Supporting Information

Building thermally and chemically reversible covalent bonds in vegetable oils based epoxy thermosets. Influence of epoxy-hardener ratio to promote recyclability

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Table S1. Structures and characteristics of the selected reagents.

Acronym	Molecular weight [g/mol]	Melting Point [°C]	Epoxy Content (meq.g^{-1})
ELO	980	-	5,6
ESO	950	-	4,66
DTBA	306,35	287-290	/
IM	68,077	89 - 91	/

Table S2. Formulations composition of the curing systems

Formulations	Ratio (e/a)	Epoxide (mol)	DTBA (mol)
ELO/DTBA-0.83	1:1.2	$2.5 \cdot 10^{-4}$	$8.4 \cdot 10^{-4}$
ELO/DTBA-1	1:1	$2.5 \cdot 10^{-4}$	$7 \cdot 10^{-4}$
ELO/DTBA- 1.25	1:0.8	$2.5 \cdot 10^{-4}$	$5.6 \cdot 10^{-4}$
ELO/DTBA- 2	1:0.5	$2.5 \cdot 10^{-4}$	$3.5 \cdot 10^{-4}$
ELO/DTBA-IM -3.33	1:0.3	$2.5 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$
ESO/ DTBA-IM -0.83	1:1.2	$2.6 \cdot 10^{-4}$	$6.9 \cdot 10^{-4}$
ESO/DTBA-IM -1	1:1	$2.6 \cdot 10^{-4}$	$5.8 \cdot 10^{-4}$
ESO/DTBA-IM-1.25	1:0.8	$2.6 \cdot 10^{-4}$	$4.6 \cdot 10^{-4}$
ESO/DTBA-IM-2	1:0.5	$2.6 \cdot 10^{-4}$	$2.9 \cdot 10^{-4}$
ESO/DTBA- IM-3.33	1:0.3	$2.6 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$
ESO/ELO/DTBA-IM-0.83	1:1.2	$7.7 \cdot 10^{-4}$	$2.4 \cdot 10^{-3}$
ESO/ELO/DTBA-IM-1	1:1	$7.7 \cdot 10^{-4}$	$2 \cdot 10^{-4}$

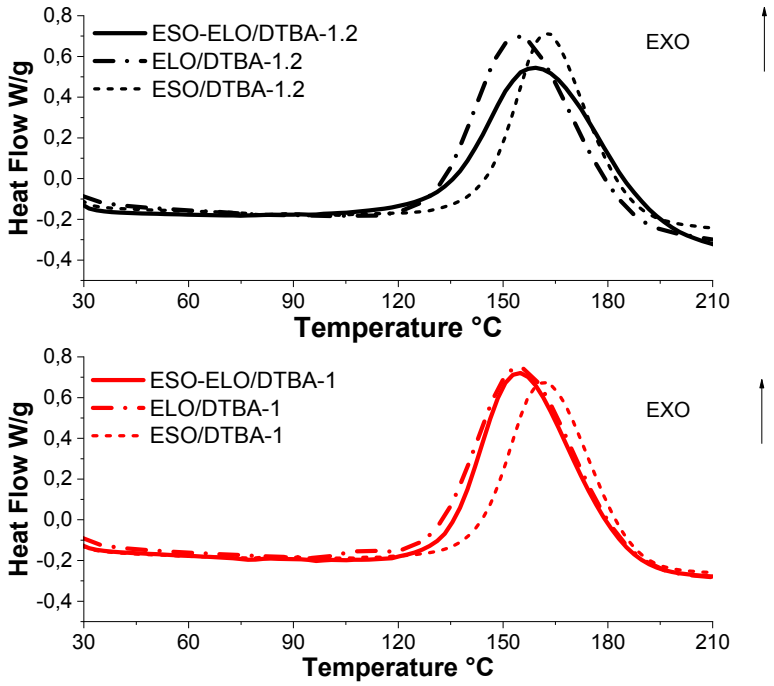

Figure S1. DSC thermograms during heating at 10 °C/min of the mixture ELO+ESO in comparison with the reference ELO and ESO, ratios 0.83 and 1

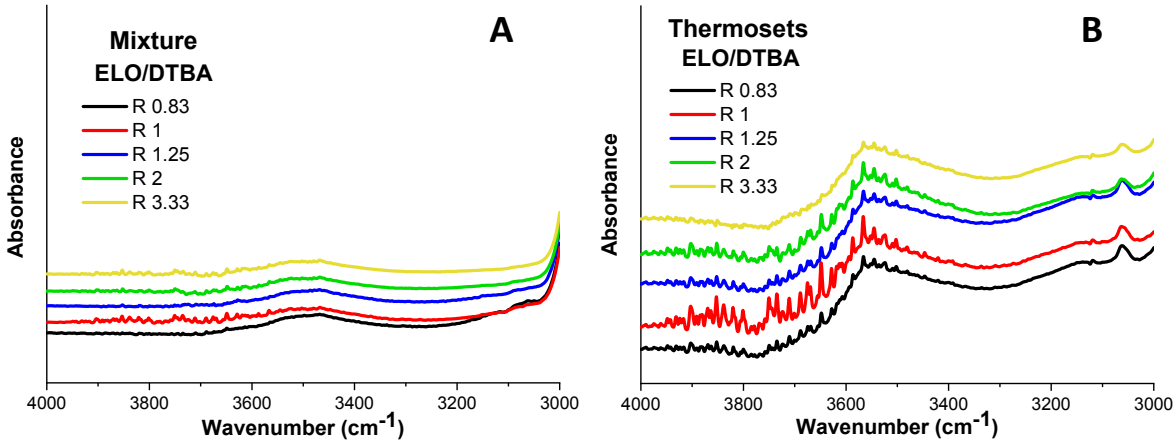

Figure S2. FTIR spectra at -OH stretching regions (3700–3300 cm-1) for ELO/DTBA systems in function of the ratio at the beginning (A) and at the end of the curing (B).

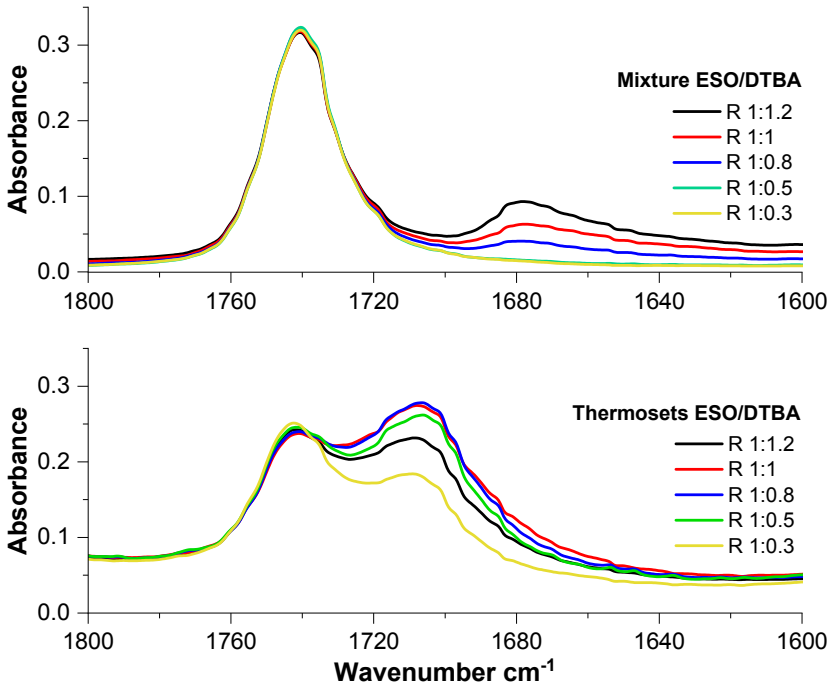

Figure S3. FTIR spectra of ESO/DTBA systems at different ratios in ester-acid regions: the starting mixture (A) and the cured resins (B)

Table S3. Aspect and reprocessing duration at 160 °C and 60 bars for ESO/DTBA and ESO/ELO/DTBA resins.

Ratio	0.83	1	1.25
ESO/DTBA M-Reprocessed resins			
Time / min	15	10	5

Ratio	0.83	1
ESO/ELO/DTBA M-Reprocessed resins		
Time / min	15	10

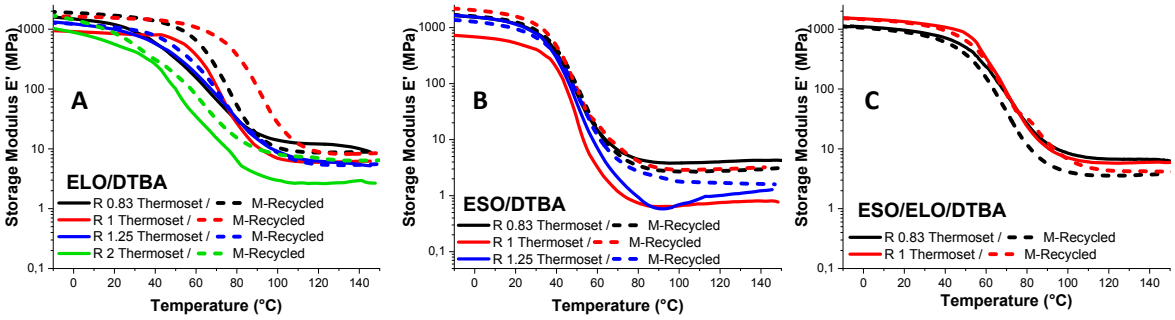

Figure S4. Storage modulus E' vs. temperature for the virgin and mechanically reprocessed (M) thermosets

Table S4. Thermomechanical properties of the virgin and reprocessed ESO/DTBA thermosets

Parameters	ESO/DTBA					
Virgin/M-Recycled	V*	M-R*	V*	M-R*	V*	M-R*
Ratio	0.83		1		1.25	
tan δ	53	60	52	60	58	58
tan δ_{max}	0.94	1.07	0.96	1.14	0.95	0.98
$E'_{glassy\ state}$ (MPa)	1900	1800	900	2330	2000	1450
$E'_{rubbery\ state}$ (MPa)	3.18	3.41	0.69	3.20	1.14	0.47
Crosslinking density (mmol/cm^3)	0.41	0.28	0.082	0.31	0.12	0.18

Table S5. Thermomechanical properties of the virgin and reprocessed ESO/ELO/DTBA thermosets.

Parameters	ESO/ELO/DTBA			
Virgin/M-Recycled	V*	M-R*	V*	M-R*
Ratio	0.83		1	
tan δ	78	74	79	83
tan δ_{max}	0.56	0.82	0.66	0.82
$E'_{glassy\ state}$ (MPa)	1000	1170	1750	1580
$E'_{rubbery\ state}$ (MPa)	3.04	4.09	4.45	4.21
Crosslinking density (mmol/cm^3)	0.45	0.36	0.58	0.42

Table S6.TGA results for the resins and recycled materials during heating at 10 °C/min under air.

EVOs/DTBA	Ratio		$T_{5\%}$ (°C)	1st Residue (%)	1st Degradation peak (°C)	2nd Residue (%)	2nd Degradation peak (°C)
ELO	0.83	V*	271	23.6	310	0.25	517
		M-R*	271	23.1	310	0.23	517
	1	V*	275	19.4	307	0.67	517
		M-R*	275	23.4	310	0.20	526
	1.25	V*	281	21.3	310	0.73	517
		M-R*	281	22.0	310	0.35	526
	2	V*	291	23.6	310	0.29	536
		M-R*	291	27.9	310	0.20	526
ESO	0.83	V*	271	19.9	310	0.29	526
		M-R*	271	18.4	310	0.99	517
	1	V*	271	18.4	310	0.42	526
		M-R*	271	19.9	310	0.53	517
	1.25	V*	281	24.1	310	0.22	507
		M-R*	281	24.1	310	0.46	517
ESO/ELO	0.83		271	18.8	310	0.35	517
		M-R*	271	25.0	310	0.15	517
	1	V*	271	25.5	300	0.14	517
		M-R*	271	28.4	300	0.53	517

V* virgin, M-R* mechanical recycled

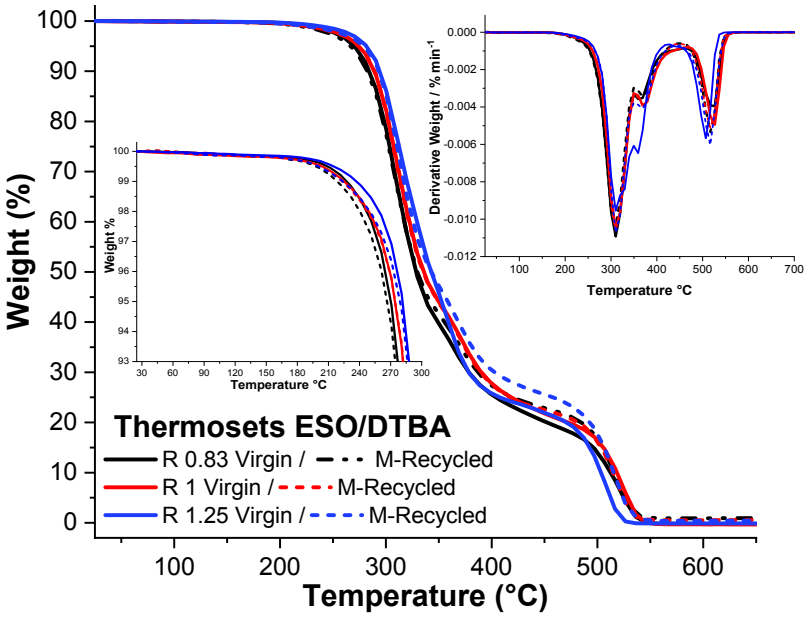

Figure S5.TGA, DTG and zoom in the region from 25 to 300 °C for the systems ESO/DTBA (heating at 10 °C/min, under air).

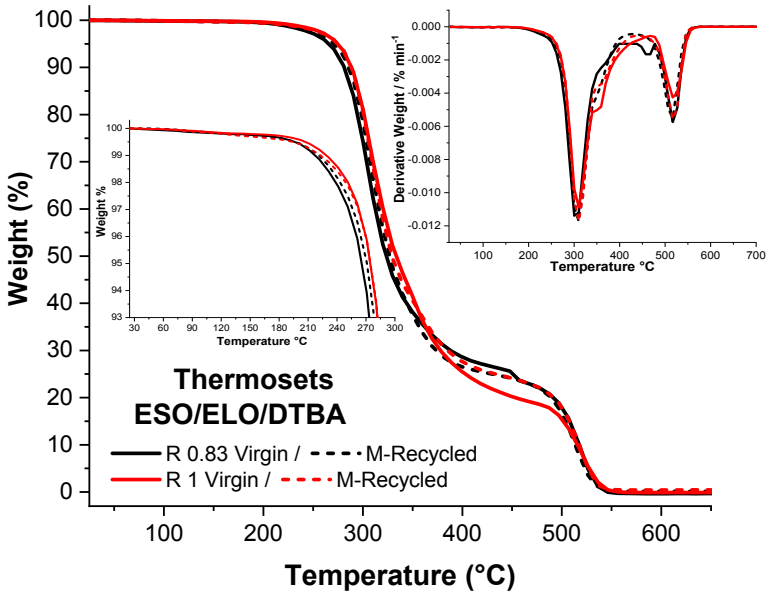

Figure S6. TGA, DTG and zoom in the region from 25 to 300 °C for the systems ESO/ELO/DTBA (heating at 10 °C/min, under air).

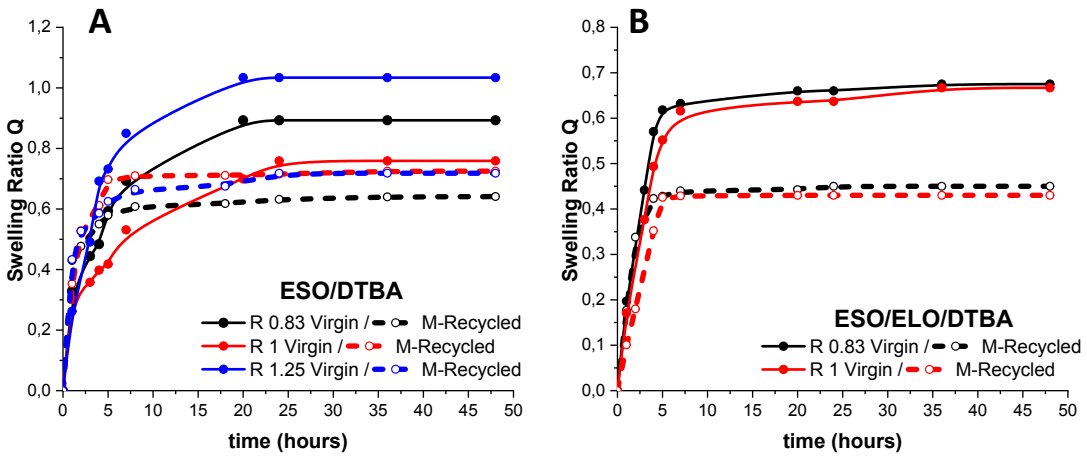

Figure S7.Swelling ratio Q for the virgin and recycled ESO/DTBA (A) and ESO/ELO/DTBA (B) thermoset resins.

Table S7. Solvent solubility in acetone and THF after 48 hours.

EVOs/DTBA	Ratio	Solubility % in acetone	Solubility % in THF
ELO/DTBA	0.83	0.70	0.095
	1	0.30	0.068
	1.25	0.15	0.057
	2	0.11	0.036
ESO/DTBA	0.83	0.87	0.12
	1	0.74	0.81
	1.25	0.55	0.055
ESO/ELO/DTBA	0.83	0.75	0.088
	1	0.51	0.064

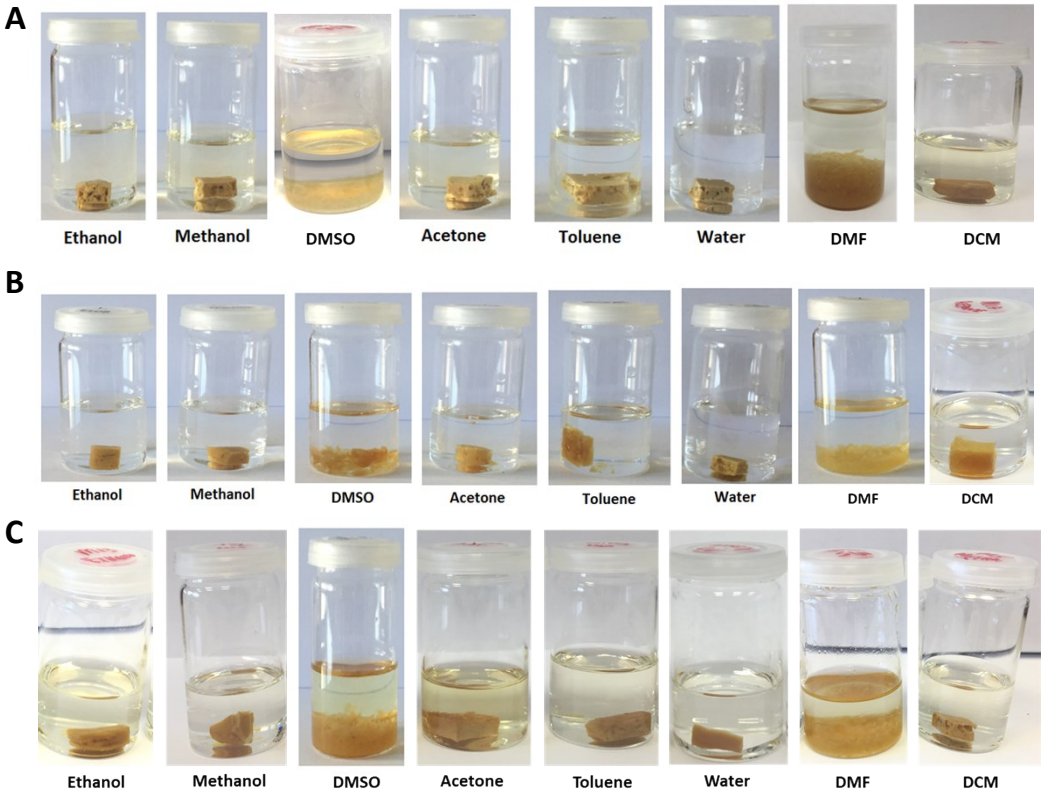

Figure S8. Solvent stability test after 48 hours at room temperature for ELO/DTBA R =0.83 (A), ESO/DTBA R =0.83 (B) and ESO/ELO/DTBA R =0.83.

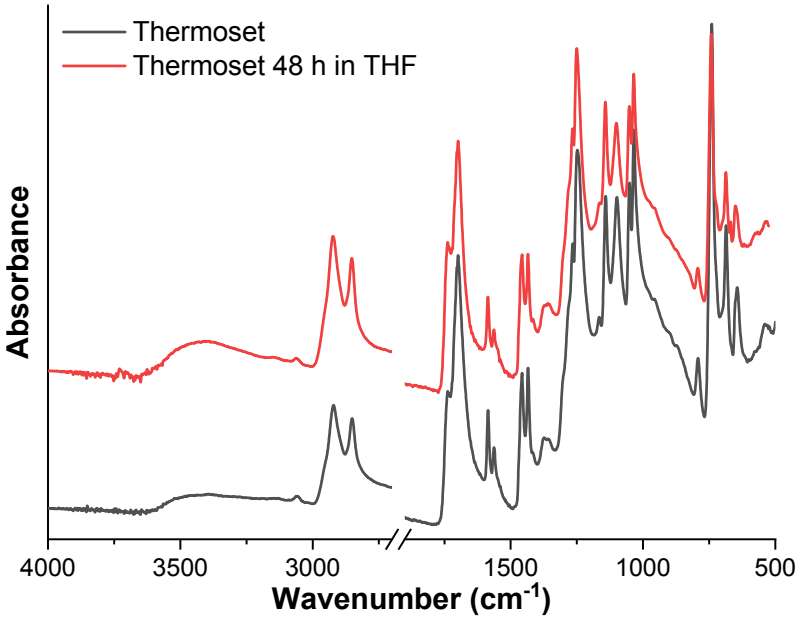

Figure S9. FT-IR of the crosslinked resin ELO/DTBA-IM R 0.83 before and after 48 hours in THF.

Table S8. TGA results for the ELO/DTBA recycled thermosets: mechanical (M) and chemical and mechanical recycling (C-M).

EVOs/DTBA	Ratio		$T_{5\%}$ (°C)	1st Residue (%)	1st Degradation peak (°C)	2nd Residue (%)	2nd Degradation peak (°C)
ELO	0.83	M-Recycled	271	23.1	310	0.23	517
		Recycled C-M	250	23.8	307	0.16	517
	1	M-Recycled	275	23.4	310	0.20	526
		Recycled C-M	265	28.3	308	0.13	513
	1.25	M-Recycled	281	22.0	310	0.35	526
		Recycled C-M	280	28.9	307	0.13	518
	2	M-Recycled	291	27.9	310	0.20	526
		Recycled C-M	290	20.9	310	0.09	520

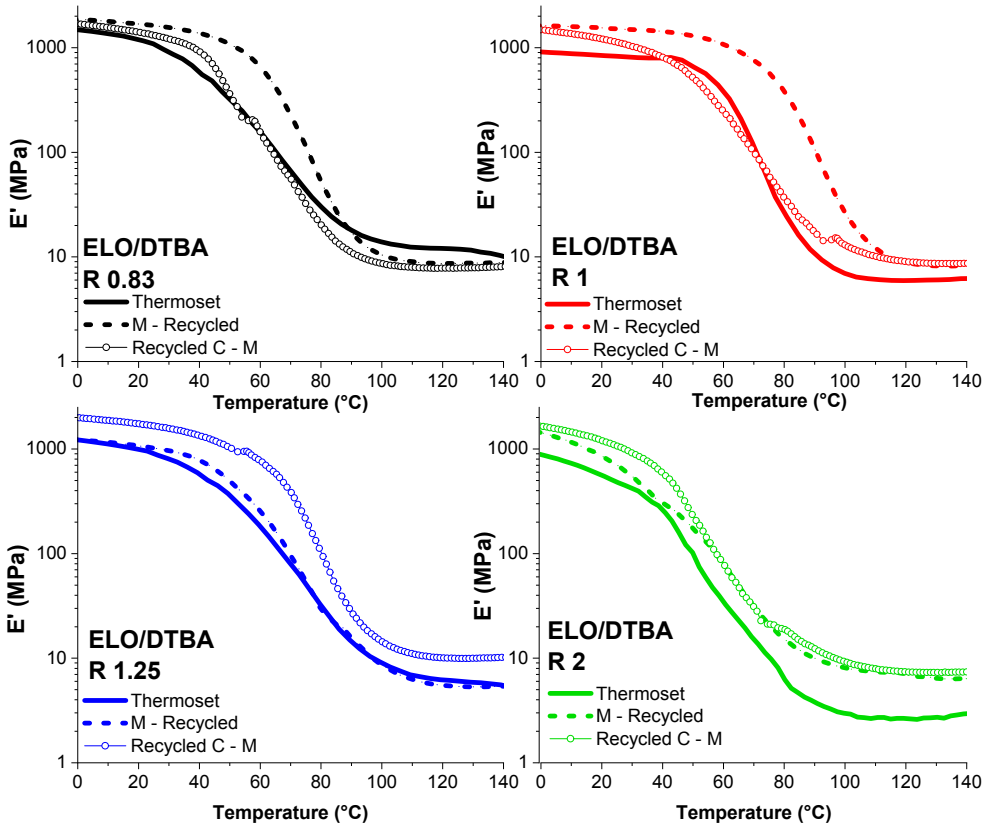

Figure S10. Storage modulus E' vs. temperature curves for virgin resin ELO/DTBA compared with the resin recycled mechanically (M) and chemically-mechanically (C-M).