Polyhydroxyalkanoate block-polymer adhesives derived from long-chain aliphatic β-lactones and lactide

Peter V Kelly,[1] *Alison Block,*[2] *Brenden D. Hoehn,*[1] *Pathikrit Saha,*[2] *Christopher J. Ellison,*[1,]* *Marc A. Hillmyer,*[2,]*

[1]Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455, United States

[2]Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, United States

*Corresponding authors: cellison@umn.edu, hillmyer@umn.edu

Experimental

Materials

1,2-epoxydodecane (EDD), aluminum phthalocyanine chloride (~85% dye content) (AlPcCl), dicobalt octacarbonyl ($Co_2(CO)_8$), triethyl aluminum (25 wt.%) in toluene, anhydrous ethyl acetate, tetrahydrofuran (THF), dichloromethane (DCM), and methanol were purchased from Sigma Aldrich and used as received. 1,4-benzenedimethanol was purchased from Alfa Aesar and was recrystallized three times in toluene before use. L-lactide was provided by Nature Works, LLC and recrystallized three times in anhydrous ethyl acetate and three times in anhydrous toluene under nitrogen before use. Deuterated chloroform ($CDCl_3$) with 0.05 vol% tetramethylsilane (TMSs) was purchased from Cambridge Isotope Laboratories and used as received. The rosin ester tackifier Sylvalite RE 80HP was generously provided by Kraton.

Synthesis of β-tridecalactone:

In a glovebox aluminum phthalocyanine chloride (AlPcCl) (500 mg, 0.87 mmol) and dicobalt octacarbonyl ($Co_2(CO)_8$) (445 mg, 1.30 mmol) were dissolved in anhydrous tetrahydrofuran (THF) (216 mL). This mixture was removed from the glovebox and allowed to dissolve overnight while stirring under nitrogen. The carbonylation of the EDD was carried out in a 1 L Parr pressure reactor. The catalyst solution and EDD (40 g, 0.217 mol) were added to the Parr reactor quickly and purged with argon gas three times by cycling between 100 psig and 25 psig. An additional three cycles were carried out using carbon monoxide (CO) gas before charging the pressure vessel to 560 psig with CO and heating to 60 °C. The reaction was run for 18 hours at which point the vessel was cooled and the CO gas was vented. THF was removed from the crude product by rotary evaporation with the resultant liquid washed through a silica plug with dichloromethane (DCM) to remove the majority of the catalyst mixture. DCM was removed from the filtrate by rotary evaporation and the sample was dried overnight over calcium hydride. Fractional short-path vacuum distillation was carried out to purify the TDL of residual catalyst and side products. Under reduced pressure (~0.24 Torr) the monomer mixture was heated, with the dodecan-2-one distilling over at a vapor temperature of ~70 °C followed by the TDL at a vapor temperature of ~110 °C. A second vacuum distillation was carried out over calcium hydride to remove trace impurities, after which the TDL was pumped into the glovebox and dried over 5 Å molecular sieves for at least 24 hours before use. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.50 (quintet, J = 5.8 Hz, 1H), 3.51 (dd, J = 16.3, 5.1 Hz, 1H), 3.05 (dd, J = 16.3, 4.3 Hz, 2H), 1.93 – 1.80 (m, 1H), 1.80 – 1.68 (m, 1H), 1.52 – 1.17 (m, 16H), 0.88 (t, J = 6.6 Hz, 4H) ^{13}C NMR (101 MHz, CDCl3) δ = 168.48, 71.43, 43.00, 34.81, 32.00, 29.67, 29.59, 29.53, 29.41, 29.28, 25.01, 22.79, 14.22.

Synthesis of PLLA-PTDL-PLLA Triblock Polymers:

The synthesis of poly(L-lactide)-*block*-poly(β-tridecalactone)-*block*-poly(L-lactide) (LTL) triblock polymers (M_n target of 19 kg/mol) was conducted in a 25 mL pressure vessel. In the glovebox TDL (5.31 g, 25 mmol), 1,4-benzene dimethanol (BDM) (35 mg, 0.25 mmol), 25 wt.% (1.86 M) triethyl aluminum (Et_3Al) in toluene (0.27 mL, 0.5 mmol), and toluene (19 mL) were added into a pressure vessel. The vessel was sealed, removed from the glovebox, and placed in an 85 °C oil bath for 40 hours (80 hours for the 200:1:2 M:I:C system). Following PTDL homopolymer synthesis, the pressure vessel was pumped back into the glovebox and L-lactide (2.39 g, 16.6 mmol) was added to the viscous solution. The pressure vessel was sealed again and placed into a 90 °C oil bath for an additional 6 hours (12 hours for the 200:1:2 M:I:C system), at which point the reaction was cooled and the sample was precipitated from DCM into cold methanol twice. The triblock polymer product was dried overnight at 40 °C under reduced pressure. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 (s, 4H), 5.28 – 5.11 (m, 187H), 5.09 (d, J = 3.6 Hz, 4H), 4.35 (quintet, *J* = 7.0 Hz, 2H), 2.53 (m, 152H), 1.58 (d, *J* = 7.1 Hz, 565H), 1.25 (s, 1532H), 0.88 (t, *J* = 6.7 Hz, 259H).

Mechanical Testing:

Peel and loop tack testing were conducted on a Shimadzu ASG-X universal testing machine. Peel testing was conducted by adhering a 1 cm wide strip of the coated PSA onto a PSTC 304 BRT, 18 Gauge polished stainless-steel test panel with a single pass of a 2 kg rubber roller. Films were then peeled from the substrate in a 180° orientation at a crosshead speed of 305 mm/min. At least three replicates of each film were tested, and a sample's peel force was calculated by averaging the force measurements in the plateau regions of every replicate and dividing by the width of the film. A plateau region was identified as beginning when the force stopped increasing and ending when the sample detached from the substrate.

Loop tack testing was conducted by cutting a 1 cm wide strip of the solvent cast PSA and pinching both ends together to form a loop with PSA facing outward. This pinched area was mounted into tensile grips with the PSA facing down at a stainless-steel plate oriented parallel to the ground. The loop was brought into contact with the substrate by lowering the crosshead until approximately 2 cm^2 of the PSA were in contact. At this point the test was started, and the loop was pulled from the substrate at 305 mm/min. At least three replicates of each film were run with the loop tack strength being equal to the maximum force measured divided by the width of the film.

Shear resistance testing was conducted by cutting a 1.27 cm by 1.27 cm square of the solvent cast PSA and adhering it to a stainless-steel test panel held perpendicular to the ground. A 250 g mass was suspended from the PSA and monitored over a 10-day period. The reported value for shear resistance is the average time taken for three replicates to fall. If none of the samples fell after 10 days the test was stopped manually and the shear resistance was reported as >240 hours.

Characterization:

NMR Spectroscopy: ^{1}H and ^{13}C NMR spectra were taken using a Bruker Avance III HD 400 MHz with a 5 mm BBFO SmartProbe at 298 K. Polymer samples were run with a delay time of 10 seconds while small molecules were measured with a 1 second delay time. All samples were run in $CDCl_3$ with chemical shifts reported in ppm and referenced to either a TMS internal standard at (0.0 ppm) or to the residual $CHCl_3$ peak (7.260 ppm).

Size Exclusion Chromatography (SEC): SEC analyses of polymer samples were conducted on an Agilent 1260 series liquid chromatography instrument equipped with a Wyatt diffractive refractive index detector. THF was used as the mobile phase at 1.0 mL/min with three Styragel HR columns at 35 °C. Polymer samples were dissolved overnight at between 2-4 mg/mL in THF and filtered through 0.2 μm syringe filters before analysis. Sample molar masses and dispersity were determined using refractive index detection against a polystyrene standard.

Differential Scanning Calorimetry (DSC): DSC analysis was conducted using a TA Instruments Discovery Series DSC 2500. Aluminum Tzero pans were loaded with 3-6 mg of the as-cast PSA formulation and hermetically sealed. Samples were run through a heat-cool-heat procedure. The first heating cycle included a ramp from room temperature to 180 °C at 10 °C/min followed by an isothermal hold for 5 minutes. Samples were cooled at 35 °C/min to -80 °C and help isothermally for 5 minutes. The second heating cycle ramped from -80 °C to 180 °C at 10 °C/min. Melting points (T_m) were measured at the peak max of the melting endotherm and glass transition temperatures (T_g) were determined by a midpoint half-height analysis.

To calculate the T_g of the PTDL midblock from LTL PSA formulations the Fox equation (eq 1) was employed.

$$\frac{1}{T_{g,blend}} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \qquad \text{(eq 1)}$$

Where $T_{g,\mathrm{blend}}$ is the measured T_g of the PSA, w_1 and $T_{g,1}$ are the mass fraction and T_g of component 1 respectively, and w_2 and $T_{g,2}$ are the mass fraction and T_g of component 2 respectively. To calculate the mass fractions of the PTDL and the tackifier we assumed that the tackifier fully segregated into the PTDL phase as was evidenced by the DSC analysis of the triblock PSAs. The T_g of the tackifier was measured at 30.2 °C using the procedure above.

X-Ray Scattering: The microstructures of the LTL PSA formulations, as-cast, were analyzed with small-angle X-ray scattinerg (SAXS) and wide-angle X-ray scattering (WAXS) at the DND-CAT at Sector 5 of the Advanced Photon Source at Argonne National Lab. SAXS data was collected using a photon wavelength of 0.7188 Å and a Rayonix MarMosaic225 detector. WAXS data was collected on a Rayonix LX170HS detector. One-dimensional scattering patterns were produced by azimuthally integrating the two-dimensional scattering patterns.

Rheology: Analysis of the viscoelastic properties of the PSA formulations were conducted on a TA-instruments ARES-G2 rheometer equipped with an 8 mm parallel-plate fixture. Samples were loaded into the parallel plates, heated to ~160 °C, and compressed to the test gap height of 1 mm. Excess sample was trimmed and the tests were conducted under nitrogen. Frequency sweeps were conducted at 0.5% strain which was determined to be in the linear viscoelastic region from a strain amplitude sweep run at 100 °C. Frequency sweeps were run from 0.4 rad/s to 100 rad/s with 12 points per decade at -20 °C, -10 °C, 0 °C, 20 °C, 40 °C, 60 °C, and 80 °C with 20 °C used as the reference temperature for the time-temperature superposition (TTS) analysis. TTS was conducted in TA-instrument's TRIOS software using the built-in feature.

Table S1: Synthetic conditions used for the carbonylation of 1,2-epoxydodecane

[EDD] (M)	EDD:AlPcCl	Temp (°C)	Time (hours)	Conversion (%)[a]	TDL Fraction[b]
0.50	25	60	6	100	0.89
0.50	100	60	30	100	0.95
0.50	250	60	30	100	0.97
1.0	250	60	30	100	0.97
1.0	500	60	30	30	0.98

[a] Conversion of 1,2-epoxydodecane calculated from the relative integrations of ^{1}H NMR peaks of 1,2-epoxy dodecane, β-tridecalactone, and dodecan-2-one. When no peaks from the 1,2-epoxydodecane are present the conversion is said to be 100%. [b] The mole fraction of TDL obtained was calculated from the integration ratios of β-tridecalactone and dodecan-2-one from ^{1}H NMR spectroscopy.

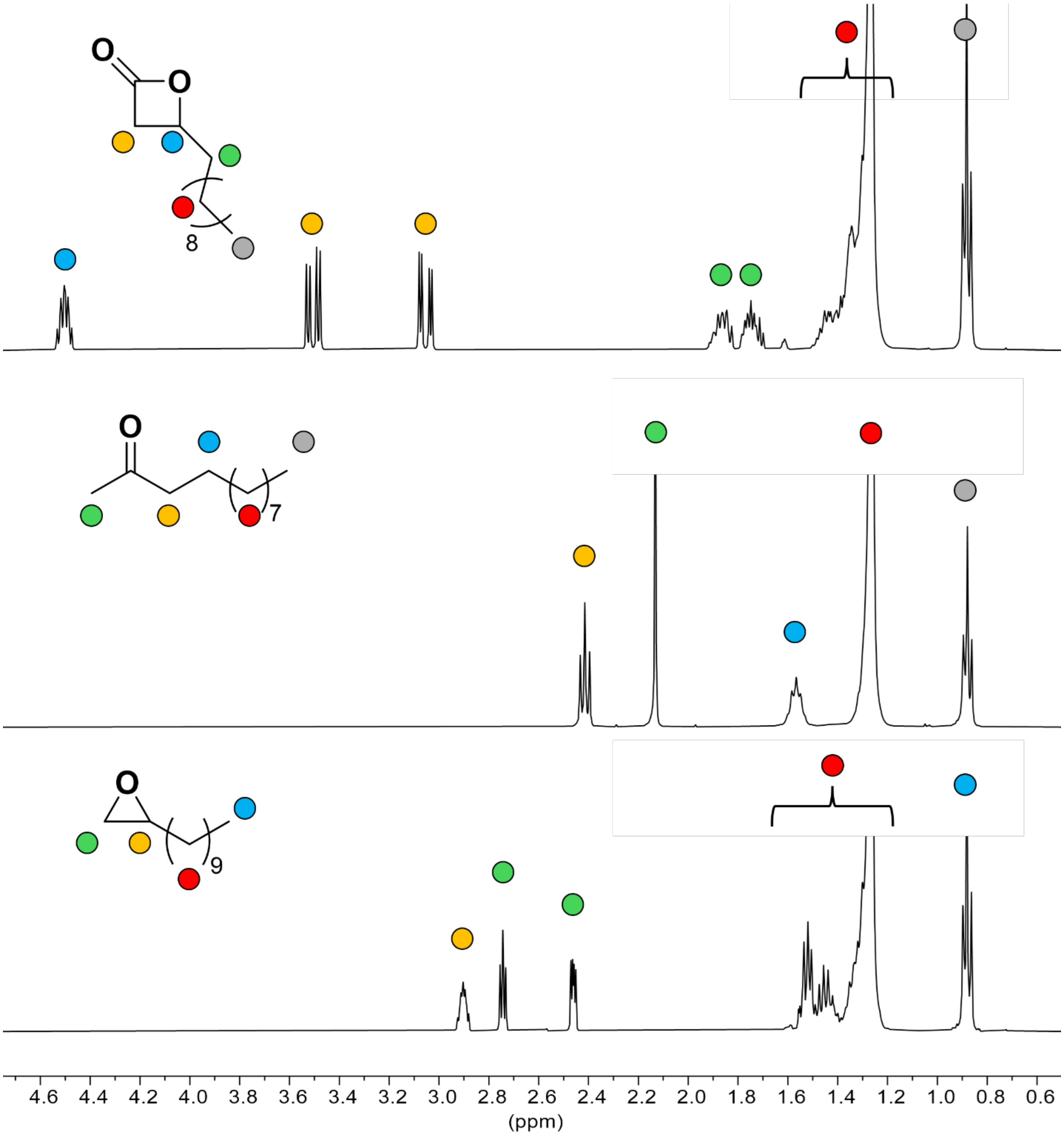


Figure S1: ^{1}H NMR (400 MHz, CDCl$_3$) spectra of β-tridecalactone monomer, dodecan-2-one impurity, and 1,2-epoxy dodecane starting material.

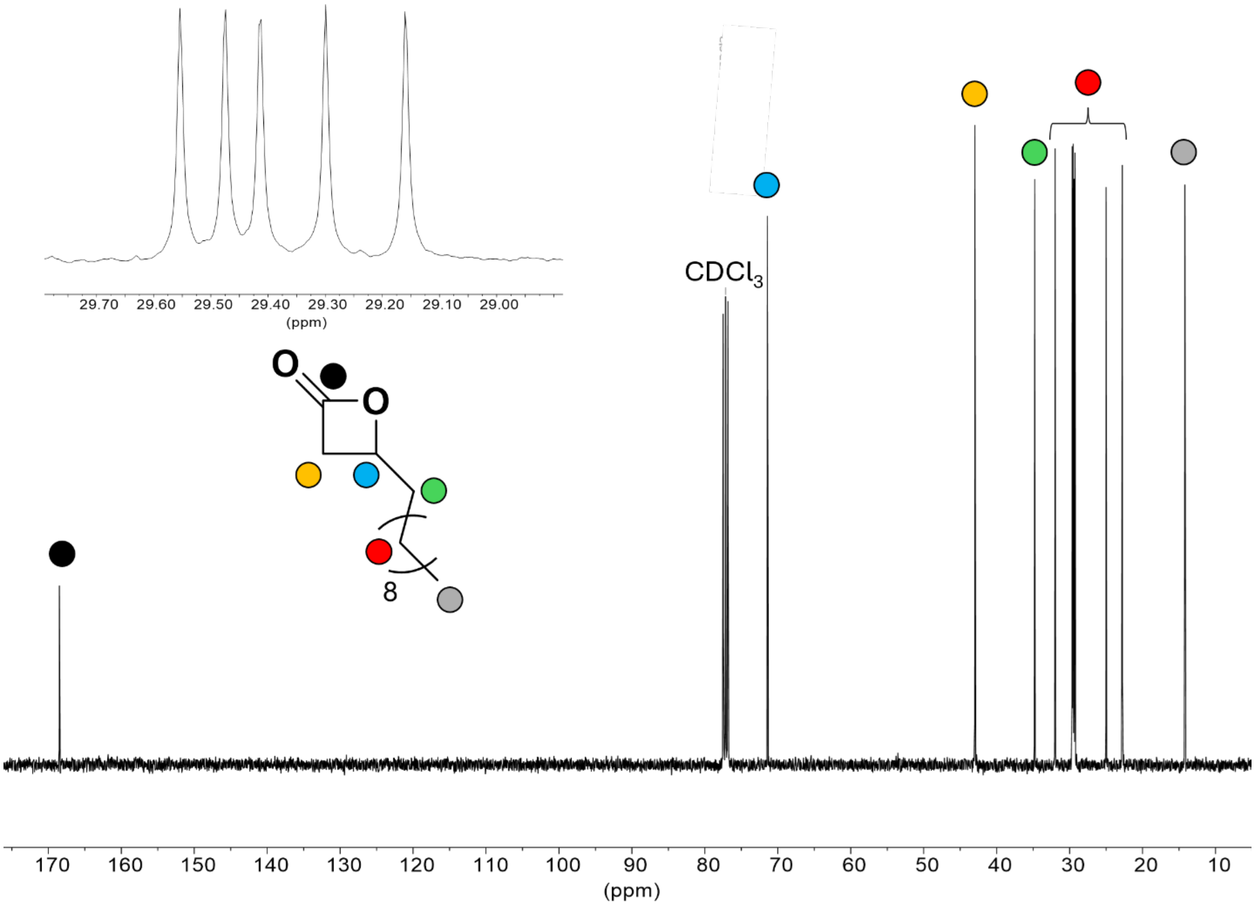


Figure S2: ^{13}C NMR (101 MHz, $CDCl_3$) spectra of β-tridecalactone with insert showing an expanded region between 30 and 28 ppm to resolve peaks in the side chain.

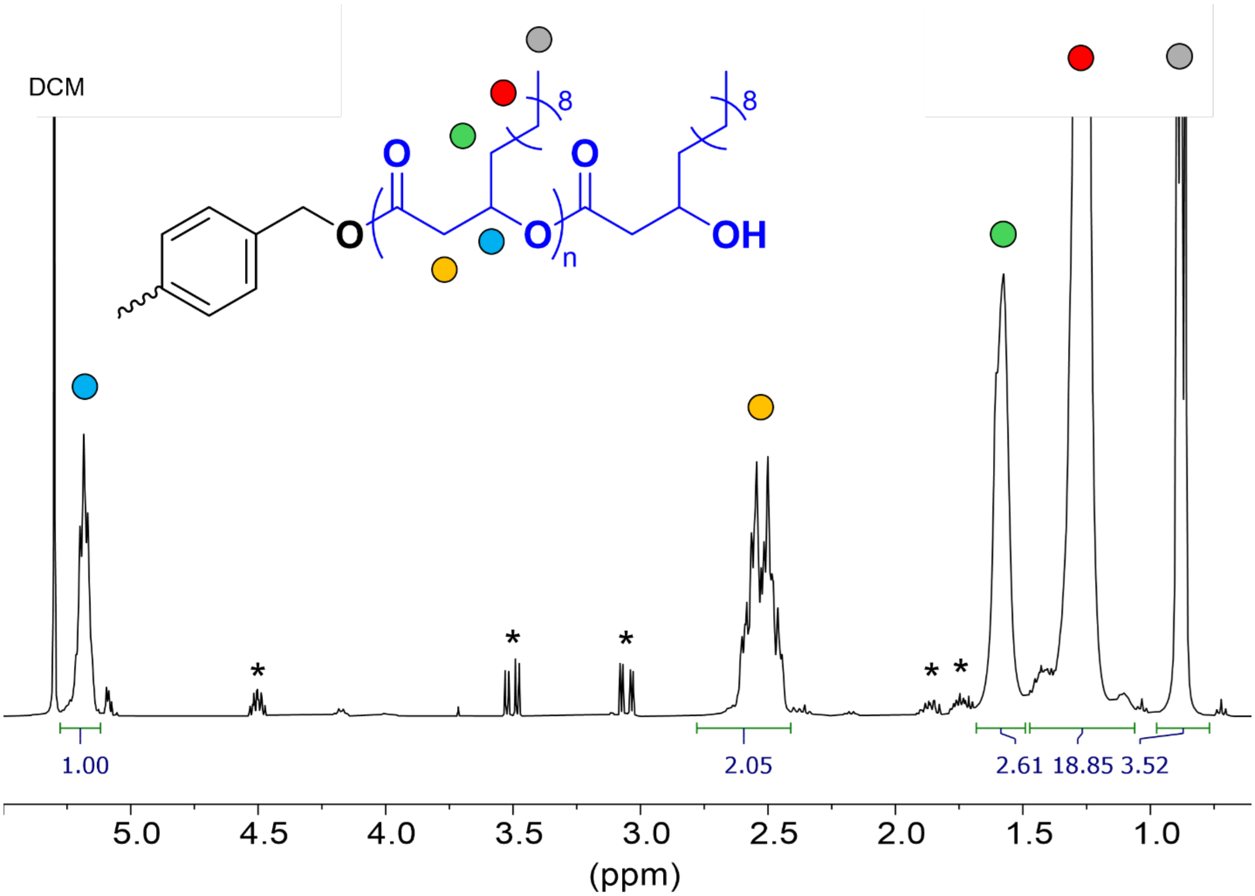


Figure S3: Expanded ^{1}H NMR (400 MHz, CDCl3) spectra of the crude 17 kg/mol PTDL homopolymer showing the peaks corresponding to the repeat units. Integrations of the alkyl-chain protons are higher than expected due to underlying monomer peaks. *Residual monomer.

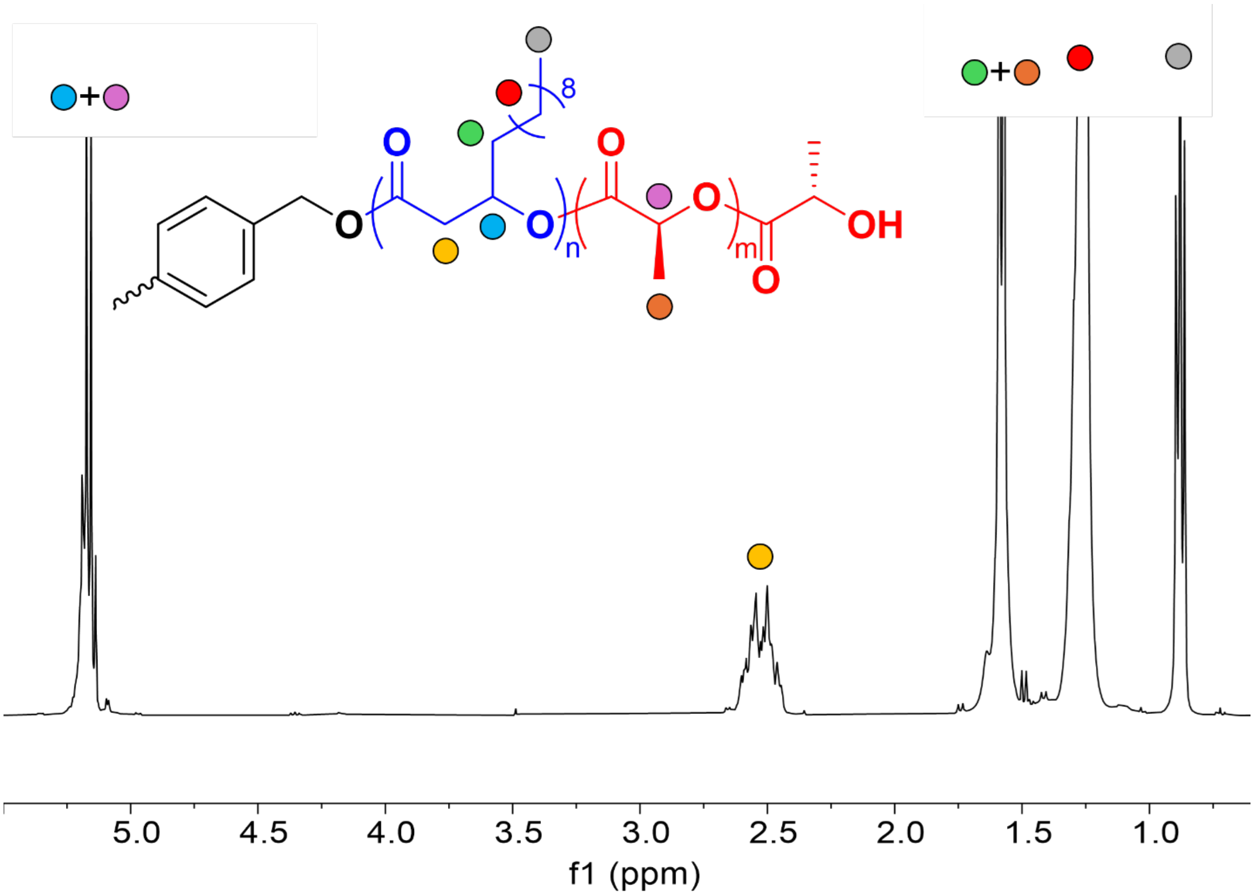


Figure S4: Expanded ^{1}H NMR (400 MHz, CDCl3) spectra of the LTL (17k, 0.35) showing the peaks corresponding to the repeat units. Methine protons in the PLLA and PTDL backbones overlap in the 5.12 – 5.22 ppm region. Methyl protons in the PLLA and the methylene protons closest to the backbone in the PTDL overlap in the 1.52 – 1.67 ppm region.

Table S2: Polymerization conditions and SEC RI analysis of PTDL macroinitiators and corresponding LTL triblocks

Sample	[M] (M)	M:I:C	$M_{n,RI}$ (kg/mol)[a]	$M_{w,RI}$ (kg/mol)[a]	LTL *Đ*[a]
PTDL (16k)	1.0	100:1:2	13	15	1.1
LTL(16k, 0.18)	-	-	19	23	1.2
PTDL (17k)	1.0	100:1:2	16	18	1.1
LTL(17k, 0.35)	-	-	22	30	1.4
PTDL (34k)	1.0	200:1:2	18	23	1.3
LTL(34k, 0.21)	-	-	21	28	1.3
PTDL (35k)	1.0	200:1:2	19	23	1.2
LTL(35k, 0.31)	-	-	25	34	1.3

[a] Calculated from RI SEC traces relative to polystyrene standards

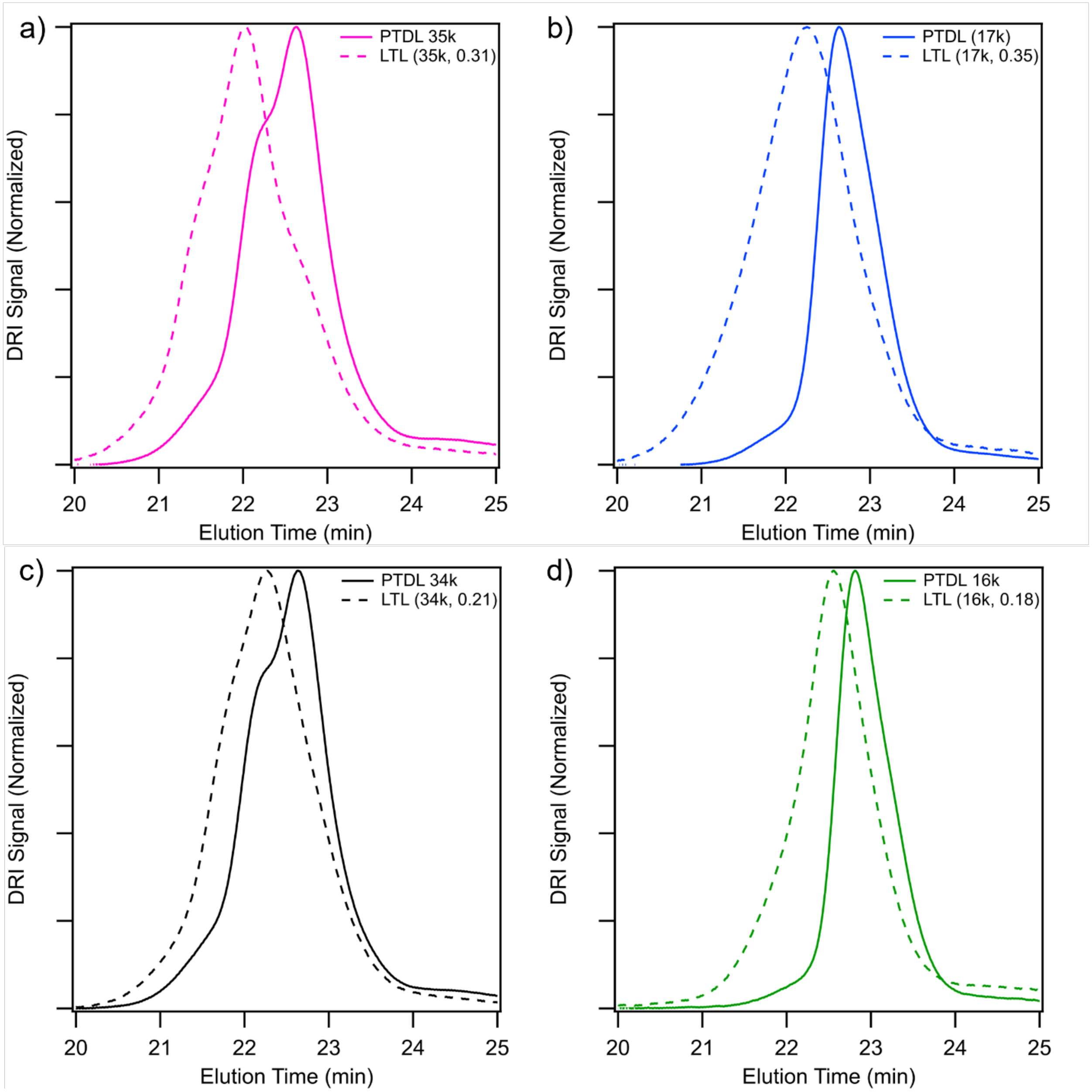
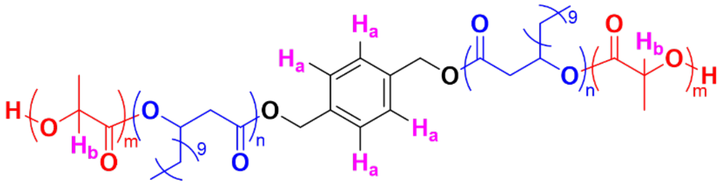
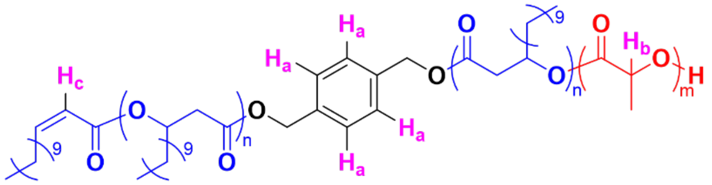


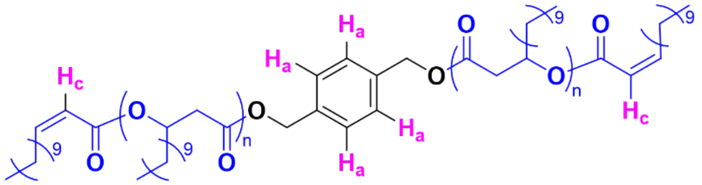
Figure S5: SEC elution curves of a) PTDL (35k) and LTL (35k, 0.31), b) PTDL (17k) and LTL (17k, 0.35), c) PTDL (34k) and LTL (34k, 0.21), and d) PTDL (16k) and LTL (16k 0.18).



PLLA-PTDL-PLLA



PTDL-PLLA



PTDL

Figure S6: The three species produced from the polymerization of TDL followed by chain extension with L-lactide accounting for no dehydration of the propagating PTDL end groups (PLLA-PTDL-PLLA), one dehydration event (PTDL-PLLA), and two dehydration events (PTDL) with the respective end group protons labeled.

Table S3: ^{1}H NMR Integrations of end groups present in LTL triblock samples with respect to the BDM initiator protons.

Sample	H_a	H_b	H_c	R_d[a]	EG:I[b]
LTL(16k, 0.18)	4	1.28	0.47	0.24	1.68
LTL(17k, 0.35)	4	1.13	0.55	0.28	1.75
LTL(34k, 0.21)	4	2.06	1.02	0.51	2.95
LTL(35k, 0.31)	4	1.94	1.01	0.51	3.08

[a] The ratio of protons H_c and H_a was used to calculate the chain-end fidelity of the produced triblock polymers. [b] The ratio of ($H_c + H_b$) to H_a indicates the total number of chain ends to initiator species.

Table S4: Thermal properties and microstructure of LTL triblock polymer films and corresponding PSA formulations DSC and SAXS analysis

Sample	$T_{\mathrm{g,\,PTDL}}$ (°C)[a]	$T_{\mathrm{m,\,PTDL}}$ (°C)[a]	$T_{\mathrm{g,\,PLLA}}$ (°C)[a]	D (nm)[b]
LTL (16k, 0.18) 0 wt.%	-	-25.8	44.0	21.2
LTL (16k, 0.18) 20 wt.%	-42.1	-	46.0	22.8
LTL (16k, 0.18) 40 wt.%	-29.4	-	51.2	24.1
LTL (16k, 0.18) 60 wt.%	-18.2	-	39.8[c]	27.6
LTL (17k, 0.35) 0 wt.%	-	-23.9	48.4	26.6
LTL (17k, 0.35) 20 wt.%	-39.5	-	49.5	25.0
LTL (17k, 0.35) 40 wt.%	-29.8	-	45.6	26.6
LTL (17k, 0.35) 60 wt.%	-15.6	-	52.5[c]	27.6
LTL (34k, 0.21) 0 wt.%	-	-22.7	39.1	22.6
LTL (34k, 0.21) 20 wt.%	-41.5	-	39.3	22.3
LTL (34k, 0.21) 40 wt.%	-33.9	-	40.7	22.3
LTL (34k, 0.21) 60 wt.%	-33.8	-	40.4[c]	23.3
LTL (35k, 0.31) 0 wt.%	-	-22.3	52.1	32.3
LTL (35k, 0.31) 20 wt.%	-38.4	-	53.2	31.3
LTL (35k, 0.31) 40 wt.%	-28.0	-	50.5	27.3
LTL (35k, 0.31) 60 wt.%	-13.4	-	49.2[c]	26.6

[a] Determined from the second DSC heating cycle of solvent cast films. [b] Calculated from the q* peak determined by SAXS of cast thin films. [c] Accurate T_g measurement was difficult due to the weak transition observed in DSC.

Table S5: Form factor fitting parameters for neat LTL triblocks analyzed by SAXS.

Sample	*D* (nm)[a]	form factor	R_{fit} (nm)[b]
LTL (17k, 0.35) 0 wt.%	26.6	sphere	12.0
LTL (17k, 0.35) 0 wt.%	26.6	cylinder	10.7
LTL (35k, 0.31) 40 wt.%	32.3	sphere	11.3
LTL (35k, 0.31) 60 wt.%	32.3	cylinder	9.9

[a] Calculated from the principle scattering peaks in the 1D SAXS patterns. [b] Determined by fitting form-scattering scattering functions to the experimental data

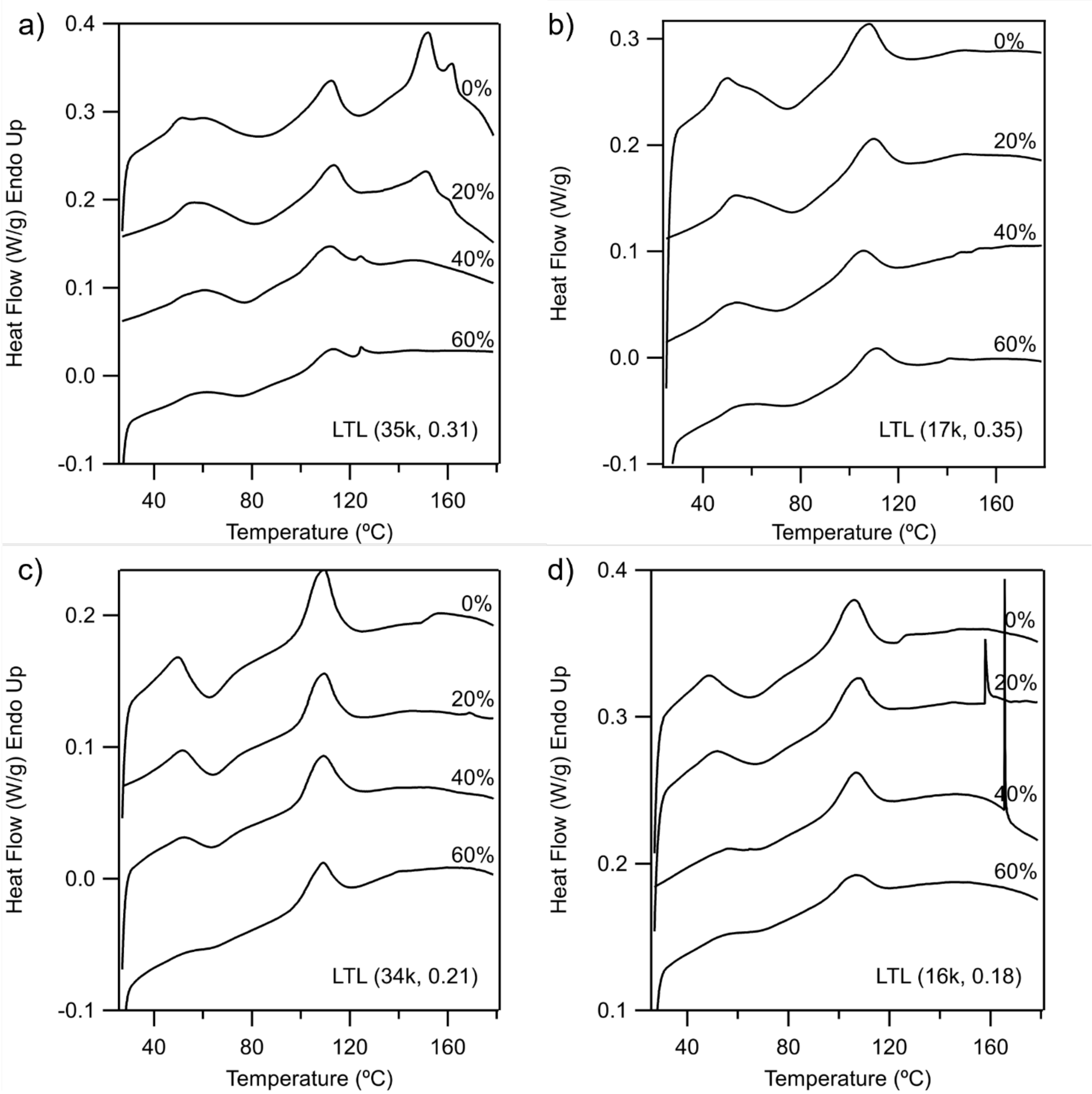


Figure S7: DSC first heating traces for thin films of a) LTL (35k, 0.31), b) LTL (17k, 0.35), and c) LTL (34k 0.21), and d) LTL (16k, 0.18) with the wt.% tackifier loading denoted by the numbers on the right hand side of the traces. Plots vertically shifted for clarity.

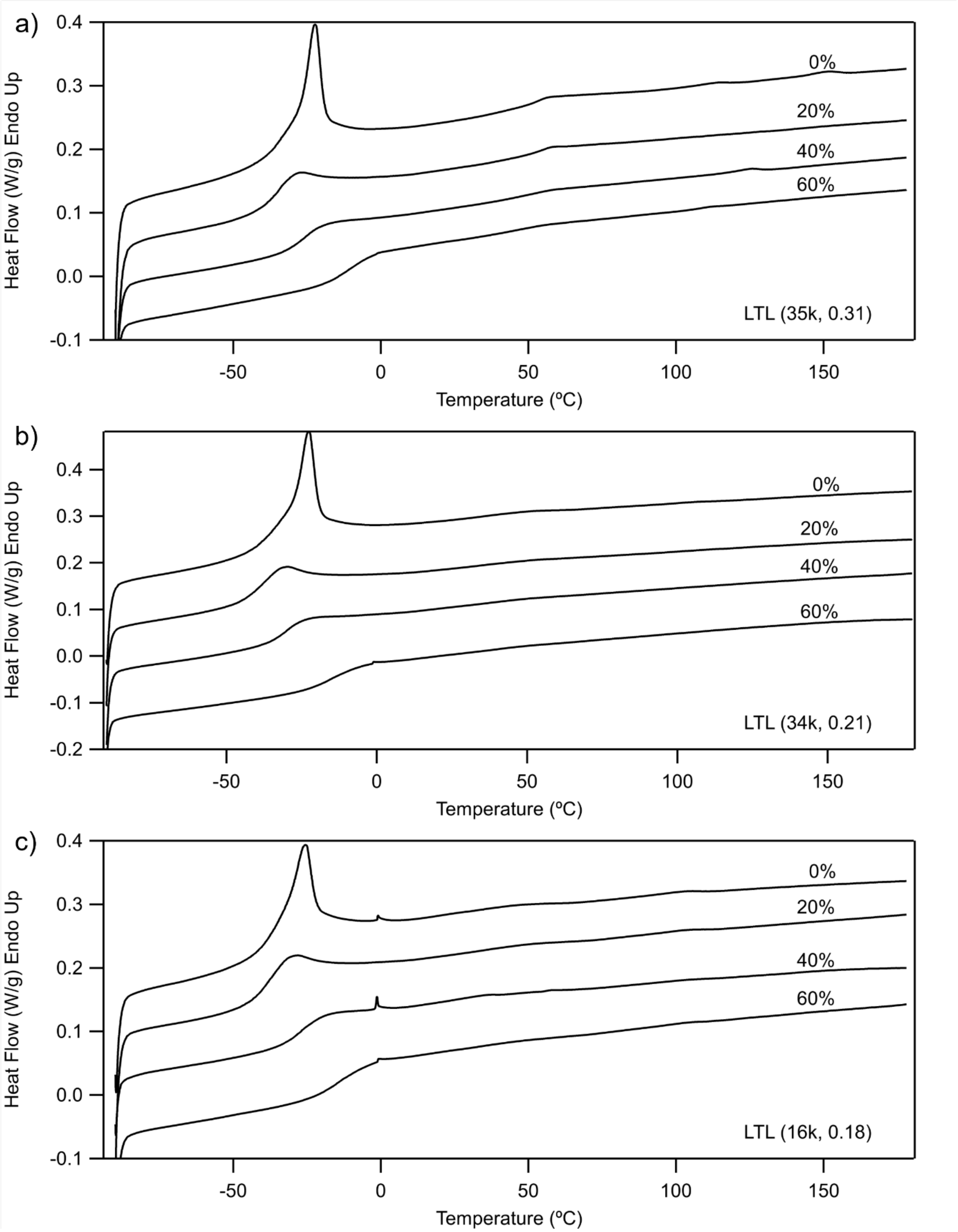


Figure S8: DSC second heating traces for thin films of a) LTL (35k, 0.31), b) LTL (34k, 0.21), and c) LTL (16k 0.18) with the wt.% tackifier loading denoted by the numbers on the right of the traces. Plots vertically shifted for clarity.

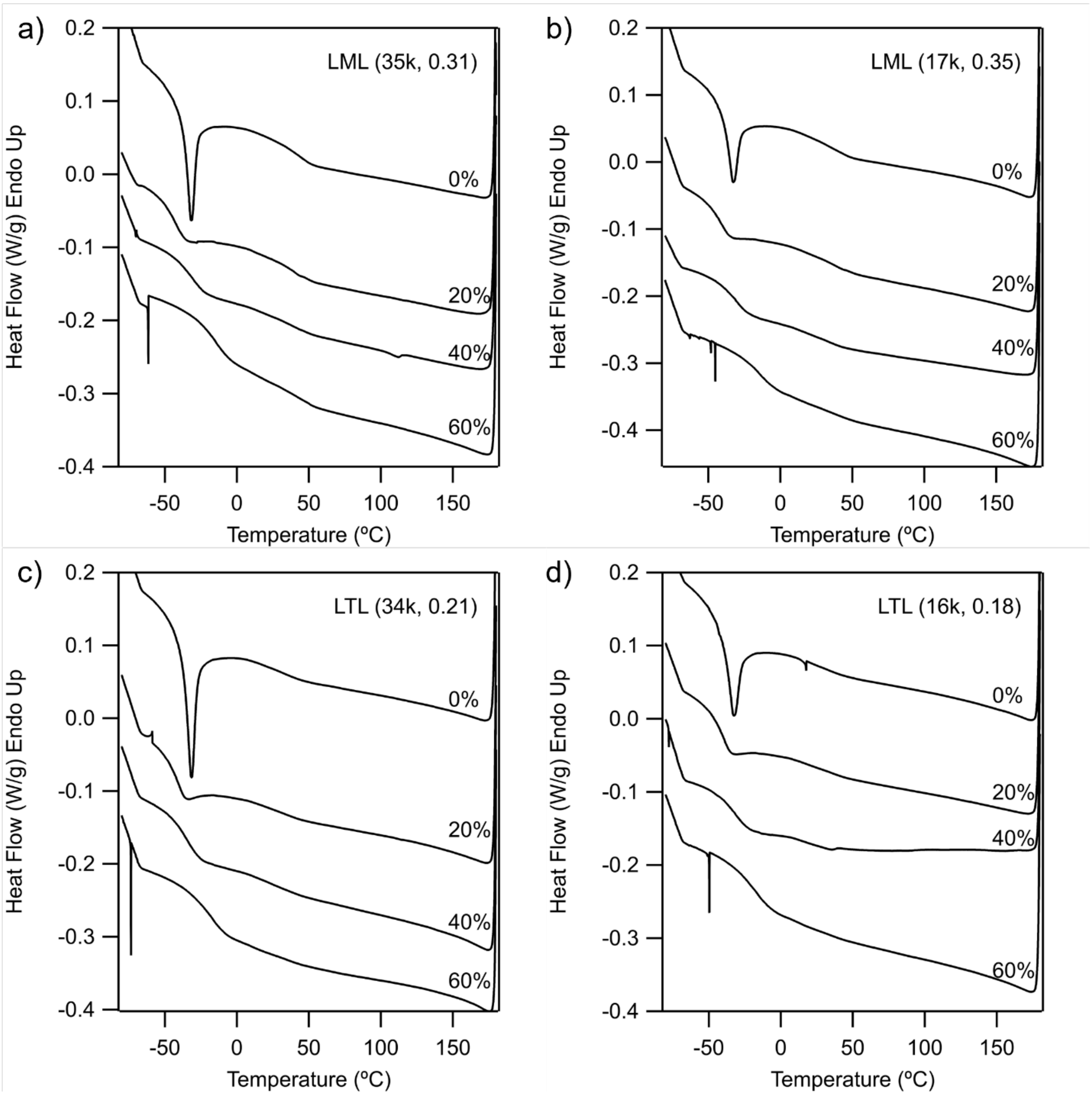


Figure S9: DSC cooling traces for thin films of a) LTL (35k, 0.31), b) LTL (17k, 0.35), and c) LTL (34k 0.21), and d) LTL (16k, 0.18) with the wt.% tackifier loading denoted by the numbers on the right hand side of the traces. Plots vertically shifted for clarity.

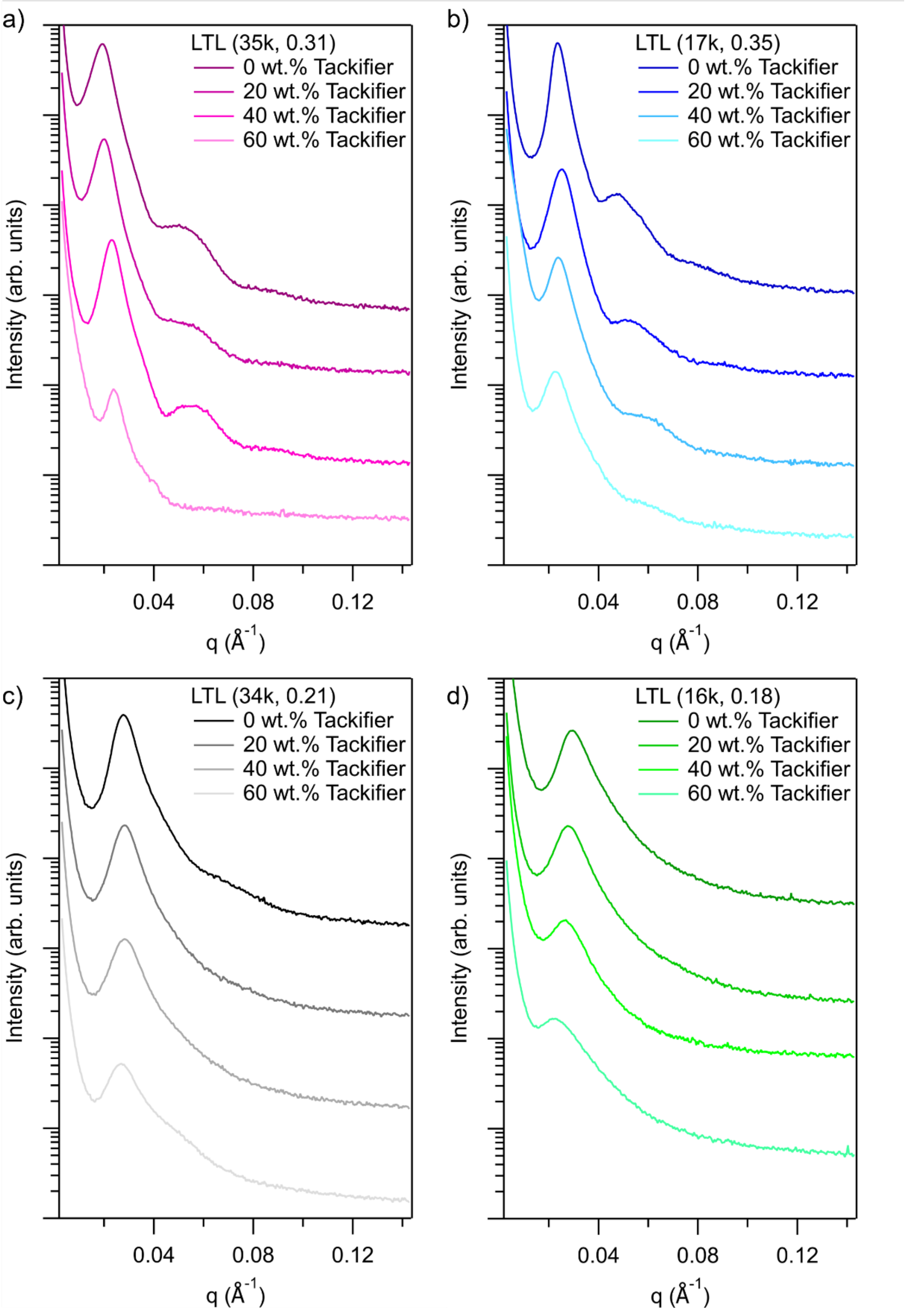


Figure S10: SAXS data of solvent cast a) LTL (35k, 0.31), b) LTL (17k, 0.35), c) LTL (34k, 0.21), and d) LTL (16k, 0.18) triblock samples with different loading levels of tackier.

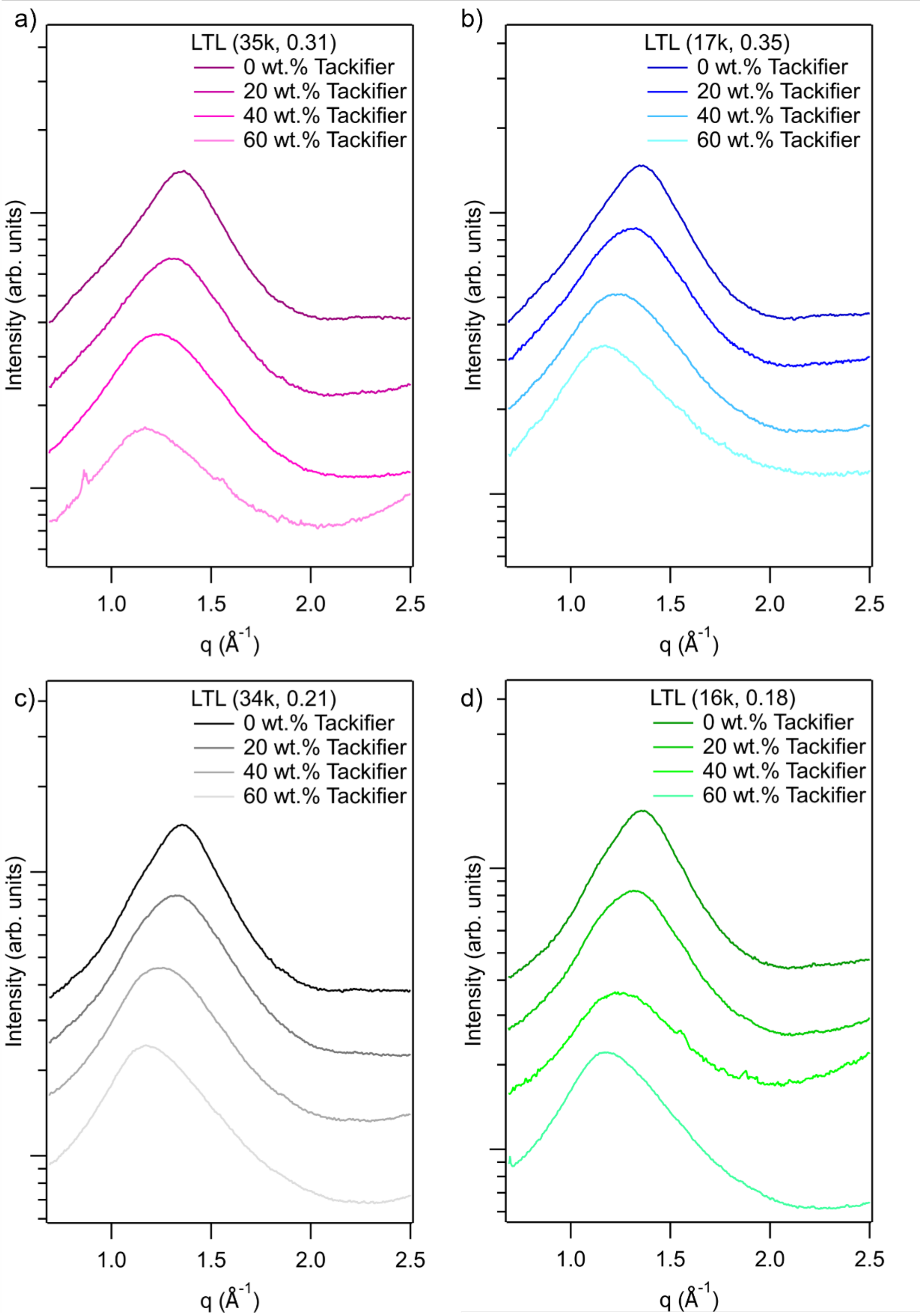


Figure S11: WAXS data of solvent cast a) LTL (35k, 0.31), b) LTL (17k, 0.35), c) LTL (34k, 0.21), and d) LTL (16k, 0.18) triblock samples with different loading levels of tackier.

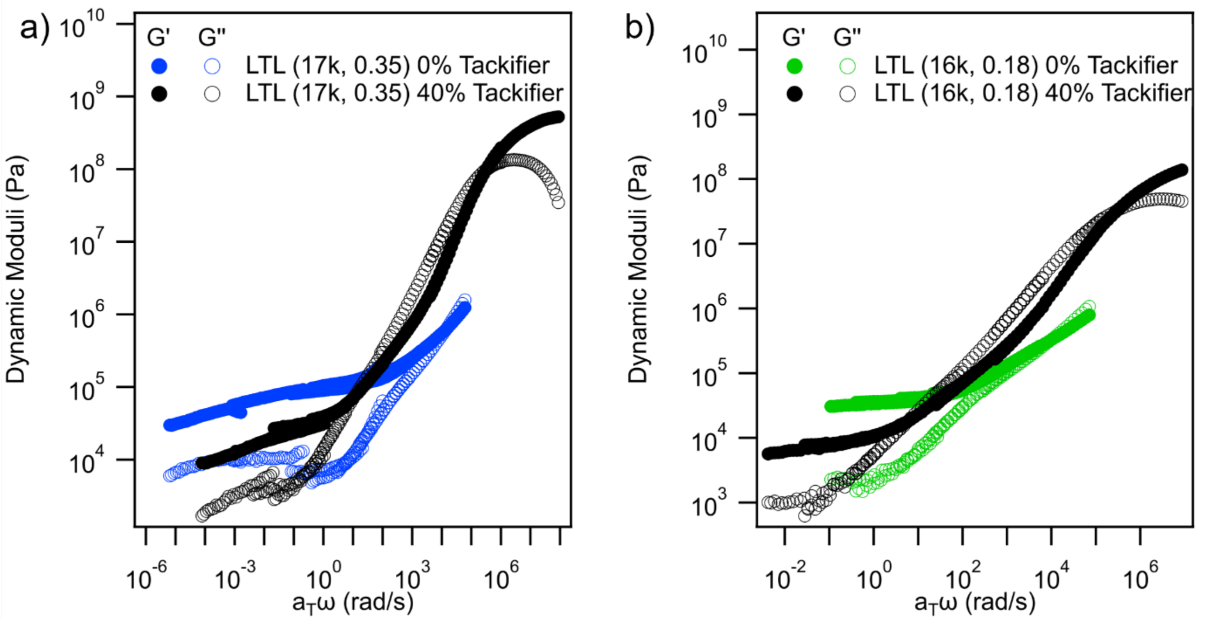


Figure S12: Storage (closed circles) and loss (open circles) moduli master curves of a) LTL (17k, 0.35) PSA formulations at 0 wt.% and 40 wt.% tackifier loadings and b) LTL (16k, 0.18) PSA formulations at 0 wt.% and 40 wt.% tackifier loadings.

Table S6: Mechanical Properties of LTL triblock PSA formulations at different tackifier loading levels.

Formulation	**Peel Strength (N/cm)**[a]	**Loop Tack (N/cm)**[a]	**Shear (Hours)**[b]
LTL(16k, 0.18) 0% Tack	0.09 ± 0.02	1.6 ± 0.4	3.9 ± 0.6
LTL(16k, 0.18) 20% Tack	2.2 ± 0.3	5.8 ± 0.2	3.1 ± 0.5
LTL(17k, 0.18) 40% Tack	4.9 ± 0.6	13.2 ± 0.6	4.6 ± 1.1
LTL(17k, 0.35) 0% Tack	0.09 ± 0.01	0.9 ± 0.2	>240
LTL(17k, 0.35) 20% Tack	0.9 ± 0.3	2.0 ± 0.5	>240
LTL(17k, 0.35) 40% Tack	2.1 ± 0.3	3.8 ± 0.2	111 ± 15
LTL(34k, 0.21) 0% Tack	0.5 ± 0.1	3.3 ± 0.2	13.3 ± 3.3
LTL(34k, 0.21) 20% Tack	3.1 ± 0.3	10.0 ± 1.1	11.6 ± 4.2
LTL(34k, 0.21) 40% Tack	4.6 ± 0.2	16.5 ± 0.1	9.3 ± 5.4
LTL(35k, 0.31) 0% Tack	0.06 ± 0.03	0.4 ± 0.2	>240
LTL(35k, 0.31) 20% Tack	0.5 ± 0.1	2.5 ± 0.2	>240
LTL(35k, 0.31) 40% Tack	5.5 ± 0.9	8.5 ± 0.9	11 ± 6

[a] Average values ± a standard deviation calculated from at least three replicates. [b] Shear tests were conducted for 10 days and if failure was not observed the test was stopped manually at which point the shear resistance was said to be >240 hours.

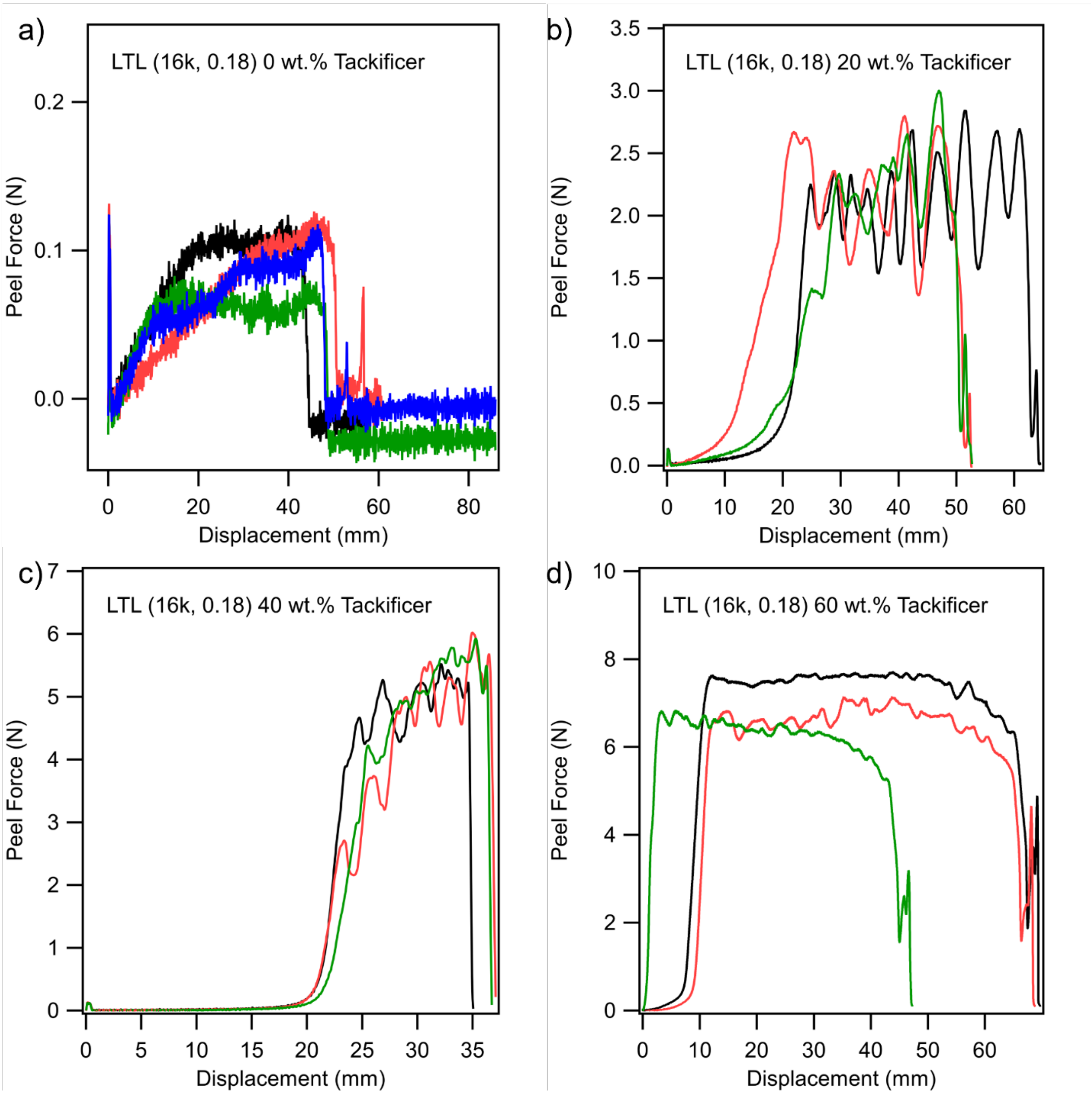


Figure S13: Peel test data for a) LTL (16k, 0.18) with 0 wt.% tackifier, b) LTL (16k, 0.18) with 20 wt.% tackifier c) LTL (16k, 0.18) with 40 wt.% tackifier, and d) LTL (16k, 0.18) with 60 wt.% tackifier. Peel testing for a) – c) were conducted using an extension rate of 305 mm/min while d) was conducted using a 30.5 mm/min extension rate.

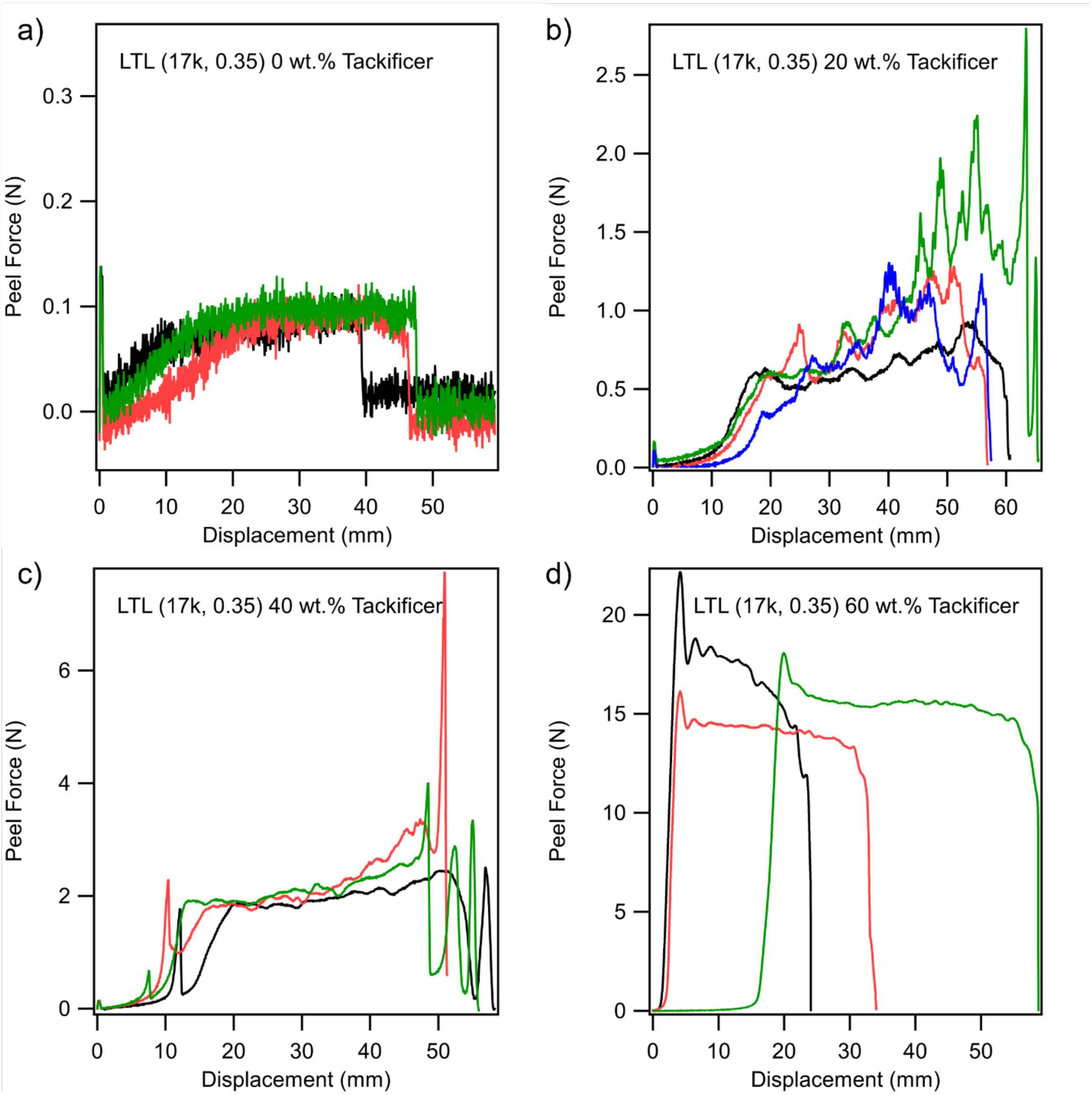


Figure S14: Peel test data for a) LTL (17k, 0.35) with 0 wt.% tackifier, b) LTL (17k, 0.35) with 20 wt.% tackifier c) LTL (17k, 0.35) with 40 wt.% tackifier, and d) LTL (17k, 0.35) with 60 wt.% tackifier. Peel testing for a) – c) were conducted using an extension rate of 305 mm/min while d) was conducted using a 30.5 mm/min extension rate.

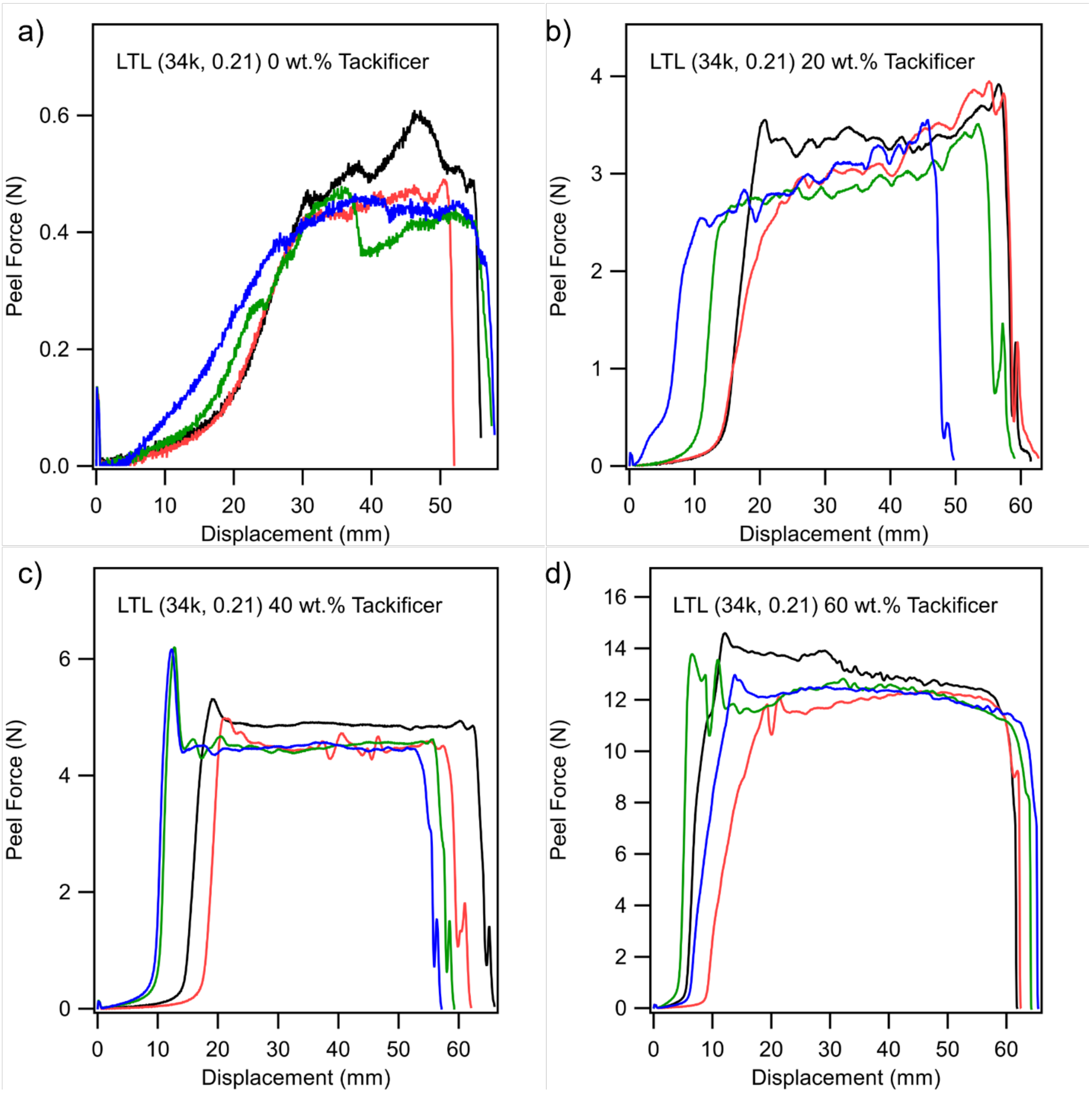


Figure S15: Peel test data for a) LTL (34k, 0.21) with 0 wt.% tackifier, b) LTL (34k, 0.21) with 20 wt.% tackifier c) LTL (34k, 0.21) with 40 wt.% tackifier, and d) LTL (34k, 0.21) with 60 wt.% tackifier. Peel testing for a) – c) were conducted using an extension rate of 305 mm/min while d) was conducted using a 30.5 mm/min extension rate.

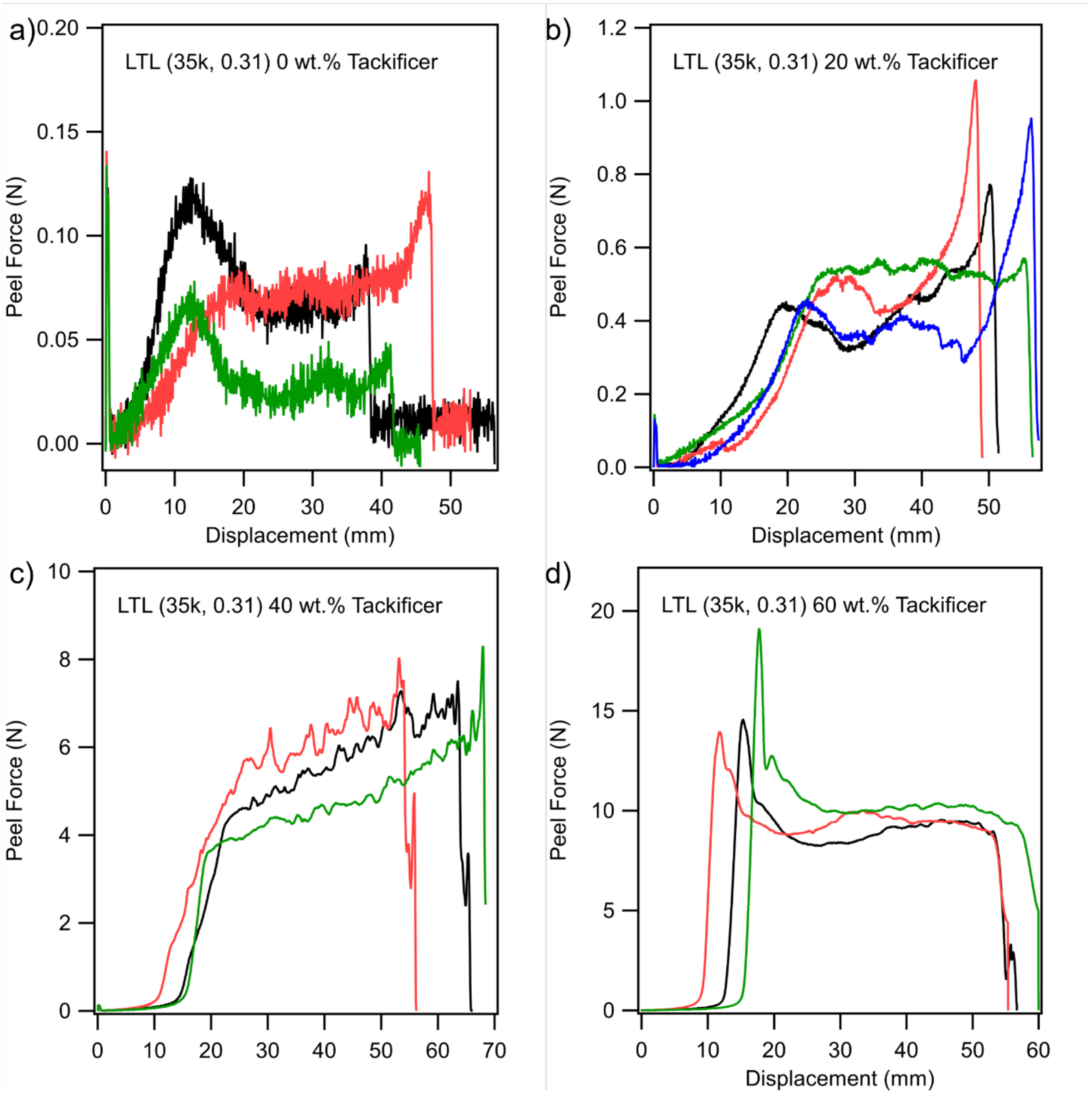


Figure S16: Peel test data for a) LTL (35k, 0.31) with 0 wt.% tackifier, b) LTL (35k, 0.31) with 20 wt.% tackifier c) LTL (35k, 0.31) with 40 wt.% tackifier, and d) LTL (35k, 0.31) with 60 wt.% tackifier. Peel testing for a) – c) were conducted using an extension rate of 305 mm/min while d) was conducted using a 30.5 mm/min extension rate.

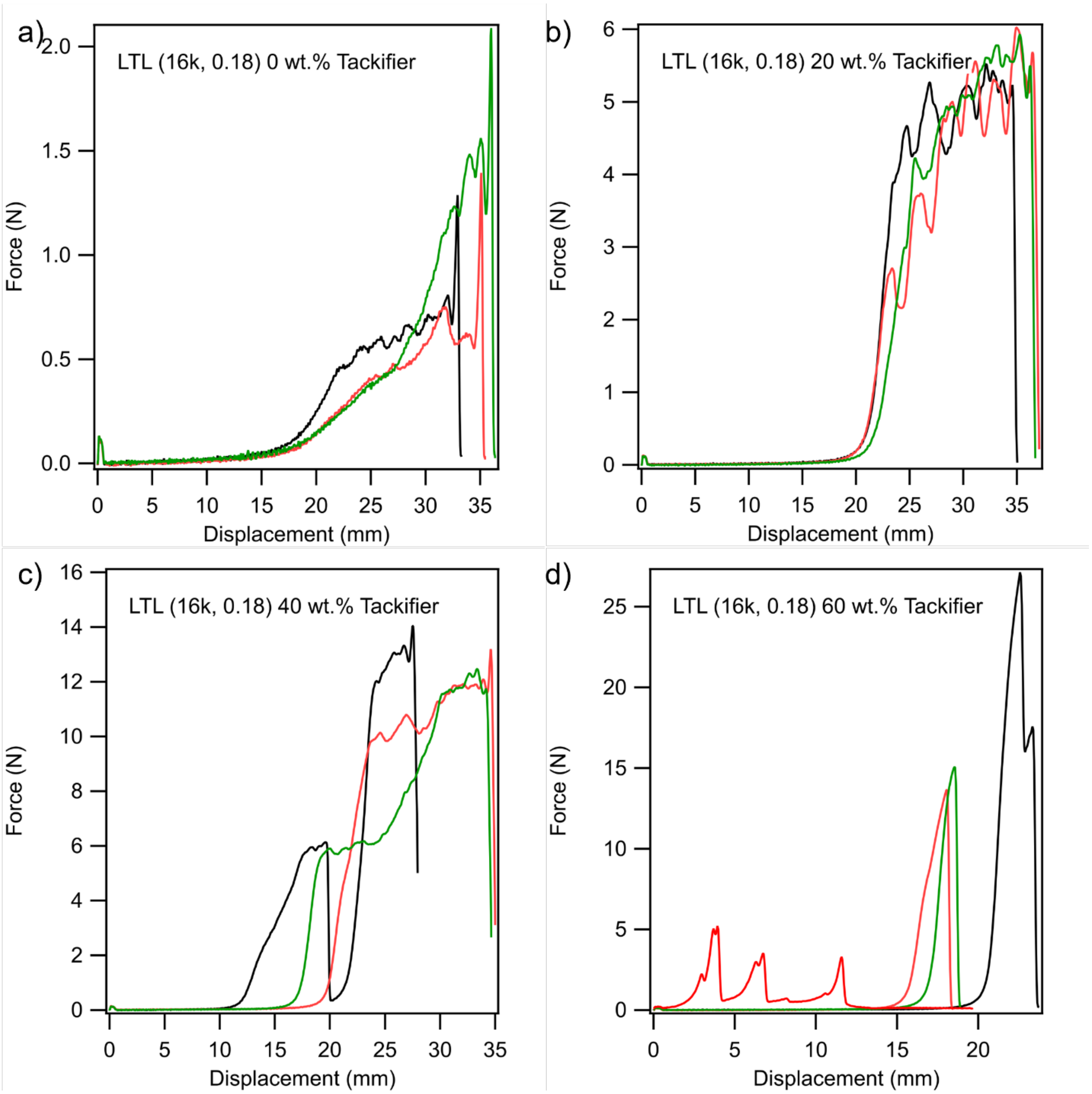


Figure S17: Loop tack test data for a) LTL (16k, 0.18) with 0 wt.% tackifier, b) LTL (16k, 0.18) with 20 wt.% tackifier c) LTL (16k, 0.18) with 40 wt.% tackifier, and d) LTL (16k, 0.18) with 60 wt.% tackifier.

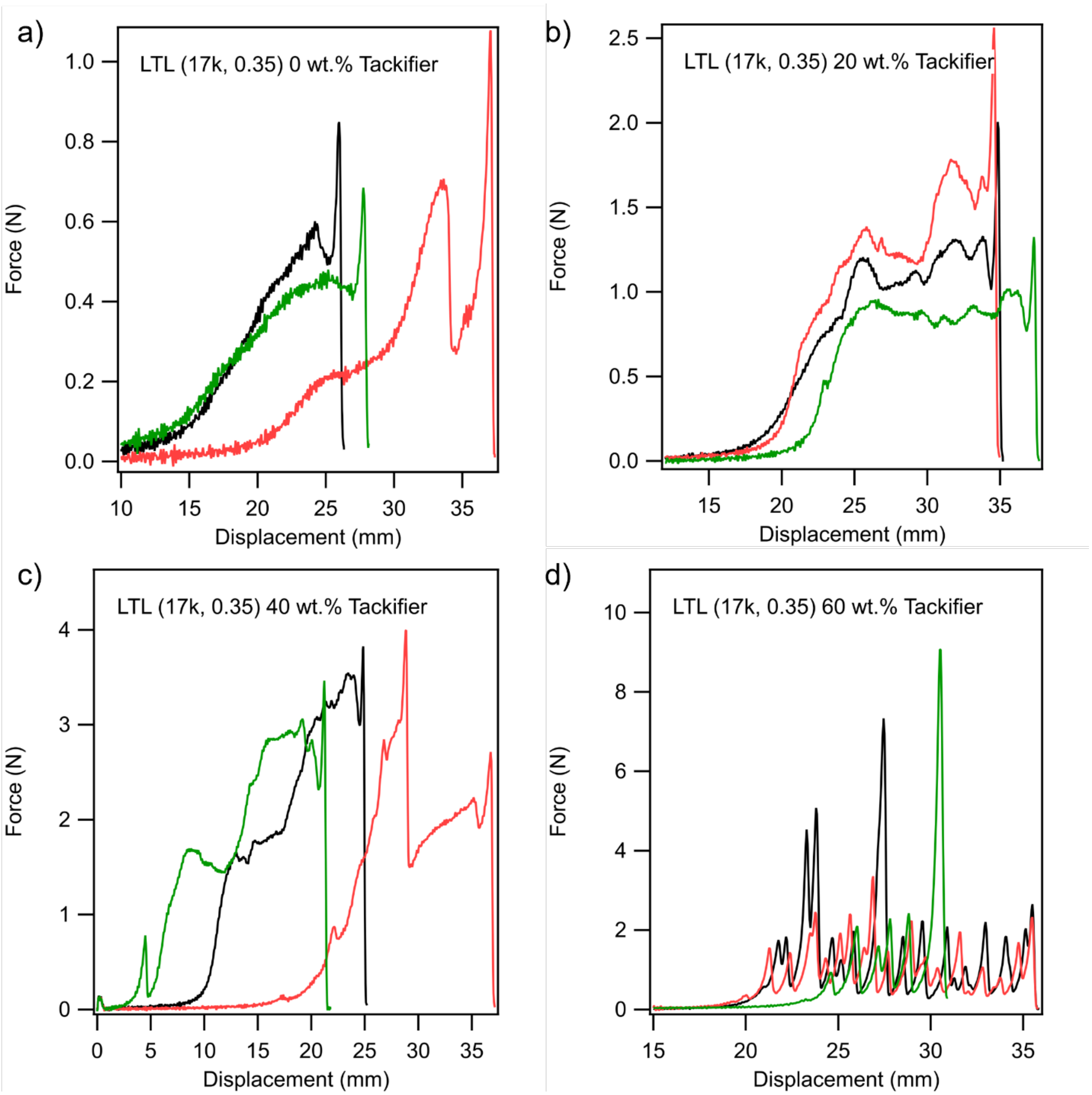


Figure S18: Loop tack test data for a) LTL (17k, 0.35) with 0 wt.% tackifier, b) LTL (17k, 0.35) with 20 wt.% tackifier c) LTL (17k, 0.35) with 40 wt.% tackifier, and d) LTL (17k, 0.35) with 60 wt.% tackifier.

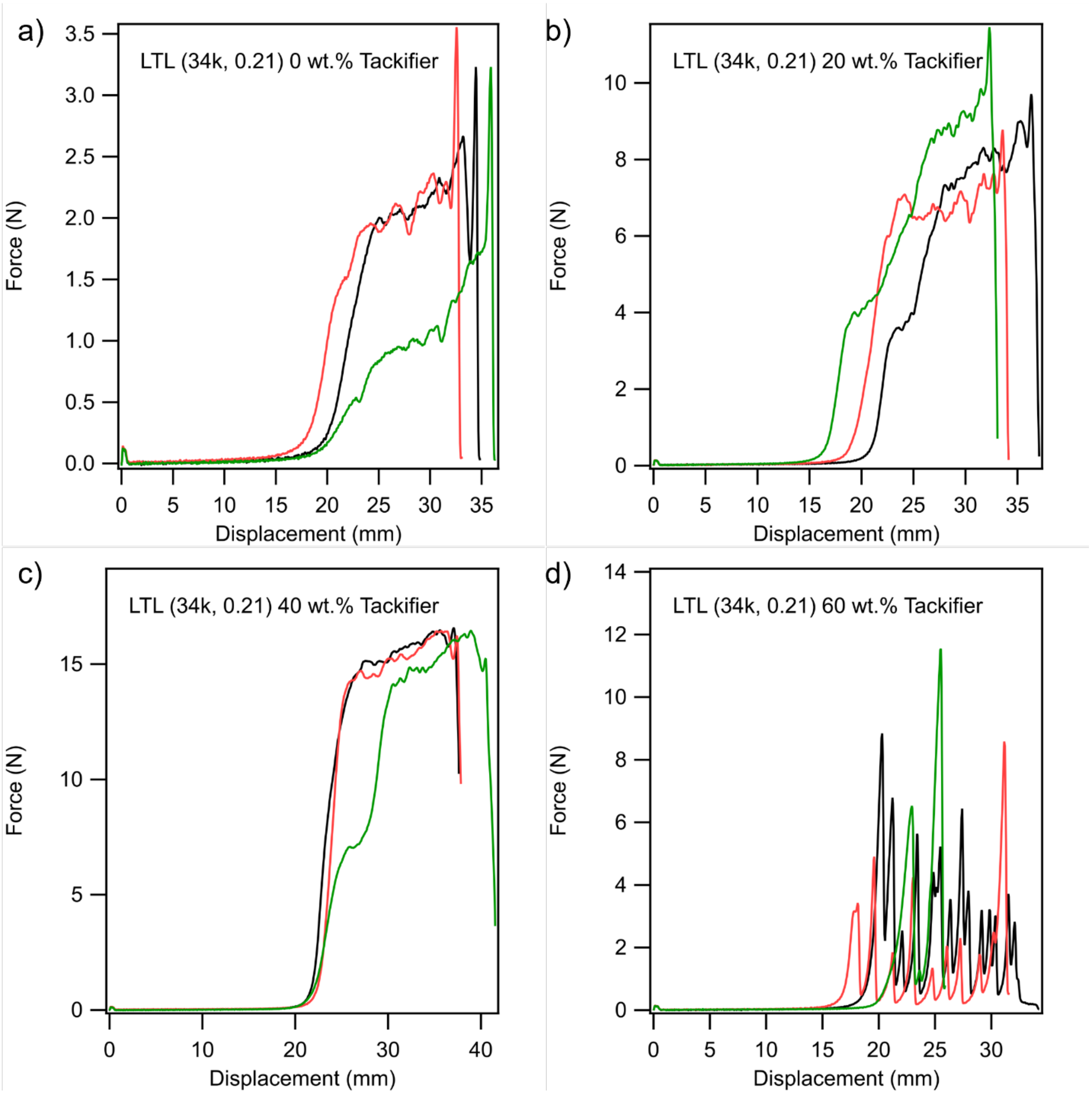


Figure S19: Loop tack test data for a) LTL (34k, 0.21) with 0 wt.% tackifier, b) LTL (34k, 0.21) with 20 wt.% tackifier c) LTL (34k, 0.21) with 40 wt.% tackifier, and d) LTL (34k, 0.21) with 60 wt.% tackifier.

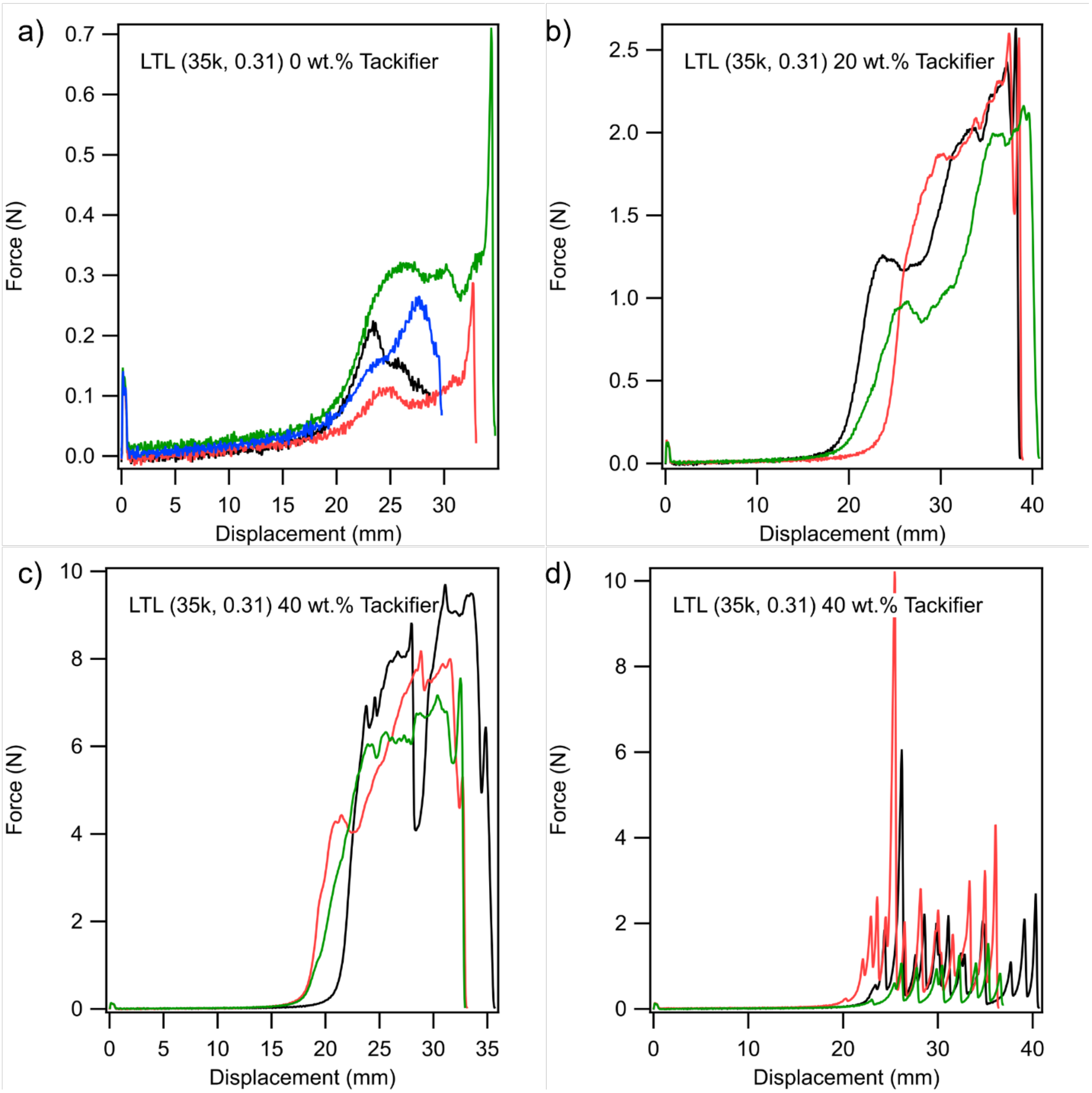


Figure S20: Loop tack test data for a) LTL (35k, 0.31) with 0 wt.% tackifier, b) LTL (35k, 0.31) with 20 wt.% tackifier c) LTL (35k, 0.31) with 40 wt.% tackifier, and d) LTL (35k, 0.31) with 60 wt.% tackifier.

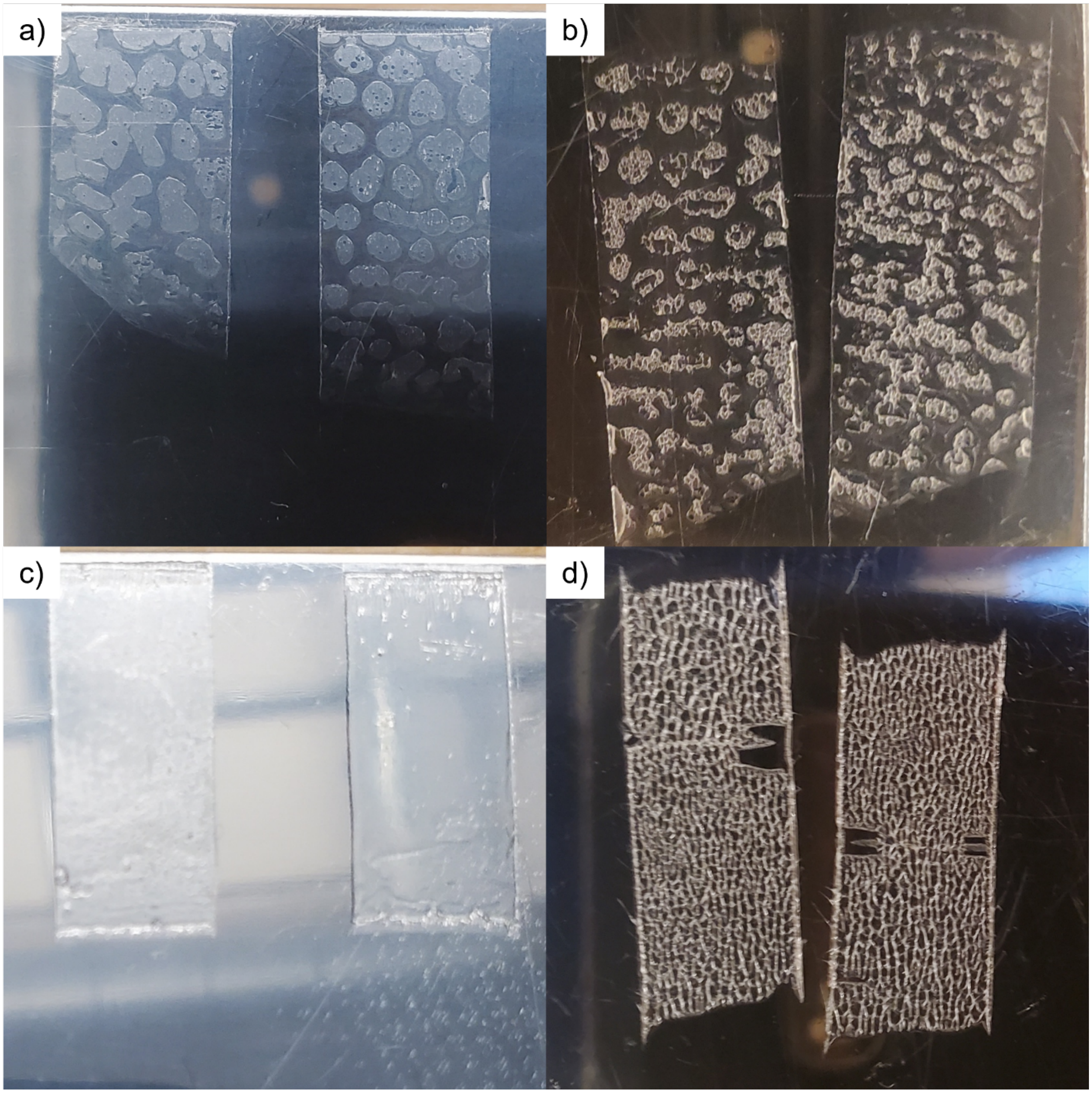


Figure S21: Images of stainless-steel substrates after peel and loop tack testing respectively for a) and b) LTL (16k, 0.18) 20 wt.% tackifier and c) and d) LTL(34k, 0.21) 40 wt.% tackifier demonstrating cohesive failure of the PSAs.

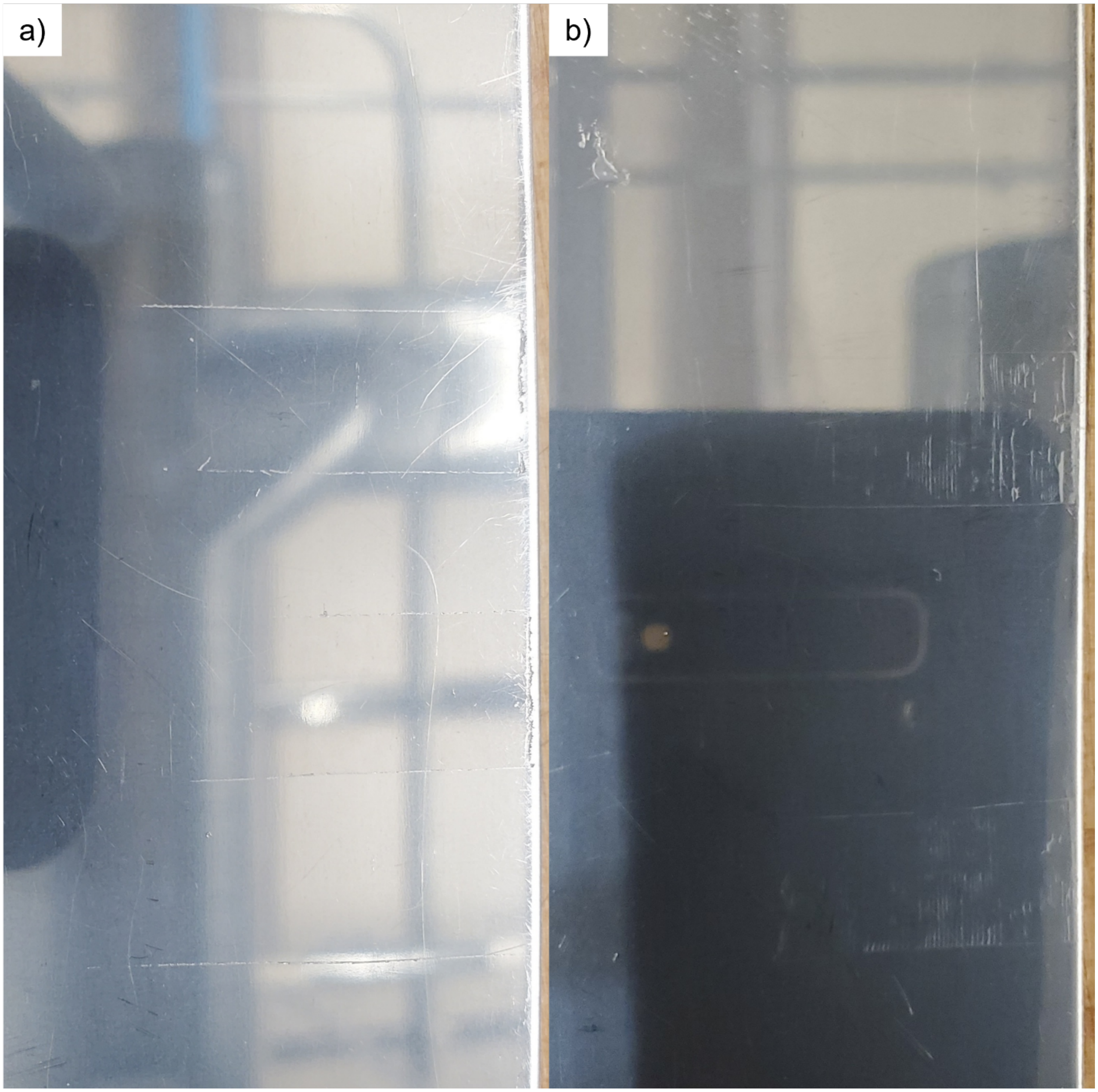


Figure S22: Images of stainless-steel substrates after peel testing for a) LTL (35k, 0.31) 40 wt.% tackifier and b) LTL(17k, 0.35) 20 wt.% tackifier demonstrating adhesive failure of the PSAs.

Figure S23: Image of shear-testing setup. 250 g of sand is suspended from a 1.27 cm x 1.27 cm square of PSA adhered to a stainless-steel substrate.