Electronic Supplementary Information

High performant, recyclable and sustainable by design natural polyphenol-based epoxy polyester thermosets

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1. Characteristics of anhydrides

Table S1. Physico-chemical characteristics of the selected anhydrides

Anhydride	Molar mass (g/mol)	Density (g/cm^3)	Melting temperature (°C)
maleic anhydride (MA)	98.06	1.50	51-56
succinic anhydride (SA)	100.07	1.50	118-120
cis-1,2,3,6- tetrahydrophthalic anhydride (THPA)	152.15	1.22	98
phthalic anhydride (PA)	148.12	1.53	131-134
1,2,4-benzenetricarboxylic anhydride (TA)	192.13	1.54	163-166

2. DSC

➢ <u>variation of the TGPh/TGEN ratio :</u>

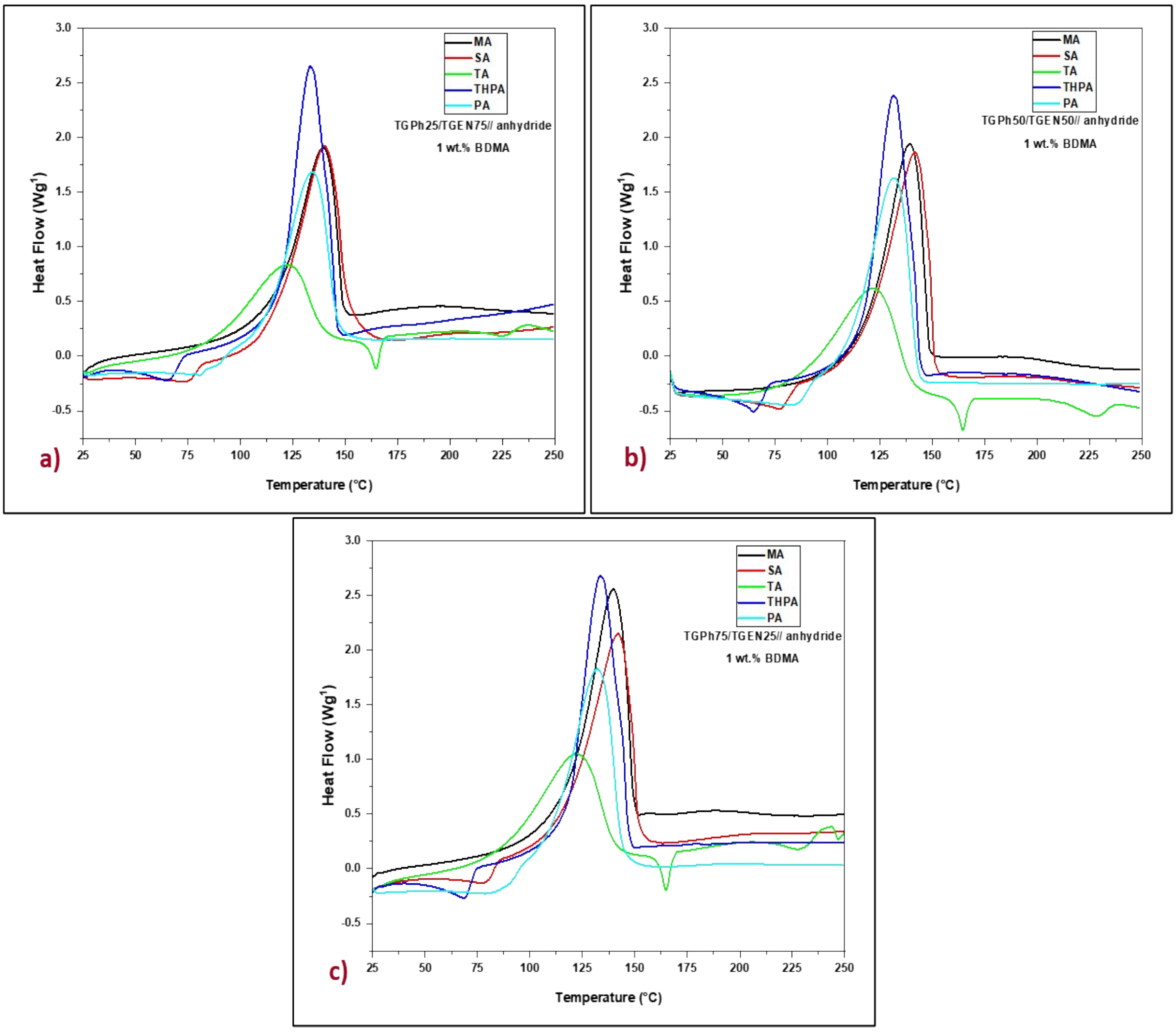


Fig. S1. DSC dynamic curves of the a) TGPh25/TGEN75//anhydride, b) TGPh50/TGEN50//anhydride and c) TGPh75/TGEN25//anhydride formulations during crosslinking initiated by 1 wt.% BDMA

Table S2. DSC data of TGPh/TGEN//anhydride crosslinking systems initiated by 1 wt.% BDMA

Hardener	Reaction T_{max} (interval) (°C) TGPh/TGEN ratios			Enthalpy of reaction ($J.g^{-1}$) TGPh/TGEN ratios		
	25-75	50-50	75-25	25-75	50-50	75-25
MA	139 (70-238)	**139 (69-235)**	140 (64-234)	244	317	**341**
SA	140 (74-175)	**142 (78-163)**	142 (78-166)	315	331	**333**
TA	122 (50-156)	**122 (52-155)**	122 (45-156)	167	215	**221**
THPA	134 (65-153)	**132 (65-151)**	134 (69-152)	335	360	**364**
PA	134 (86-233)	**132 (83-217)**	132 (80-221)	238	314	**318**

Table S3. Glass transition values obtained by DSC of TGPh/TGEN crosslinking systems initiated by 1 wt.% BDMA

Hardener	Glass transition (°C) TGPh/TGEN ratios		
	25-75	50-50	75-25
MA	170	**175**	173
SA	140	**141**	125
TA	200	**210**	197
THPA	140	**148**	135
PA	132	**138**	137

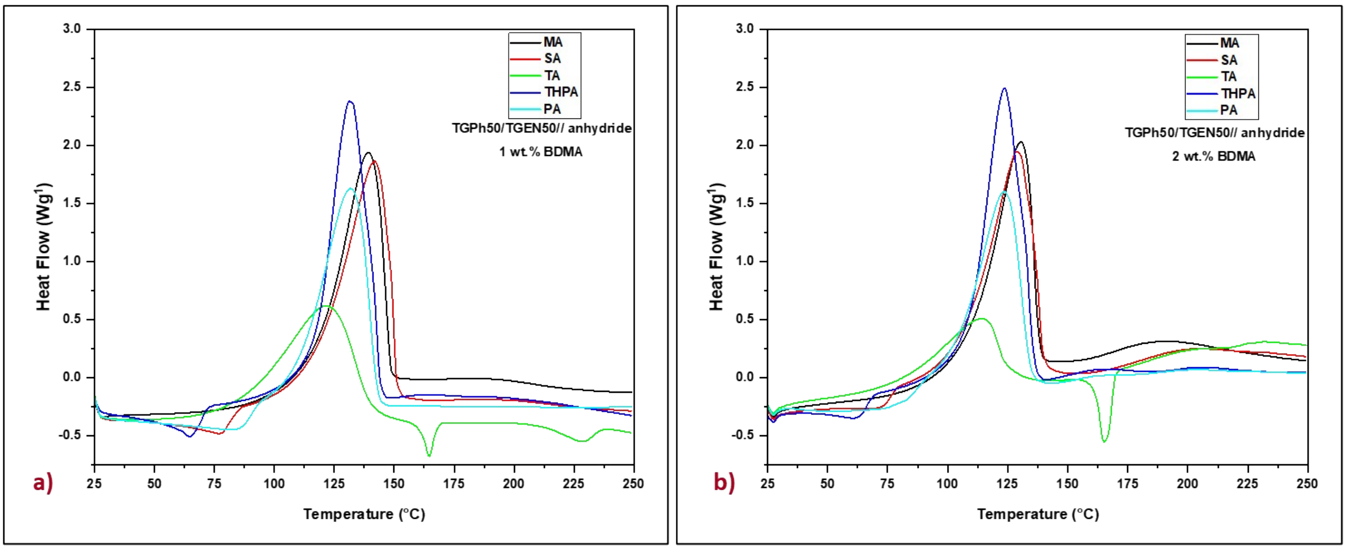


Fig. S2. DSC dynamic curves of TGPh50/TGEN50//anhydride crosslinking initiated by a) 1 wt.% BDMA and b) 2 wt.% BDMA

➢ <u>variation of the initiator percentage</u>

Table S4. Glass transition obtained by DSC for TGPh50/TGEN50//anhydride mixtures initiated by various percentage of BDMA

Hardener	Glass transition (°C) TGPh50/TGEN50		
	0.5% BDMA	**1% BDMA**	**2% BDMA**
MA	**180**	175	173
SA	**142**	141	118
TA	**199**	210	207
THPA	**134**	148	123
PA	**149**	138	149

➢ <u>comparison of mono-epoxy//anhydride formulations *vs.* TGPh50/TGEN50//anhydride mixture</u>

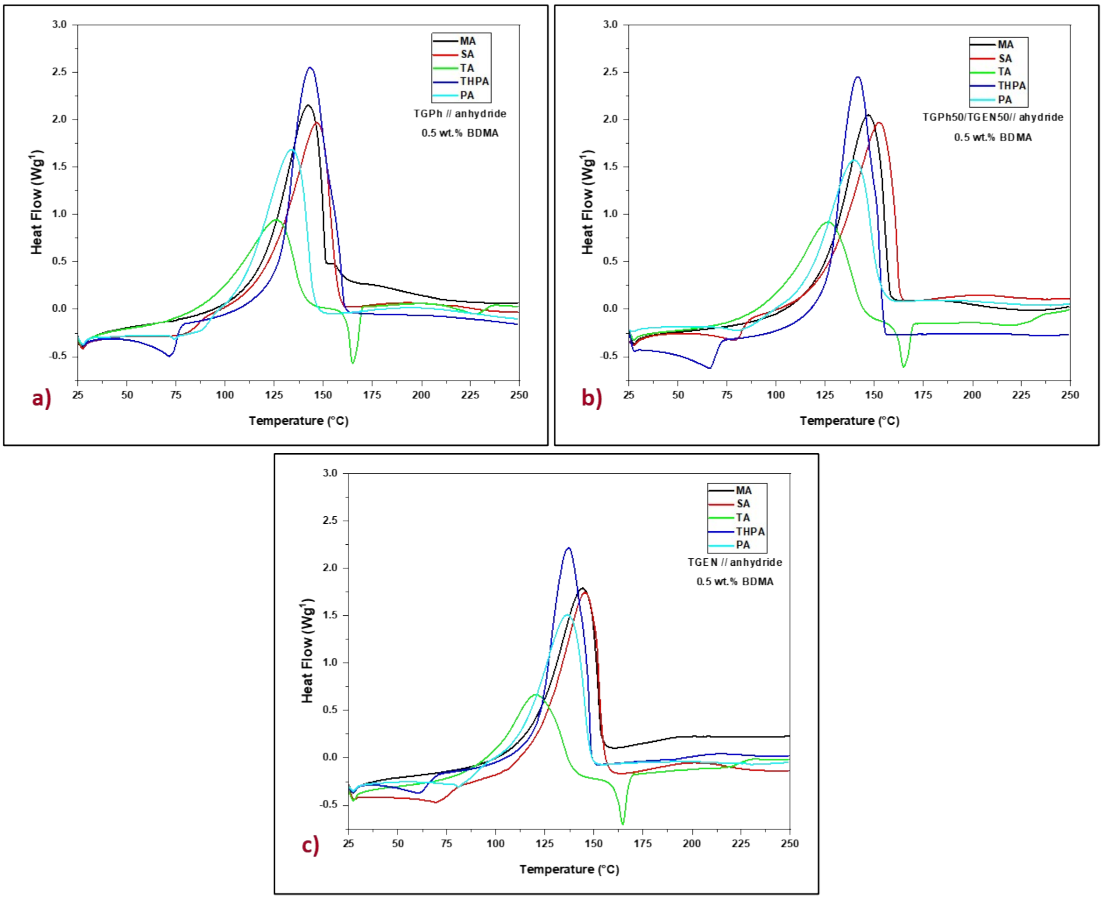


Fig. S3. DSC dynamic curves of the a) 100% TGPh, b) 50-50% TGPh-TGEN and c) 100% TGEN samples crosslinked with various anhydrides and initiated by 0.5 wt.% BDMA

Table S5. DSC data of crosslinking the individual epoxy monomers, and of the TGPh50/TGEN50//anhydride mixture initiated by 0.5 wt.% BDMA

Hardener	Reaction T_{max} (interval) (°C)			Enthalpy of reaction ($J.g^{-1}$)		
	TGPh	50/50 TGPh/TGEN	TGEN	TGPh	50/50 TGPh/TGEN	TGEN
MA	142 (60-230)	147 (60-228)	144 (66-242)	365	**392**	280
SA	147 (75-245)	153 (80-233)	146 (69-238)	392	**487**	370
TA	126 (58-151)	126 (46-158)	120 (56-150)	165	**238**	150
THPA	143 (72-168)	142 (66-162)	137 (61-240)	397	**428**	377
PA	134 (80-240)	140 (81-236)	137 (80-240)	346	**352**	335

Table S6. Glass transition values obtained by DSC for TGPh//anhydride, TGEN//anhydride and TGPh50/TGEN50//anhydride materials (crosslinked with 0.5 wt.% BDMA)

Hardener	Glass transition (°C)		
	TGPh	50/50 TGPh/TGEN	TGEN
MA	128	**180**	190
SA	84	**142**	109
TA	-	**199**	165
THPA	126	**134**	107
PA	123	**149**	143

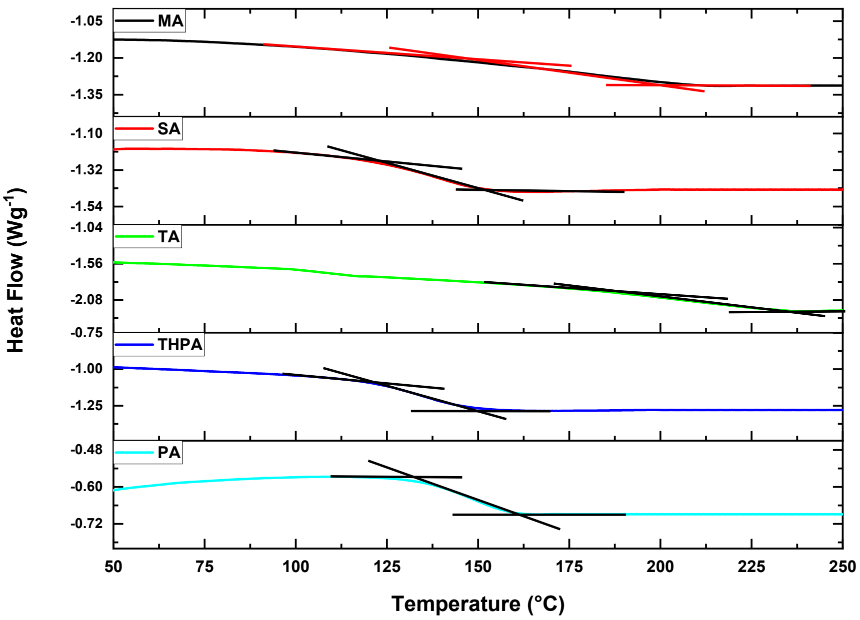


Fig. S4. DSC thermograms showing the glass transitions of TGPh50/TGEN50//anhydride thermosets

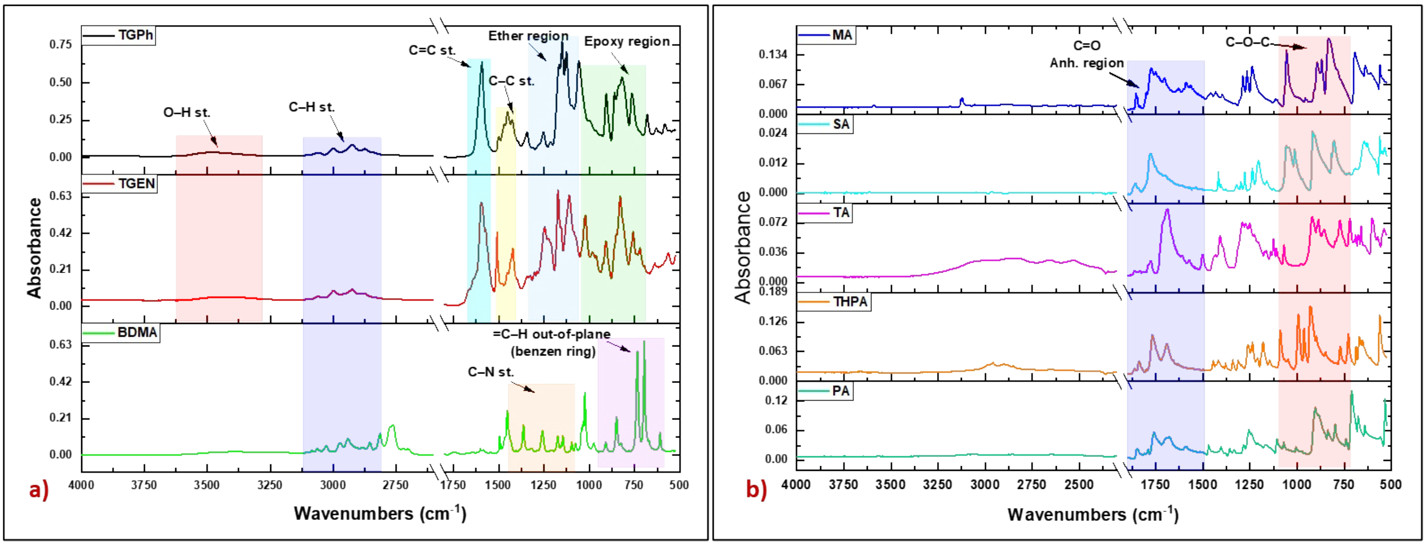


Fig. S5. FT-IR spectra of the raw compounds: a) TGPh, TGEN and BDMA, and b) MA, SA, TA, THPA and PA

3. FT-IR spectroscopy

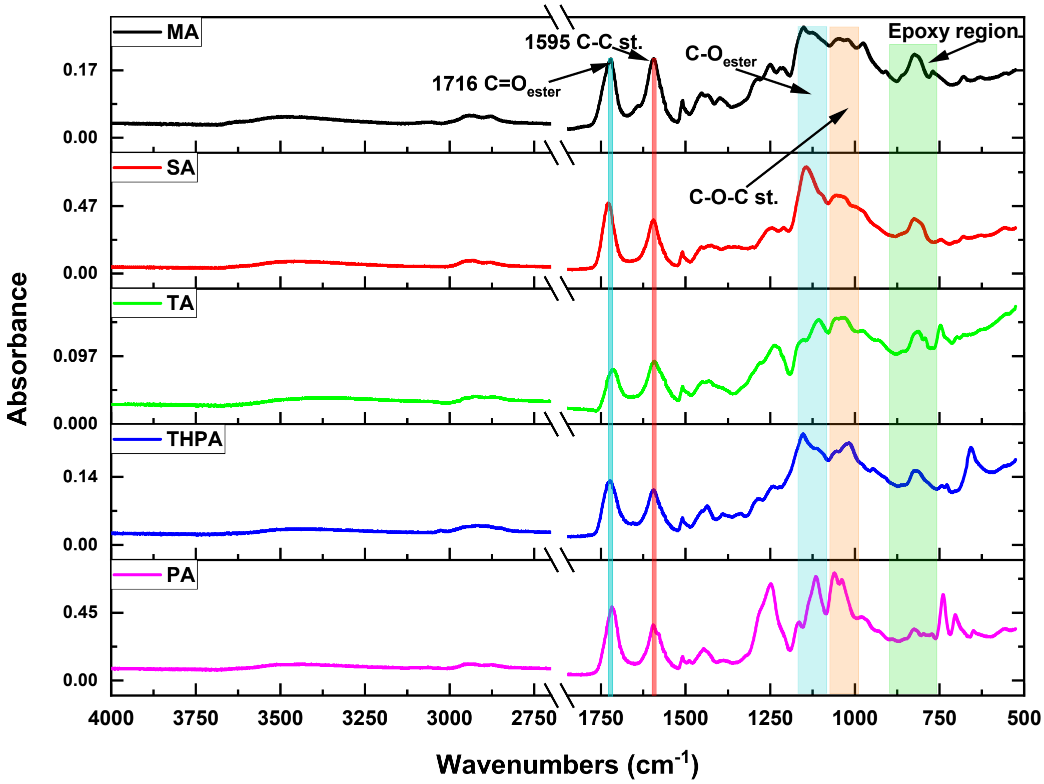


Fig. S6. FT-IR spectra of TGPh50/TGEN50 mixture crosslinked with indicated anhydride

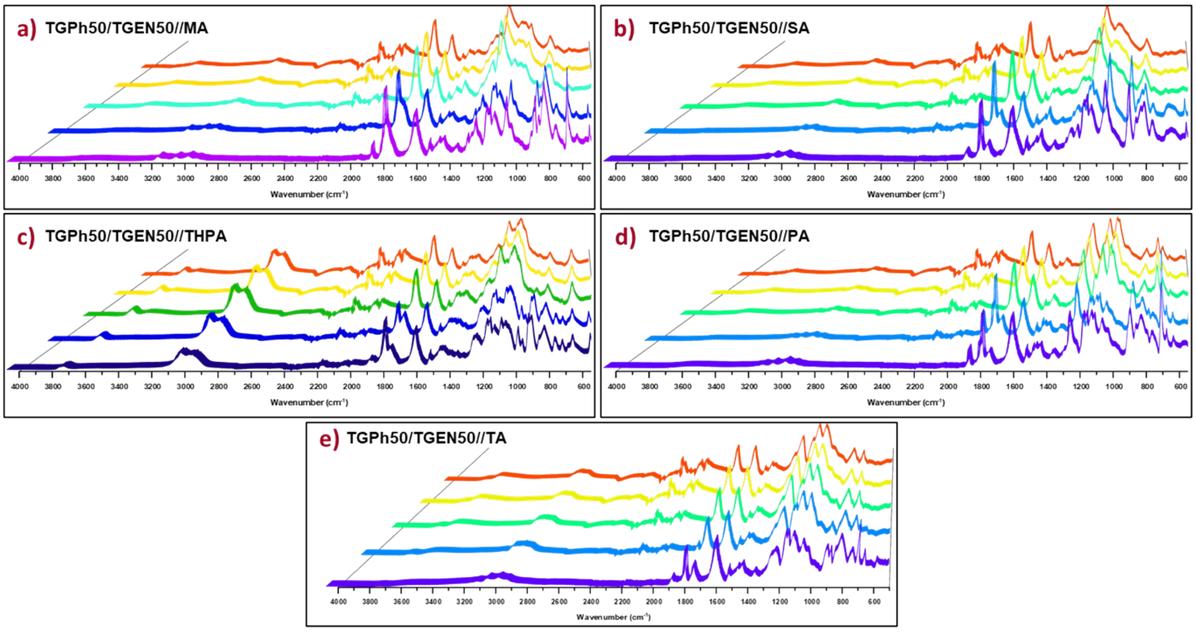


Fig. S7. Temperature-dependent FT-IR spectra during dynamic curing of a) TGPh50/TGEN50//MA, b) TGPh50/TGEN50//SA, c) TGPh50/TGEN50//THPA, d) TGPh50/TGEN50//PA and e) TGPh50/TGEN50//TA systems

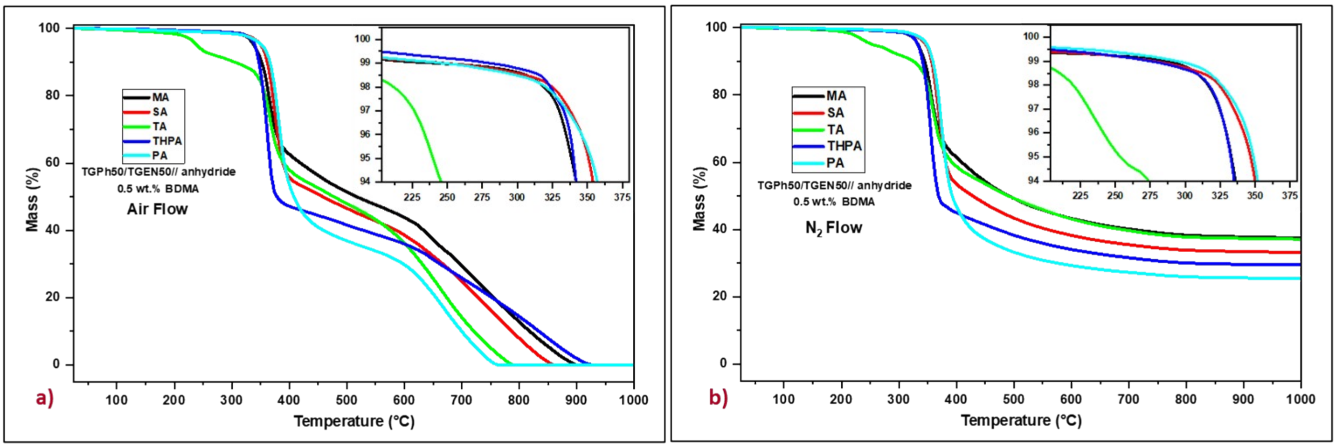


Fig. S8. Thermogravimetric curves of the epoxy/anhydride systems in a) air flow, and b) N_2 flow, at 10 °C/min

4. TGA

Table S7. TGA results obtained for the designed bio-based epoxy/anhydride thermosets

Thermosets	$T_{1\%}$ (°C)		$T_{5\%}$ (°C)		$T_{30\%}$ (°C)		T_{dmax} (°C)		T_s		Cy_{850} (%)		LOI (%)	
	Air	N_2	Air	N_2	Air	N_2	Air	N_2	Air	N_2	Air	N_2	Air	N_2
TGPh50/TGEN50// MA	241	281	335	335	375	370	369	357	176	175	5.3	38	N/A	32.7
TGPh50/TGEN50// SA	241	271	355	340	380	375	379	369	181	177	0.7	33.6	N/A	30.9
TGPh50/TGEN50// TA	300	192	335	351	370	365	369	360	174	176	0	37.5	N/A	32.5
TGPh50/TGEN50// THPA	275	271	345	335	360	355	359	350	174	170	7.8	29.8	N/A	29.4
TGPh50/TGEN50// PA	245	291	355	340	385	375	379	370	183	177	0	25.7	N/A	27.8

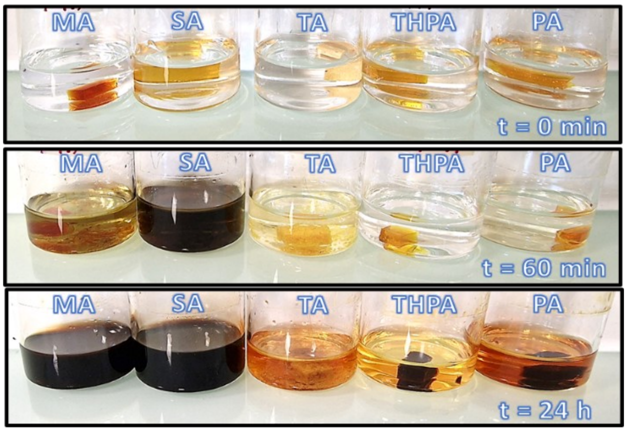
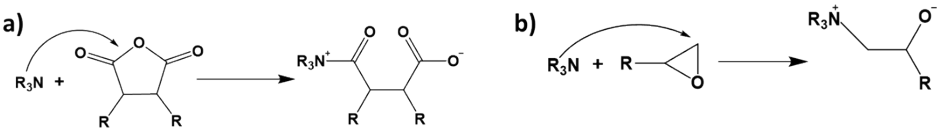


Fig. S9. Physical appearance of the thermosets transesterification when immersed in EG at 170 °C

7. Chemical recycling

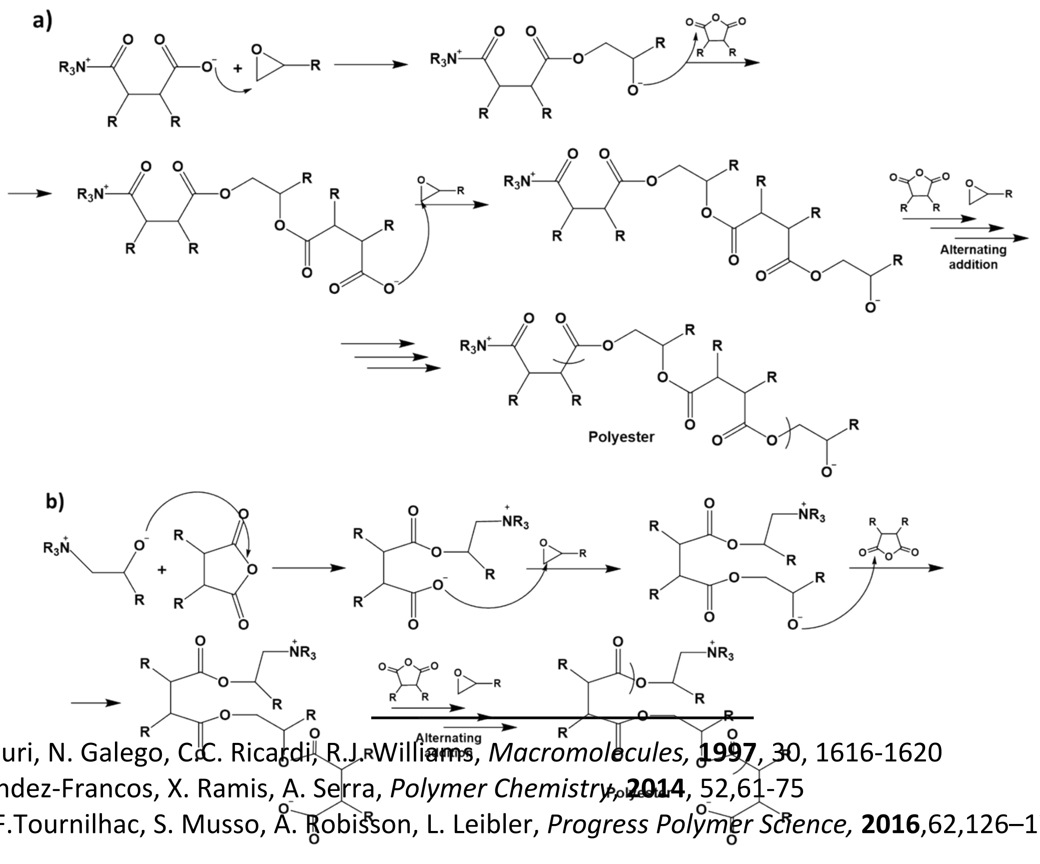
Epoxy-anhydride mechanism of curing in presence of tertiary amine initiator[1],[2],[3]



A) Chain-wise alternant anionic copolymerization

I/ Initiation step : nucleophilic attack of tertiary amine on cyclic anhydride (a) or on oxirane ring (b)

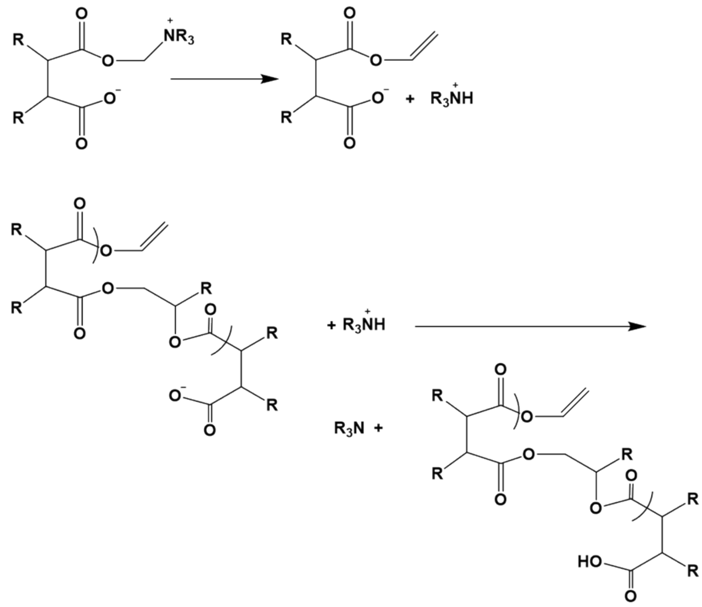
II/ Propagation

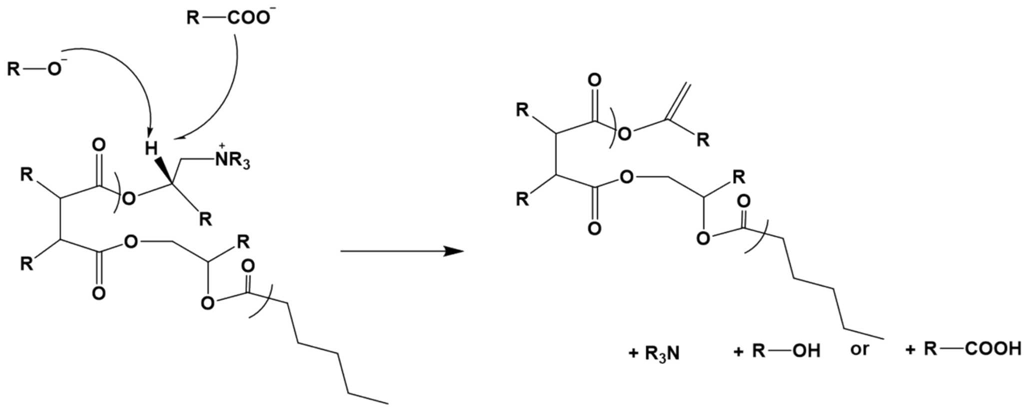


[1] A. N. Mauri, N. Galego, C.C. Ricardi, R.J. Williams, *Macromolecules,* **1997**, 30, 1616-1620
[2] X. Fernandez-Francos, X. Ramis, A. Serra, *Polymer Chemistry*, **2014**, 52,61-75
[3] T. Vidil, F.Tournilhac, S. Musso, A. Robisson, L. Leibler, *Progress Polymer Science,* **2016**,62,126–179

III/ Initiator regeneration and termination of chain-wise anionic polymerization

- by unimolecular elimination followed by transfer proton:

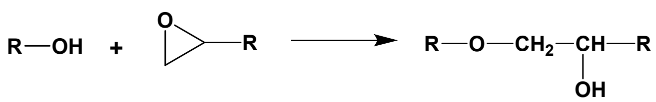




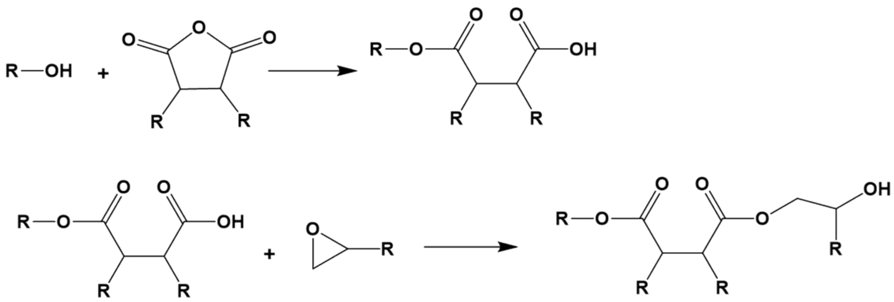
- by attack of carboxylate or alkoxide anions with hydrogen abstract

B) Step growth polymerizations:

- polyetherification : reaction of hydroxyl groups with epoxy groups



- polyesterification : reaction of hydroxyl groups with anhydrides



Scheme S1. A) Chain-wise anionic alternant epoxy-anhydride copolymerization; B) Step growth epoxy-anhydride polyaddition