Supporting Information for:

Enhanced reduction of polymerization-induced shrinkage stress via combination of radical ring opening and addition fragmentation chain transfer

Sebastian Schoerpf,[†,‡] *Yohann Catel,*[‡,∥] *Norbert Moszner,*[‡,∥] *Christian Gorsche*[†,‡,*] *and Robert Liska*[†,‡]

[†]Institute of Applied Synthetic Chemistry, Technische Universität Wien, Getreidemarkt 9/163 MC, A-1060 Vienna, Austria

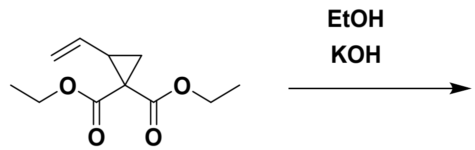
[‡]Christian Doppler Laboratory for Photopolymers in Digital and Restorative Dentistry, Technische Universität Wien, Getreidemarkt 9/163 MC, A-1060 Vienna, Austria

[∥]Ivoclar Vivadent AG, Bendererstrasse 2, FL-9494 Schaan, Liechtenstein

*corresponding author: christian.gorsche@tuwien.ac.at

1. Experimental procedures

Syntheses of 1-(ethoxycarbonyl)-2-vinylcyclopropane-1-carboxylic acid 2



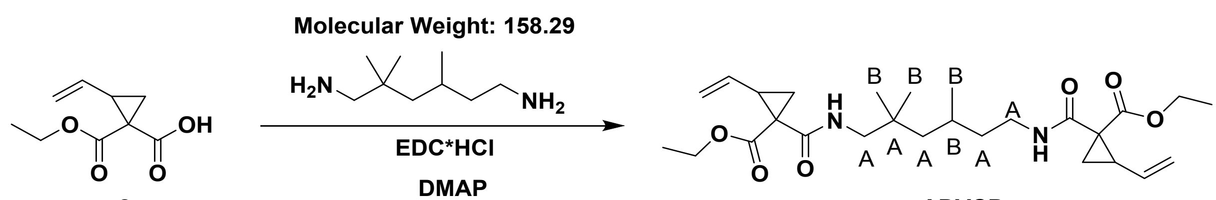
1 Molecular Weight: 212.25 g/mol

2 Molecular Weight: 184.19 g/mol

1,1-Diethoxycarbonyl-2-vinylcyclopropane **1** (157.4 g, 714.6 mmol) was dissolved in ethanol (325 mL). The mixture was cooled down to 0 °C, KOH (46.1 g, 821.6 mmol) was added in small portions and the resulting solution was stirred for 2 h at RT. Then, the solution was filtered and concentrated under reduced pressure. Distilled water (150 mL) was added to the solution and the aqueous layer was extracted with Et_2O (diethyl ether) (2x60 mL). The organic phase was discarded. HCl (120 mL, 1N) was added to the aqueous solution, which was subsequently extracted with Et_2O (3x90 mL). The organic layers were combined, dried over Na_2SO_4 and filtered. After concentration under reduced pressure, 96.25 g (522.56 mmol) of the desired product **2** were isolated.

Yield: 71%. Aspect: slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3CH_2O); 2.01 (dd, $^2J_{HH}$ = 4.6 Hz, $^3J_{HH}$ = 8.4 Hz, 1H, $CH_2CHCH{=}CH_2$); 2.17 (dd, $^2J_{HH}$ = 4.6 Hz, $^3J_{HH}$ = 9.3 Hz, 1H, $CH_2CHCH{=}CH_2$); 2.76 (q, $^3J_{HH}$ = 8.8 Hz, 1H, $CH_2CHCH{=}CH_2$); 4.22-4.37 (m, 2H, CH_3CH_2O); 5.26 (dd, $^2J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 9.8 Hz, 1H, $CH{=}CH_2$); 5.41 (dd, $^2J_{HH}$ = 1.0 Hz, $^3J_{HH}$ = 15.7 Hz, 1H, $CH{=}CH_2$); 5.64-5.76 (m, 1H, $CH_2{=}CH$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2 (OCH_2CH_3); 23.5 ($CH_2{=}CHCHCH_2$); 33.2 (COCCO); 39.1 (CCHCH); 62.9 (CH_2OCO); 120.9 ($CH{=}CH_2$); 132.2 ($CH{=}CH_2$); 171.2 (C=O); 172.9 (C=O).

Synthesis of ADVCP



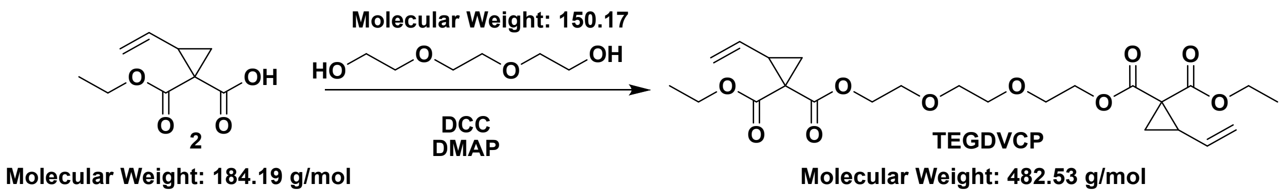
2 Molecular Weight: 184.19 g/mol

ADVCP Molecular Weight: 490.64 g/mol

Under argon atmosphere, 4-dimethylaminopyridine (DMAP, 0.2 g, 1.6 mmol) was added to a solution of 1-ethoxycarbonyl-2-vinylcyclopropanecarboxylic acid **2** (30.00 g, 162.88 mmol) and dry DCM (100 mL). The solution was cooled to 0 °C. 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC*HCl, 36.97 g, 179.16 mmol) was dissolved in dry DCM and added over a dropping funnel to the reaction mixture. The solution was stirred for 15 min and then 2,2,4(2,4,4)-trimethyl-1,6-hexandiamine (11.64 g, 81.44 mmol) was added dropwise. The solution temperature did not raise over 0 °C and it was stirred for 3 h at 0 °C and then overnight at RT. The reaction mixture was filtered and washed with distilled water (2 × 200 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography (eluent = ethyl acetate (EA)/ petrol ether (PE): 2/8). 32.36 g (65.95 mmol) of the desired compound **ADVCP** were isolated.

Yield: 81%. Aspect: colorless viscous oil, mixture of isomers. ^{1}H NMR (400 MHz; $CDCl_3$): δ = 0.68- 0.99 (m, 9H, CH_3); 1.17-1.31 (m, 8H, OCH_2CH_3 and CH_2); 1.33-1.62 (m, 2H, $NHCH_2$); 1.64-2.09 (m, 5H, $CH_2CHCH{=}CH_2$ and CH_2); 2.28-3.41 (m, 4H, CH_2CH and $NHCH_2$); 4.02-4.78 (m, 4H, OCH_2CH_3); 4.97-5.20 (m, 2H, $CH_2{=}CH$); 5.20-5.36 (m, 2H, $CH_2{=}CH$); 5.49-5.79 (m, 2H, $CH_2{=}CH$); 8.30 (s, 1H, NH); 8.48 (s, 1H, NH). ($CDCl_3$, 100 MHz, δ): 14.3 (OCH_2CH_3); 21.9 ($CH_2CHCH{=}CH_2$); 22.4 (C_B); 25.4 ($CH_2CHCH{=}CH_2$); 25.7 (C_B); 26.6 (C_B); 27.2 (C_B); 29.1 (C_B); 33.1 (C_A); 34.3 (COCCO); 36.7 (C_A); 38.8 (C_A); 41.9 (C_A); 46.8 (C_A); 47.6 (C_A); 50.1 (C_A); 61.4 (CH_2OCO); 119.5 ($CH_2{=}CH$); 133.5 ($CH_2{=}CH$); 168.0 (C=O); 171.4 (C=O).

Synthesis of TEGDVCP



4-Dimethylaminopyridine (DMAP, 0.2 g, 1.6 mmol) was added to a solution of 1-ethoxycarbonyl-2-vinylcyclopropanecarboxylic acid **2** (30.00 g, 162.88 mmol) and triethylene glycol (11.64 g, 81.44 mmol) in dry DCM (180 mL) under argon atmosphere. The solution was cooled down to 0 °C. N,N′-Dicyclohexylcarbodiimide (DCC, 36.97 g, 179.16 mmol) was added in small portions to the reaction mixture. The solution was stirred for 3 h at 0 °C. Then, the reaction mixture was filtered and washed with distilled water (2 × 60 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography (eluent = EA/PE : 2/3). 31.89 g (66.09 mmol) of the desired compound **TEGDVCP** were isolated.

Yield: 81%. Aspect: colorless, viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (t, $^{3}J_{HH}$ = 7.1 Hz, 6H, OCH_2CH_3); 1.57 (dd, $^{2}J_{HH}$ = 4.9 Hz, $^{3}J_{HH}$ = 9.0 Hz, 2H, $CH_2CHCH{=}CH_2$); 1.71 (dd, $^{2}J_{HH}$ = 4.9 Hz, $^{3}J_{HH}$ = 7.5 Hz, 2H, $CH_2CHCH{=}CH_2$); 2.59 (q, $^{3}J_{HH}$ = 8.2 Hz, 2H, $CH_2CHCH{=}CH_2$); 3.62 (s, 4H, CH_2O); 3.69 (t, $^{3}J_{HH}$ = 4.9 Hz, 4H, CH_2O); 4.12–4.34 (m, 8H, CH_2OCO); 5.10–5.16 (m, 2H, $CH_2{=}CH$); 5.25–5.33 (m, 2H, $CH_2{=}CH$); 5.36–5.50 (m, 2H, $CH_2{=}CH$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3 (CH_3); 20.6 ($CH_2CHCH{=}CH_2$); 31.4 ($CH_2CHCH{=}CH_2$); 35.9 (COCCO); 61.6 (CH_2O); 64.7 (CH_2O); 69.0 (CH_2O); 70.7 (CH_2O); 118.7 ($CH_2{=}CH$); 133.1 ($CH_2{=}CH$); 167.2 (OCO); 169.6 (OCO).

2. Photo-Reactor Study

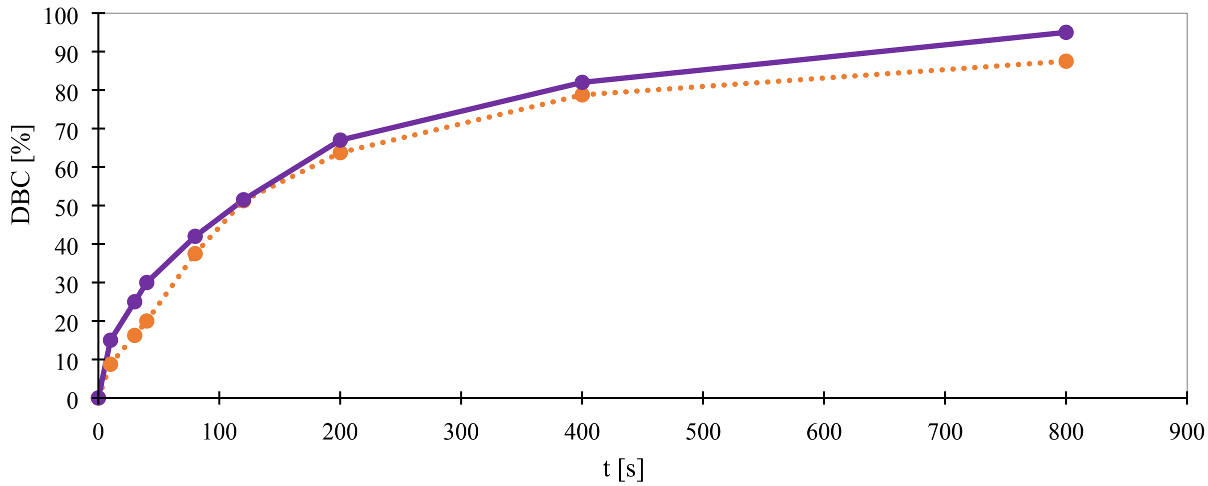


Figure S1: DBC of DVD (dot) and EVS (solid) over time in the photoreactor (irradiation source: Exfo OmniCureTM 2000 device with a broadband Hg-lamp, 300 s, 400–500 nm, ~8 mW cm^{-2} on the surface of the sample)

3. Photo-DSC

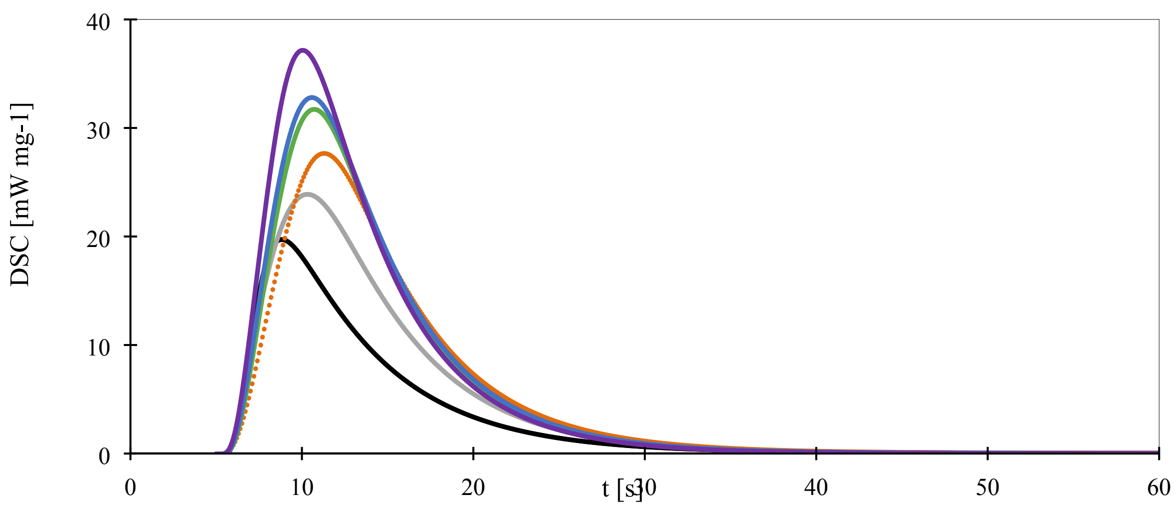


Figure S2: Photo-DSC data of all six formulations, MA (solid); VCP (solid), VCP/EVS_5 (dot), VCP/EVS_10 (short dash), VCP/EVS_15 (long dash), VCP/EVS_20 (dash dot); light irradiation starts at 5 s, light source: Omnicure 2000 with 400-500 nm filter, intensity ~20 mW cm^{-2} at 25 °C

Table S1: Results from the photo DSC measurements, (t_{max}…time until maximum of the polymerization rate is reached, $t_{95\%}$… when 95% of the overall heat was evolved, ΔH… overall reaction heat produced during photopolymerization)

formulation	t_{max} [s]	t_{95}% [s]	ΔH [J g^{-1}]
MA	2.6 ± 0.2	23.3 ± 1.5	170.8 ± 1.2
VCP	4.3 ± 0.1	21.1 ± 0.6	234.7 ± 5.4
VCP/EVS_5	4.9 ± 0.1	22.9 ± 0.7	277.4 ± 5.9
VCP/EVS_10	4.4 ± 0.1	19.3 ± 0.8	288.3 ± 2.5
VCP/EVS_15	4.5 ± 0.1	20.0 ± 0.2	305.9 ± 0.6
VCP/EVS_20	4.0 ± 0.1	18.2 ± 0.6	316.6 ± 5.4

4. RT-NIR-photorheology

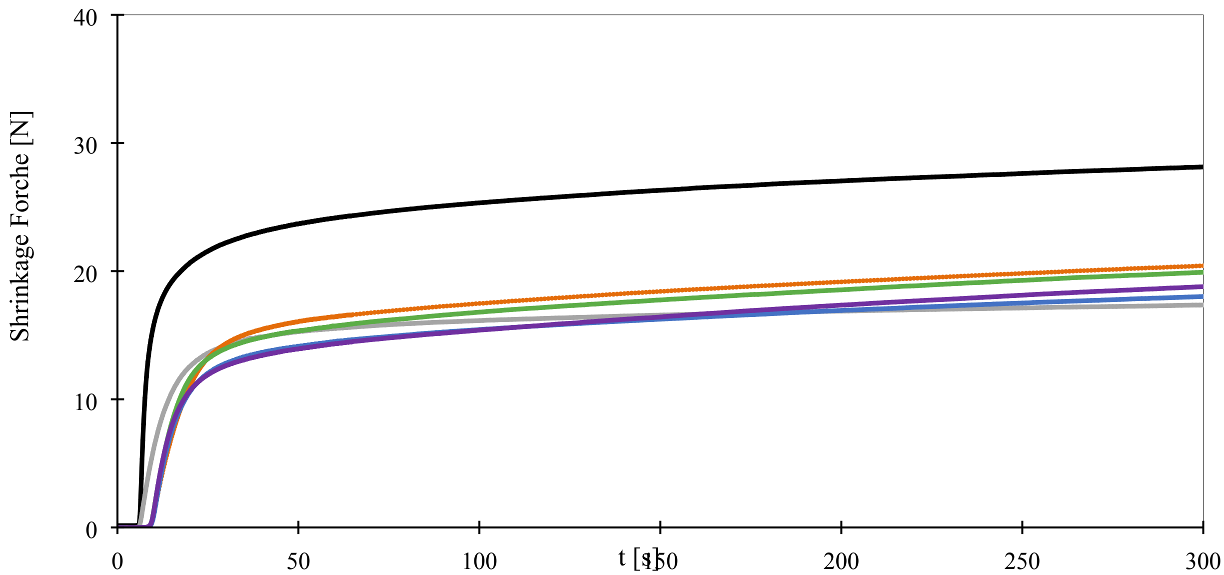


Figure S3: Shrinkage force plot from RT-NIR-photorheology measurements of all six formulations, MA (solid); VCP (solid), VCP/EVS_5 (dot), VCP/ EVS_10 (short dash), VCP/ EVS_15 (long dash), VCP/ EVS_20 (dash dot); light irradiation starts at 5 s, light source: Omnicure 2000 with 400-500 nm filter, intensity ~20 mW cm^{-2} at 25 °C

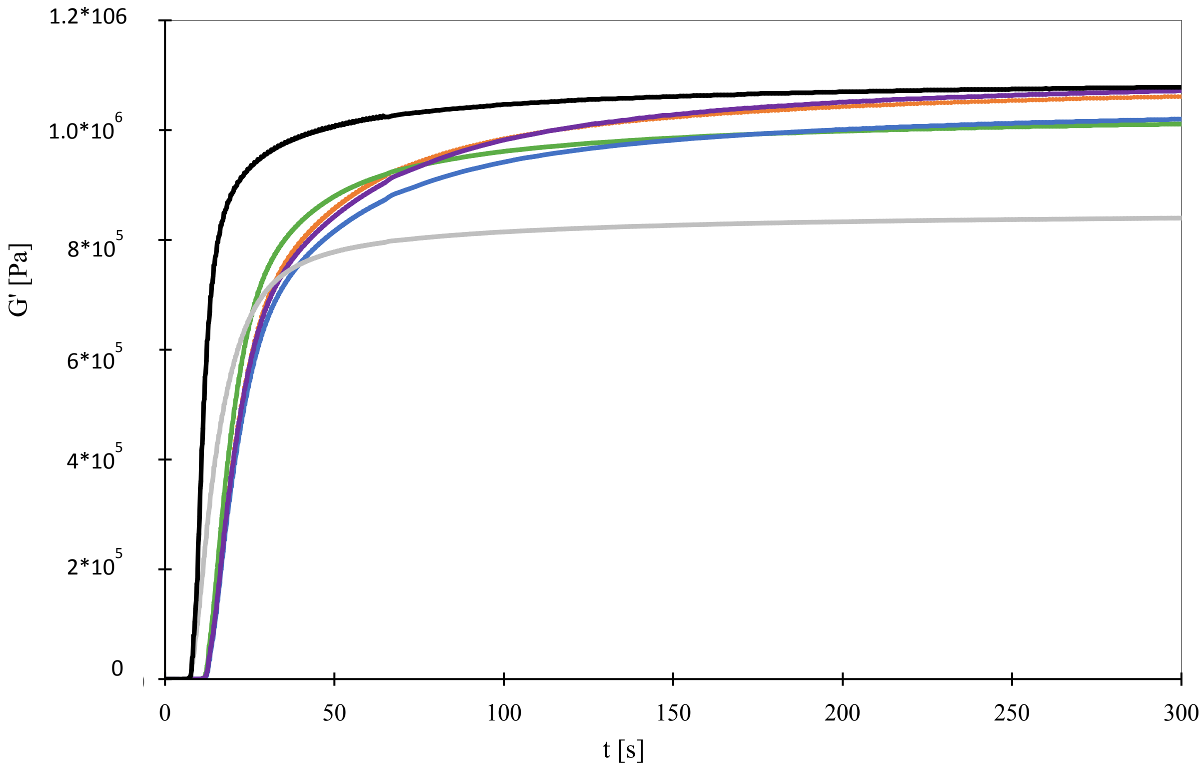


Figure S4: Storage modulus G' plot from RT-NIR-photorheology measurements of all six formulations, MA (solid); VCP (solid), VCP/EVS_5 (dot), VCP/ EVS_10 (short dash), VCP/ EVS_15 (long dash), VCP/ EVS_20 (dash dot); light irradiation starts at 5 s, light source: Omnicure 2000 with 400-500 nm filter, intensity ~20 mW cm^{-2} at 25 °C

Table S2: Results from the RT-NIR-photorheology measurements, (t_{gel}…time until gel point is reached, DBC_{gel}… double bond conversion at the gel point, $t_{95\%rheo}$... time until 95% of the final double bond conversion is reached, DBC_{final}… final double bond conversion, F_N … final normal force detected during the reaction, F_N at 70% DBC … normal force value detected at 70% DBC, G'_{final} … final storage modulus reached after photopolymerization)

formulation	t_{gel} [s]	DBC_{gel} [%]	$t_{95\%rheo}$ [s]	DBC_{final} [%]	F_N [N]	F_N at 70% DBC [N]	G'_{final} [MPa]
MA	3.0	38 ± 2	85 ± 2.0	70 ± 0.8	27.3 ± 1.8	27.3 ± 1.5	1.08 ± 0.18
VCP	2.0	17 ± 1	75 ± 1.3	73 ± 0.4	17.5 ± 0.6	16.3 ± 0.3	0.84 ± 0.19
VCP/EVS_5	4.5	23 ± 1	158 ± 1.5	79 ± 0.3	19.9 ± 0.5	15.2 ± 0.6	1.04 ± 0.04
VCP/EVS_10	5.0	32 ± 1	147 ± 1.7	83 ± 0.4	19.7 ± 0.6	14.0 ± 0.8	0.96 ± 0.03
VCP/EVS_15	6.0	44 ± 1	132 ± 3.0	87 ± 0.9	18.4 ± 0.4	10.1 ± 0.7	0.98 ± 0.05
VCP/EVS_20	6.0	55 ± 1	122 ± 2.0	93 ± 1.6	19.4 ± 0.4	7.9 ± 0.3	1.00 ± 0.08

5. Storage stability test

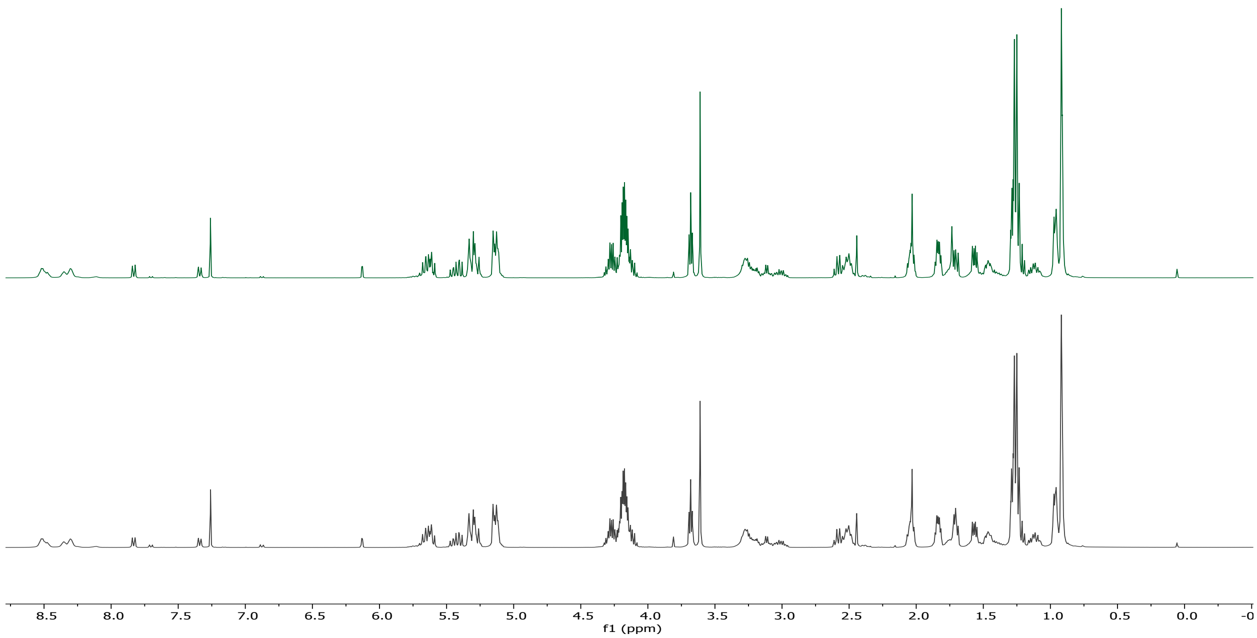


Figure S5: ^{1}H-NMR spectroscopy of the formulation VCP/EVS_5 immediately after mixing (green, solid, t=0) and after 8 weeks (black, solid).

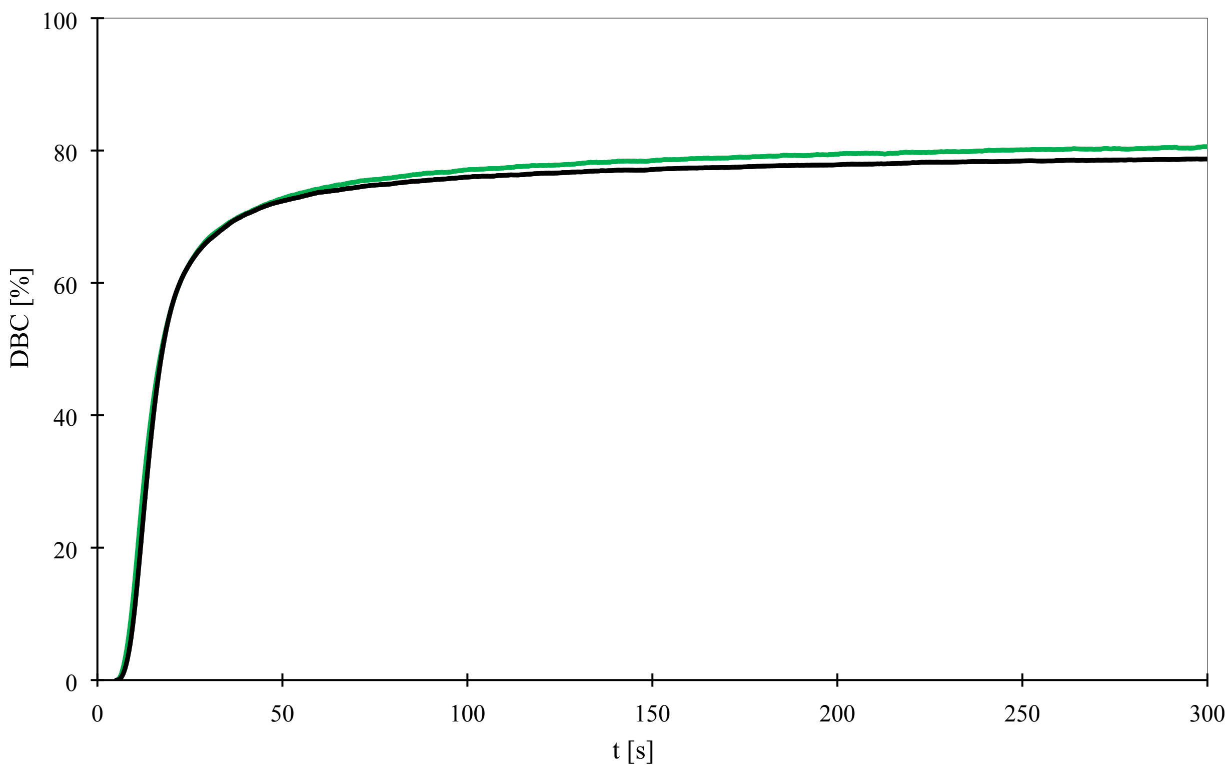


Figure S6: Double bond conversion DBC measured during RT-NIR-photorheology of the formulation VCP/EVS_5 immediately after mixing (green, solid) and after 8 weeks (black, solid); light irradiation starts at 5 s, light source: Omnicure 2000 with 400-500 nm filter, intensity ~20 mW cm^{-2} at 25 °C

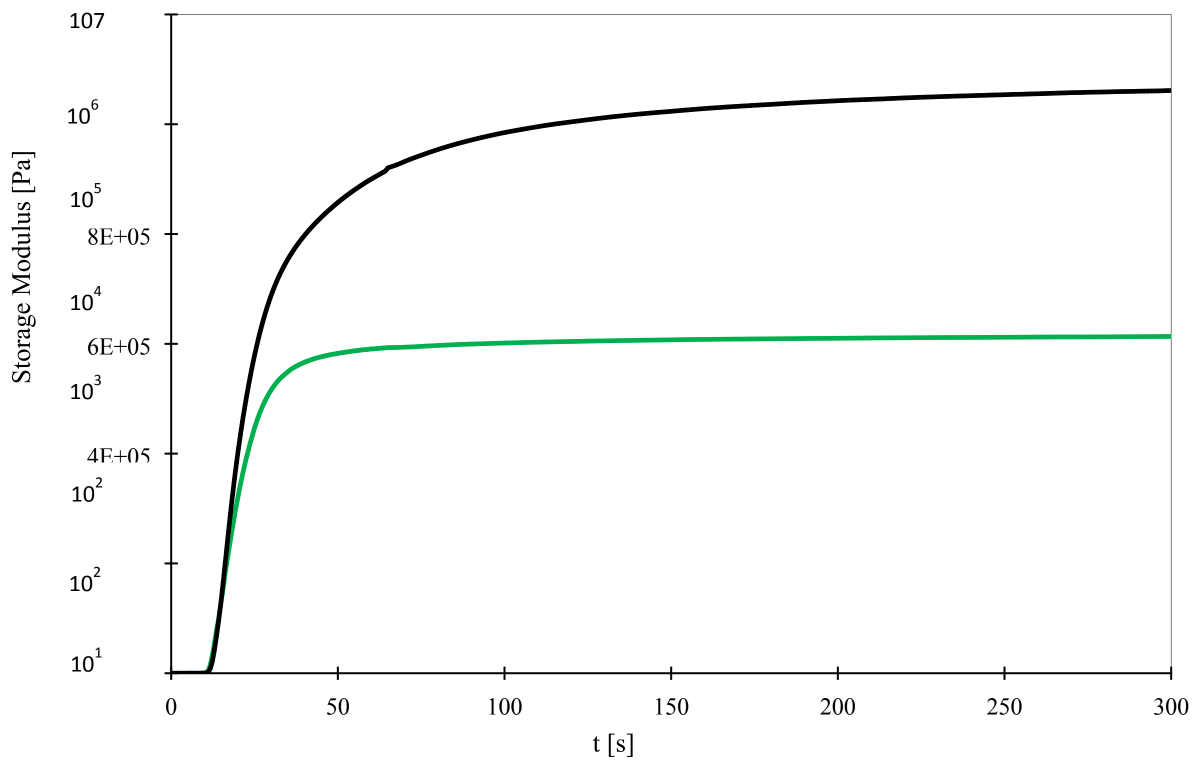


Figure S7: Storage modulus G' measured during RT-NIR-photorheology of the formulation VCP/EVS_5 immediately after mixing (green, solid) and after 8 weeks (black, solid); light irradiation starts at 5 s, light source: Omnicure 2000 with 400-500 nm filter, intensity ~20 mW cm^{-2} at 25 °C

6. Dynamic Mechanical Thermal Analysis (DMTA)

Table S3: Results from the DMTA measurement, ($G'_{37°C}$… storage modulus at 37 °C, T_g … glass transition temperature at the maximum of the tan□ plot, fwhm… full width at half maximum of the tan□ plot, G'_r… storage modulus at the rubbery plateau)

specimen	$G'_{37°C}$ [MPa]	T_g [°C]	fwhm [°C]	G'_r [MPa]
polyMA	1520	151	101	5
polyVCP	878	91	29	17
polyVCP/EVS_5	928	89	28	18
polyVCP/EVS_10	897	90	27	17
polyVCP/EVS_15	1160	81	26	14
polyVCP/EVS_20	1050	68	26	7

7. Tensile Tests

Tables S4: Stress (maximum value recorded) and stain at break values of the tensile test measurements

specimen	Stress [MPa]	Strain at break [%]
polyMA	69.10 ± 4.03	4.33 ± 1.0
polyVCP	46.18 ± 2.74	4.87 ± 0.4
polyVCP/EVS_5	48.12 ± 1.33	7.75 ± 1.2
polyVCP/EVS_10	51.33 ± 0.93	6.60 ± 1.1
polyVCP/EVS_15	53.17 ± 2.22	8.14 ± 1.1
polyVCP/EVS_20	56.61 ±1.02	6.04 ± 0.2

8. Shrinkage force measurements of composite formulations

Table S5: Shrinkage force measurement data, (F0-600… occurring shrinkage force at 0 s, 125 s, 130 s, 400 s and 600 s)

formulation	F0 [N]	F125 [N]	F130 [N]	F200 [N]	F400 [N]	F600 [N]
MA	0	46.9 ± 2.7	49.2 ± 2.9	52.4 ± 3.1	54.3 ± 3.3	55.3 ± 3.3
VCP	0	39.5 ± 1.3	41.5 ± 1.3	44.6 ± 1.4	46.1 ± 1.4	46.9 ± 1.4
VCP/EVS_5	0	38.2 ± 2.6	40.1 ± 2.8	42.8 ± 3.0	43.9 ± 3.1	44.2 ± 3.3
VCP/EVS_10	0	38.3 ± 1.6	40.3 ± 1.9	43.1 ± 2.2	44.2 ± 2.2	44.6 ± 2.3
VCP/EVS_15	0	38.9 ± 0.9	40.9 ± 1.0	43.9 ± 1.2	45.2 ± 1.3	45.8 ± 1.3
VCP/EVS_20	0	36.9 ± 1.5	38.5 ± 1.7	41.1 ± 1.9	42.1 ± 2.2	42.5 ± 2.1

9. Mechanical properties of composite formulations

Table S6: Flexural strength measuring data after 24 h stored at room temperature

specimen	Flexural strength [N mm^{-2}]	E-Modulus [MPa]
polyMA	144.9 ± 15.0	8215 ± 712
polyVCP	112.8 ± 9.2	6600 ± 628
polyVCP/EVS_5	117.1 ± 6.2	7097 ± 272
polyVCP/EVS_10	112.3 ± 4.0	6969 ± 239
polyVCP/EVS_15	109.8 ± 3.0	7160 ± 434
polyVCP/EVS_20	107.4 ± 5.2	7277 ± 360