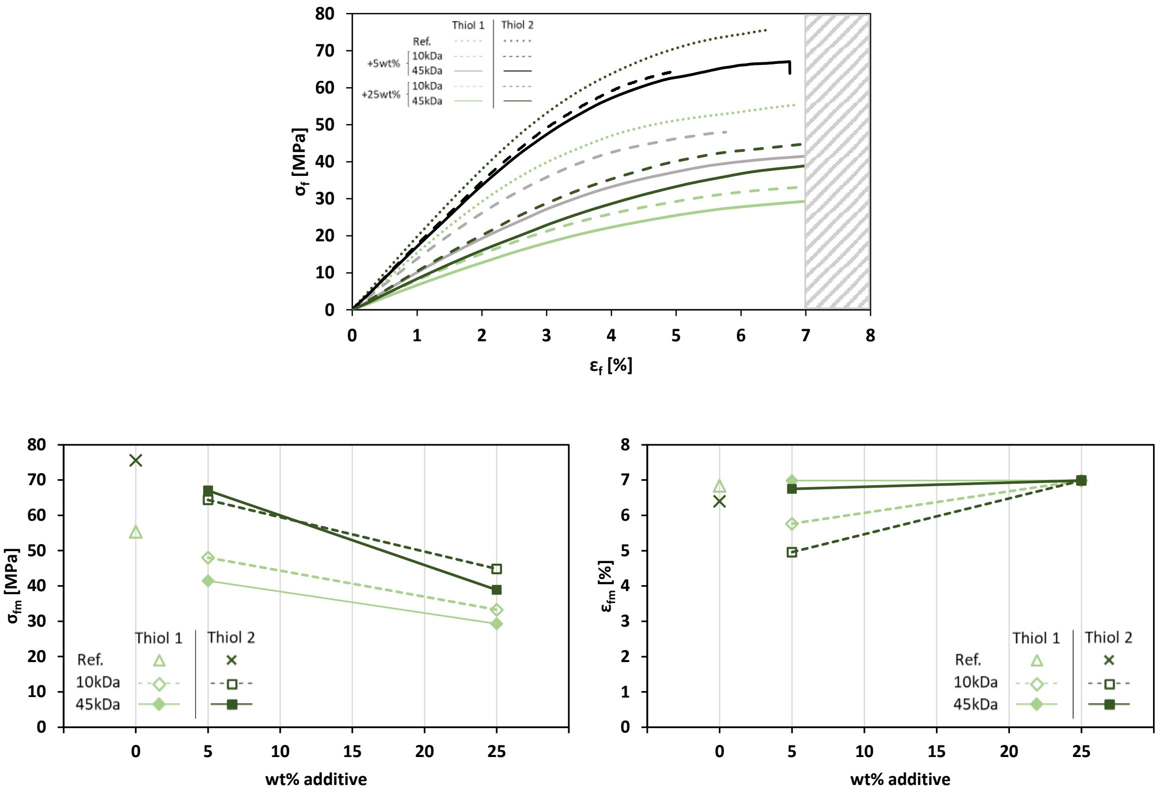

Figure S. 13. Results of 3-point bending experiments of formulations containing DVA, 15 db% thiol, 0.5 wt% Ivocerin and 0.02 wt% PYR. Empty symbols with dashed lines indicate AC10kPCL and full symbols with solid lines indicate AC45kPCL. Exemplary curves (above) and obtained values for the strength σ_{fm} and elongation ε_{fm} at room temperature.

Table S. 9. Results of 3-point bending experiments of formulations containing DVA, 15 db% thiol, 0.5 wt% Ivocerin and 0.02 wt% PYR. Ref. Thiol (without additive); containing additional 5 or 25 wt% ACxkPCL.

Thiol	additive	wt% additive	σ_{fM} [MPa]	ε_{fm} [%]
Thiol 1	Ref. Thiol 1	0	55.4	6.8
	AC10kPCL	5	48.0	5.8
		25	33.3	6.9*
	AC45kPCL	5	41.5	6.9*
		25	29.3	6.9*
Thiol 2	Ref. Thiol 2	0	75.6	6.4
	AC10kPCL	5	64.4	5.0
		25	44.8	6.9*
	AC45kPCL	5	67.1	6.8
		25	38.9	6.9*

* Indicates no break (standard strain σ_{fC} was set to 7%).