Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Limonene dioxide as building blocks for 100% bio-based thermosets

Alice Mija,*[a] Elodie Louisy,[a] Sara Lachegur,[a] Veronika Khodyrieva,[a] Philippe Martinaux,[a] Sandra Olivero [a] and Veronique Michelet*[a]

[a] *Université Côte d'Azur, Institut de Chimie de Nice, UMR 7272 CNRS 06108 Nice, France.*

**Corresponding authors:*

Veronique Michelet. Tel: +330489150150 ; e-mail address: veronique.michelet@univ-cotedazur.fr

Alice Mija. E-mail address: alice.mija@univ-cotedazur.fr

Experimental

Materials

(R)-(+)-limonene was provided by Mane SA under the name "Orange terpenes". Oxone® monosulfate compound, sodium hydrogenocarbonate, dichloromethane, diethylether, acetone (Acet), methanol (MeOH), ethanol (EtOH), Toluene (Tol), THF, dichloromethane (DCM), imidazole, glycerol, glutaric anhydride (GA), 2,2-dimethylglutaric anhydride (DGA), maleic anhydride (MA), phtalic anhydride (PhtA), pyromellitic dianhydride (PyDA), itaconic anhydride (IA) and succinic anhydride (SA) were purchased from Sigma-Aldrich and used as such.

Synthesis of limonene dioxide

(R)-(+)-Limonene (5 g, 36.7 mmol), sodium hydrogenocarbonate (16 g) and acetone (120 mL) were added to a round-bottom flask. A homogeneous solution of Oxone® (32 g, 104 mmol dissolved in 200 mL of distilled water) was added to the flask using a dropping funnel with a flow rate of 1 mL.min^{-1}. After the total adding of the Oxone solution the medium was left 2 hours under stirring. The reaction mixture was separated by liquid-liquid extraction using diethyl ether. The combined organic layers were dried over anhydrous magnesium sulfate and filtered then evaporated to give the crude dioxide which was used as such. The reaction products were monitored by ^{1}H NMR.

Sample preparation for polymerization

The limonene dioxide monomers were mixed with the selected nucleophilic molecules (glycerol, glutaric anhydride, 2,2-dimethylglutaric anhydride, maleic anhydride, phtalic anhydride, pyromellitic dianhydride, itaconic anhydride and succinic anhydride) with or without imidazole as catalyst. Various catalyst amounts were studied from 0 to 5 wt.% and different epoxide/hardener ratios, from 1/0.5 to 1/3. All the hardeners except for glycerol are solid powders at room temperature whereas limonene dioxide is viscous pale-yellow oil. The hardener and the catalyst were weighed first then the epoxide was added to reach the desired epoxide/hardener ratio. Samples were stirred at room temperature to obtain a homogeneous mixture. When needed, mild heating was applied (30 to 50 °C) to homogenize the hardener dispersion. The freshly prepared mixtures were submitted to the analysis of reactivity by DSC analysis. To produce samples, for the analysis of thermosets thermomechanical properties, the reactive mixtures were poured into molds and cured in oven at a heating program determined by DSC.

Experimental techniques

Nuclear magnetic resonance spectroscopy. ^{1}H NMR spectra were recorded in deuterated chloroform $CDCl_3$ at 300 or 400 MHz using a Brüker AVANCE instrument. Chemical shifts are reported in ppm relative to $CDCl_3$ [signals for residual $CHCl_3$ in the $CDCl_3$: 7.26 for ^{1}H NMR].

Fourier-transformed infrared spectroscopy (FT-IR). FTIR analyses were performed using a Thermo Scientific Nicolet iS50 FTIR Spectrometer equipped with OMNIC FTIR software. The number of scans was chosen to be 32 and the resolution 2.

Gas chromatography with Flame-Ionization Detection (GC-FID). GC-FID analyses were performed using a Shimadzu GC-2025 instrument with a ZB-5-MS column (30 m x 0.25 mm x 0.25 µm). Samples were heated from 60 to 250 °C at a rate of 10 °C/min. When needed, GC-MS analyses were performed using a Shimadzu GC-2010 with a ZB-5MS column (20 m x 0.18 mm x 0.18 µm) and a GCMS-QP2010S detector (electron impact at 200 °C). Samples were heated from 60 °C to 315 °C at a rate of 10 °C/min.

Differential Scanning Calorimetry (DSC). Differential scanning calorimetry was firstly used to study the thermal induced copolymerization. Uncured thermosetting resins formulations were analyzed using a Mettler-Toledo DSC 3 apparatus equipped with STARe Software. For each formulation, samples of 5–10 mg were reacted under non-isothermal condition in 40 µL aluminum pans. The thermal aspects of the resins crosslinking were analyzed in the temperature range between 25–210 °C, at a heating rate of 10 °C min^{-1}. The reversible transitions of amorphous materials from a molten or rubber state to a hard and relatively fragile state, called the glass transitions (Tg), have also been studied by DSC. Samples of 5-10 mg of cured materials were analyzed applying heating/ cooling cycles from -50 °C to 150 °C at 10 °C min^{-1} heating rate.

Thermogravimetric analysis (TGA). A TGA 2 Mettler-Toledo device was used to analyze the thermal degradation, mass loss and the derivative mass loss as function of temperature. Samples of 10–15 mg were tested in 70 µl aluminum crucibles, using a 10 °C min^{-1} dynamic heating from 25 to 1000 °C. The thermal stability of the materials was analyzed in oxidative (air) atmospheres at a debit of 50 $mL.min^{-1}$. The materials degradation temperature was considered as the temperature at which the samples lose 5% of its mass, $T_{5\%.}$

Swelling tests. The swelling behavior of cured sample was studied in methanol, ethanol, acetone, toluene, THF, dichloromethane and solution of 1 M HCl to confirm the complete crosslinking and to evaluate the samples resistance in these solvents. The dry sample (weight w_0) was immersed in solvents at room temperature for 48 h. The weight of swollen sample (w_1) was measured after wiping the surface with a filter paper. The swelling ratio (S) was calculated as follows:

$$S = 100 \times (w_1 - w_0)/w_0$$

Shore hardness tests. A Zwick Roell 3116 hardness tester was used for determining the hardness according to ISO 7619-1, ASTM D2240 and ISO 868. The Shore D hardness tester was released smoothly with a load force of 50 N ± 0.5 N until the presser foot was firmly seated on the specimens. To avoid errors, three samples of resin formulation were tested, and three measurements were performed for each sample.

Tensile tests. The tensile tests were performed with an Instron 3400 equipment with a 5 kN cell. These tests (5 samples per system) were performed at room temperature, with a crosshead speed of 10 mm.min^{-1} to access the Young's modulus, the stress at break and the strain at break of the polymer.

Dynamic Mechanical Analysis (DMA). DMA analyses were carried out on a Mettler Toledo DMA 1 instrument, equipped with STAR© software for curve analysis. The analyzed samples were prepared according to the curing protocol and had rectangular dimensions of 30 × 7 × 2 mm^3 (length × width × thickness). Elastic modulus values (E′) and damping factors (tan δ) were collected at 3 °C·min^{-1} heating rate from −50 to 170 °C and 1.0 Hz frequency. The DMA was operated using the tension method. The glass transition was assigned at the maximum of the damping factor (tan δ = E″/E′). The cross-linking density of EVO thermosets was calculated using eq 3, according to Flory theory of the rubber elasticity:

$$\nu = E'/3RT$$

where E′ is the storage modulus in the rubbery plateau region at Tg +50 °C, R is the gas constant, and T is the absolute temperature in Kelvin.

Results and discussions

1.Epoxidation of R-limonene to limonene dioxide

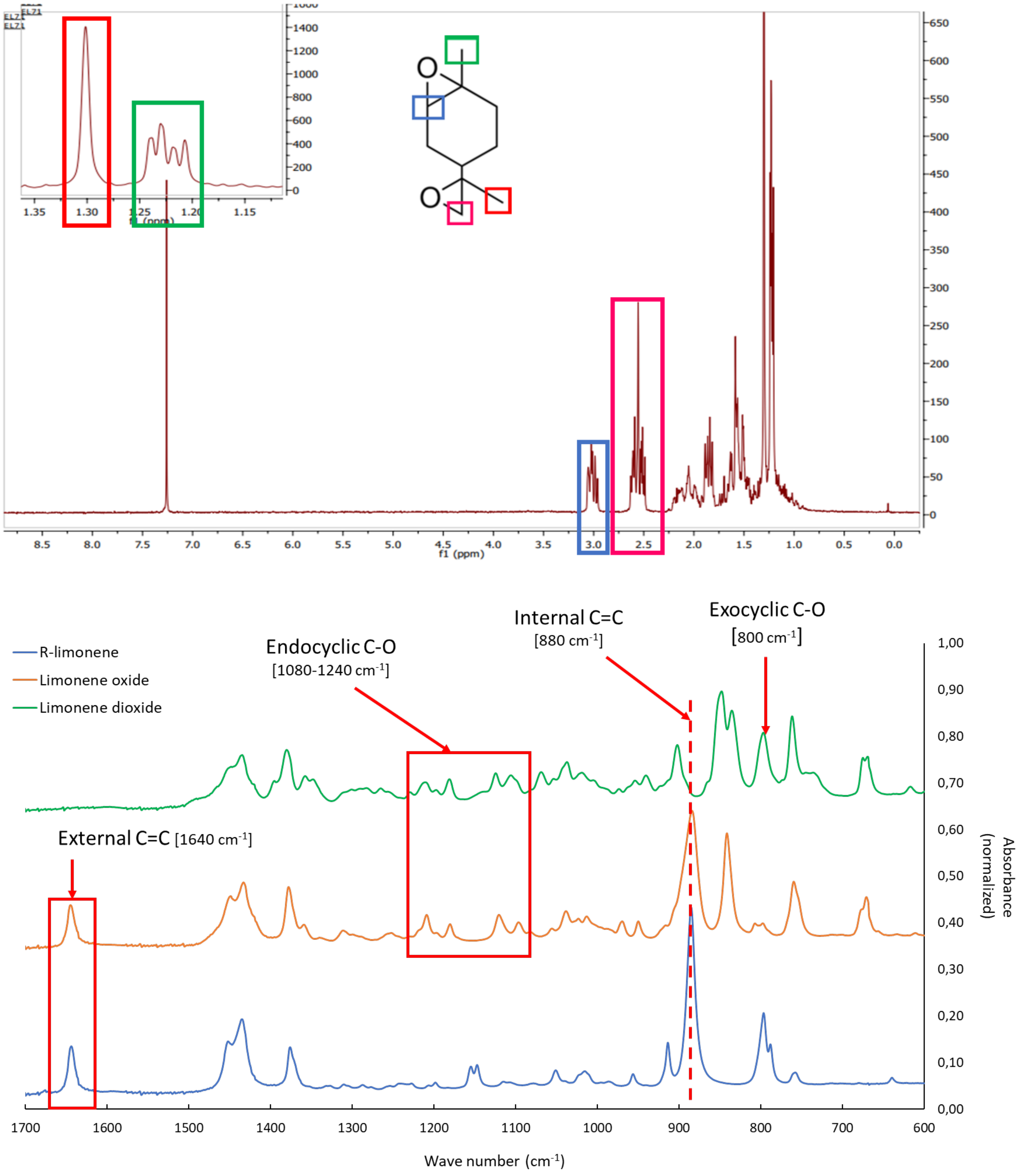
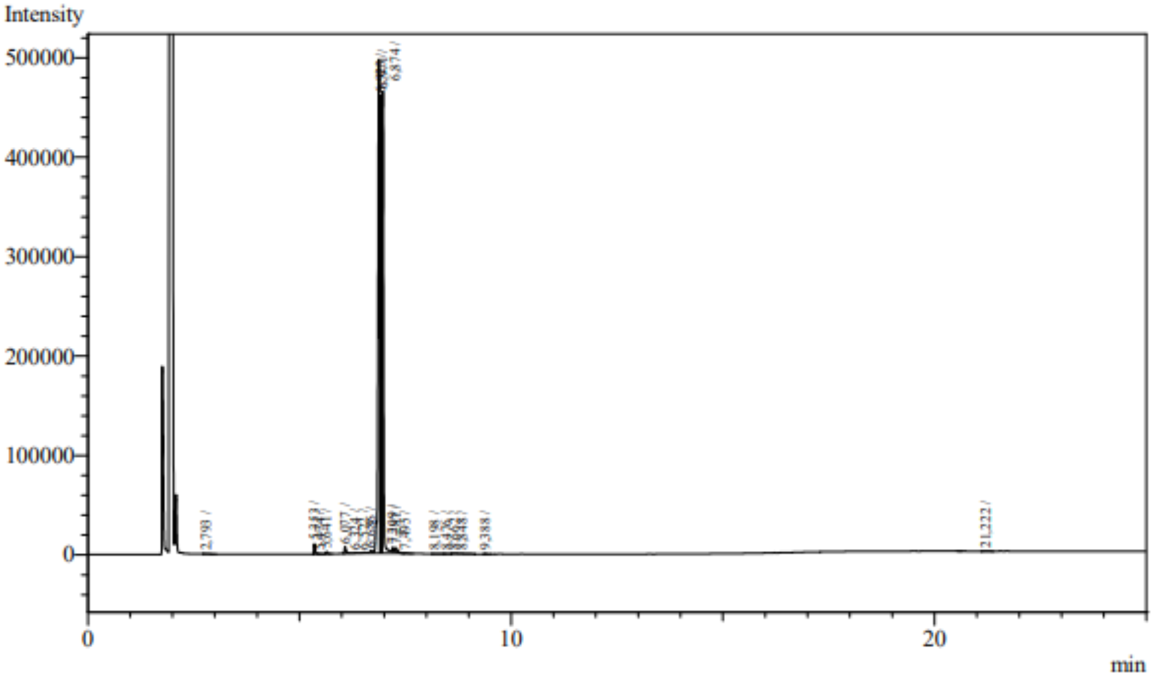


Figure S1. ^{1}H NMR (up) and FTIR (down) of synthesized limonene dioxide



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name	Area%
1	2,793	1659	284	0,052					0,0517
2	5,353	24623	10500	0,767					0,7670
3	5,474	3055	727	0,095		V			0,0952
4	5,641	6561	2482	0,204		V			0,2044
5	6,077	17474	7005	0,544					0,5443
6	6,324	3116	456	0,097					0,0971
7	6,522	4548	867	0,142		V			0,1417
8	6,686	11958	2770	0,372		V			0,3725
9	6,874	1256135	491687	39,128		V			39,1282
10	6,923	908796	457386	28,309		V			28,3087
11	6,971	928939	459485	28,936		SV			28,9362
12	7,209	10917	4300	0,340		T			0,3401
13	7,281	14003	4146	0,436		TV			0,4362
14	7,495	1883	388	0,059					0,0587
15	8,198	1523	177	0,047					0,0475
16	8,476	1061	178	0,033					0,0331
17	8,662	9187	903	0,286		V			0,2862
18	8,848	2301	373	0,072		V			0,0717
19	9,388	1088	440	0,034					0,0339
20	21,222	1474	199	0,046					0,0459
Total		3210301	1444753						100,0000

Figure S2. GC-FID of synthesized limonene dioxide

2.Polymerization of limonene epoxides - DSC Study

2.1. Influence of the catalyst amount on the polymerization

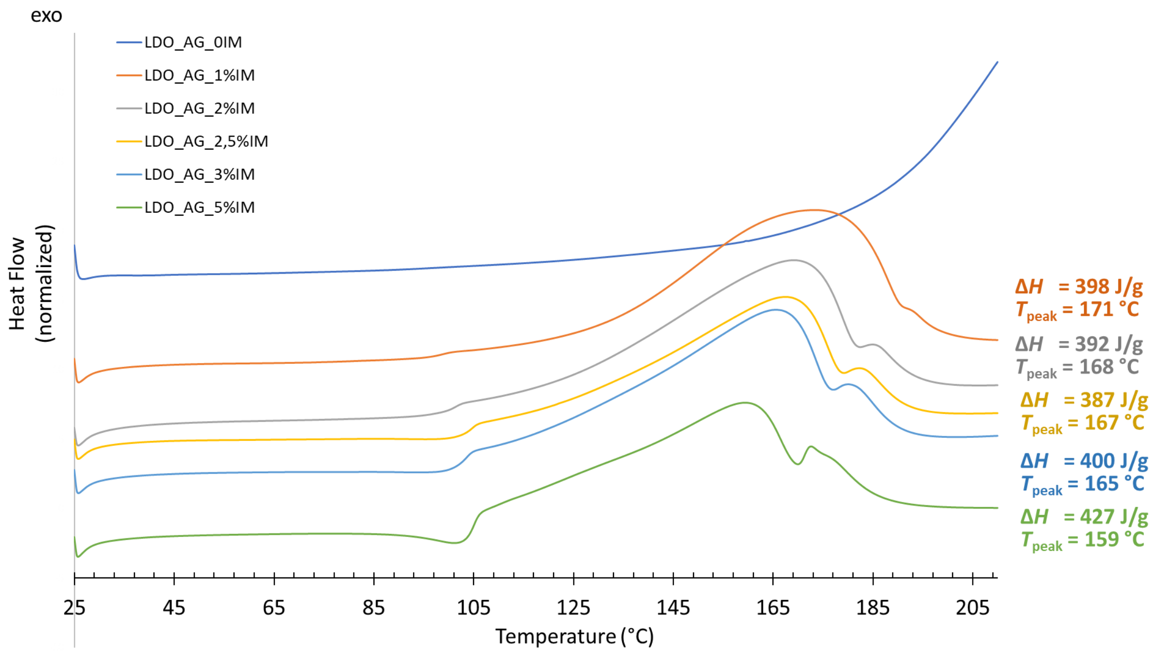


Figure S3. DSC thermograms of the polymerization reactivity regarding the amount of catalyst. Heating program: 25 to 210 °C, at a heating rate of 10 °C.min^{-1}

Table S1. Influence of initiator amount in LDO/GA copolymerization

	LDO				
Imidazole (wt.%)	T_{start} (°C)	T_{Peak} (°C)	ΔH (J.g^{-1})	T_{end} (°C)	Tg (°C)
1	92	172	398	210	59
2	94	168	392	206	50
2.5	94	167	387	203	98
3	94	164	400	202	64
5	104	159	427	204	79

2.2. Influence of the hardener equivalent on the polymerization

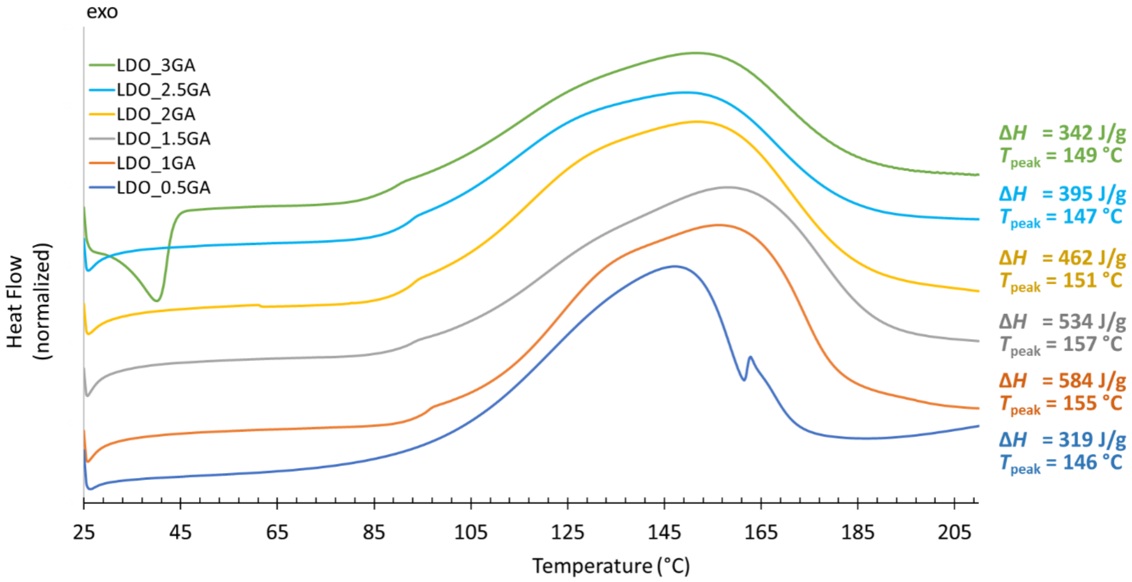
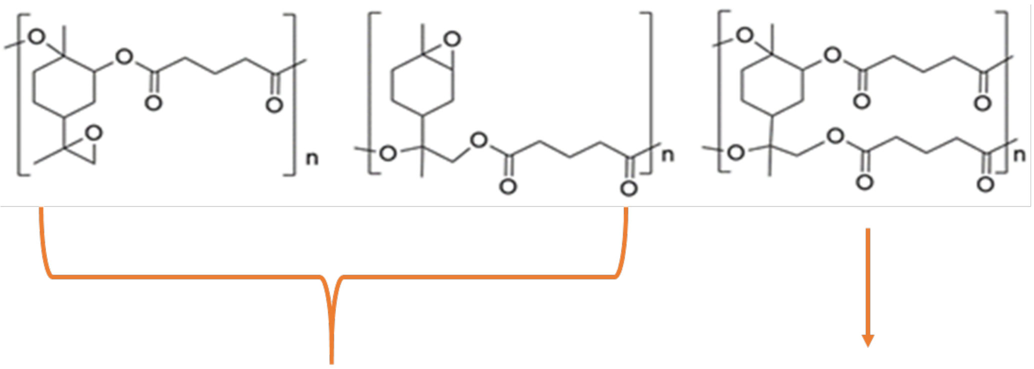


Figure S4. DSC thermograms of the polymerization reactivity regarding LDO/GA system. Heating program: 25 to 210 °C, at a heating rate of 10 °C.min^{-1}

Table S2. Influence of the hardener amount in LDO polymerization

	LDO				
GA equivalent	T_{start} (°C)	T_{Peak} (°C)	ΔH (J.g^{-1})	T_{end} (°C)	Tg (°C)
0.5	72	146	319	185	39
1	82	155	584	202	98
1.5	79	157	534	202	54
2	77	151	462	200	20
2.5	76	147	395	200	6
3	76	149	342	200	-4



Functionnality : non stoechiometric
Molar : Stoechiometric

Functionnality : stoechiometric
Molar : LDO/A = 1:2

Scheme S1. Potential structures of LDO/ GA polymers

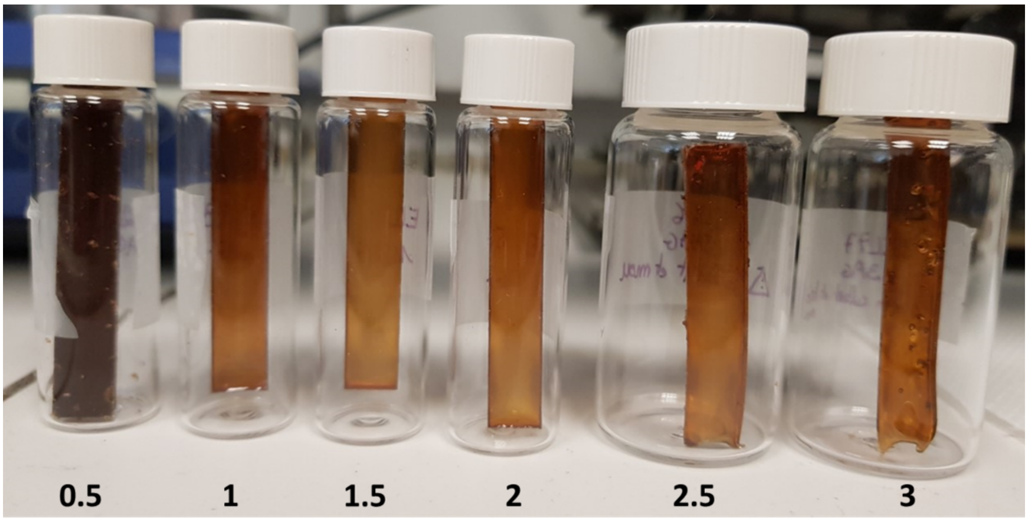


Figure S5. Aspects of polymers obtained with different GA ratios

3.Thermoset resins characterization

3.1 Glass Transition Temperatures (T_g)

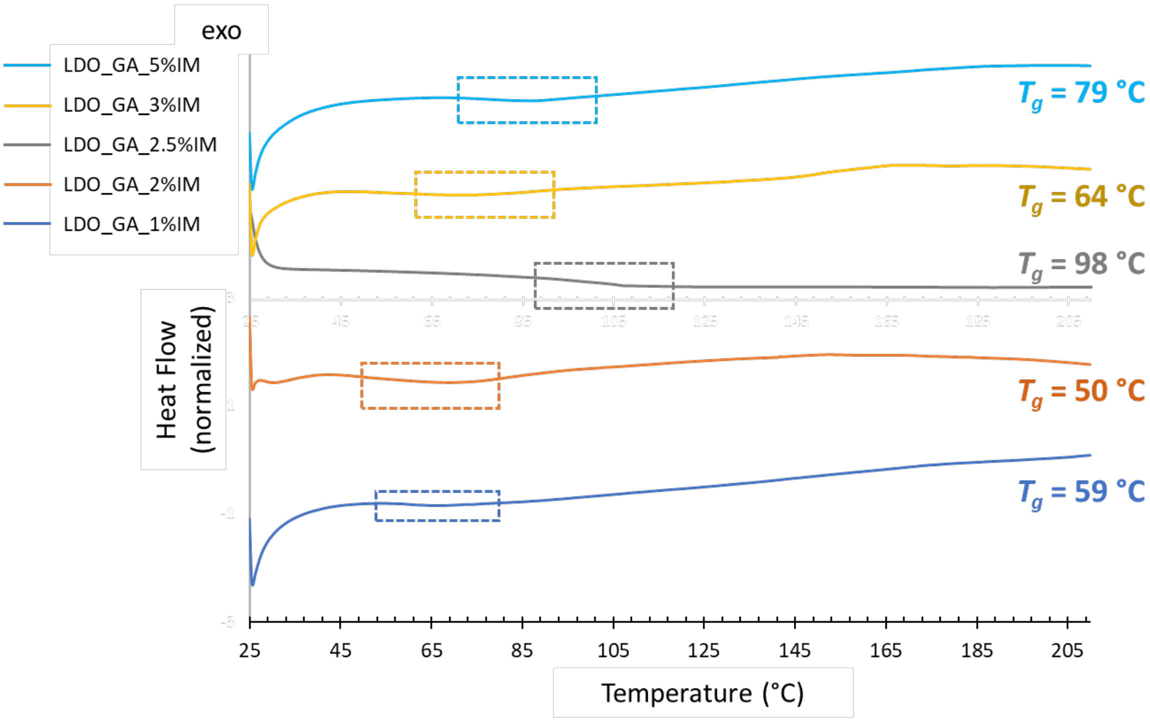


Figure S6. DSC thermograms of LDO/GA polymers (1:1) with different amount of initiator; Heating program: from 25 °C to 210 °C; heating rate: 10 °C.min^{-1}

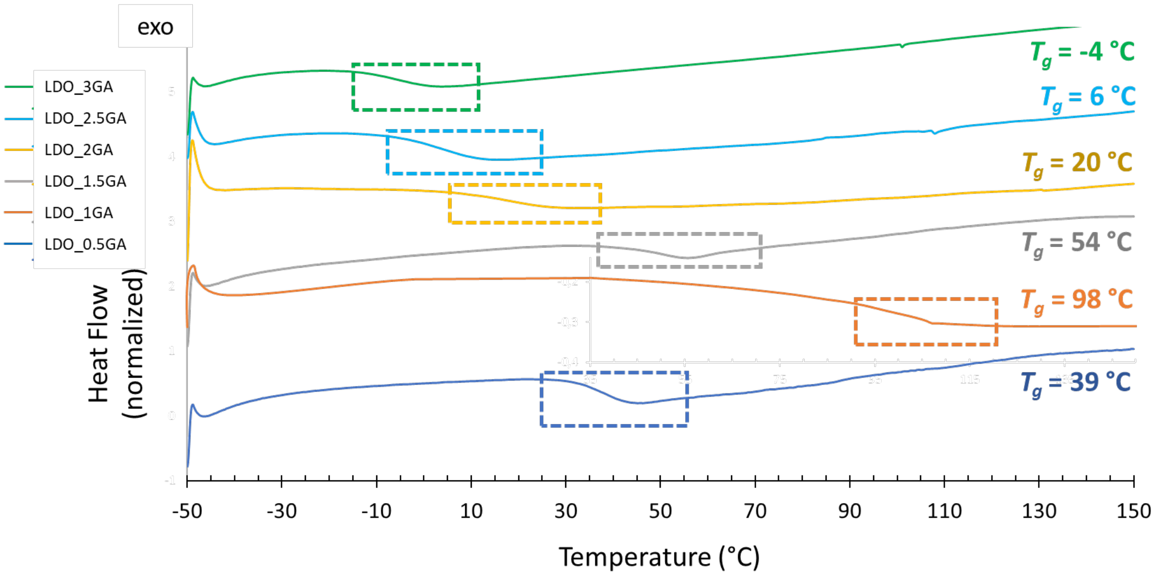


Figure S7. DSC thermograms of LDO/GA polymers (1:0.5-3; 2.5 wt% imidazole); Heating program: from -50 °C to 150 °C; heating rate: 10 °C.min^{-1}

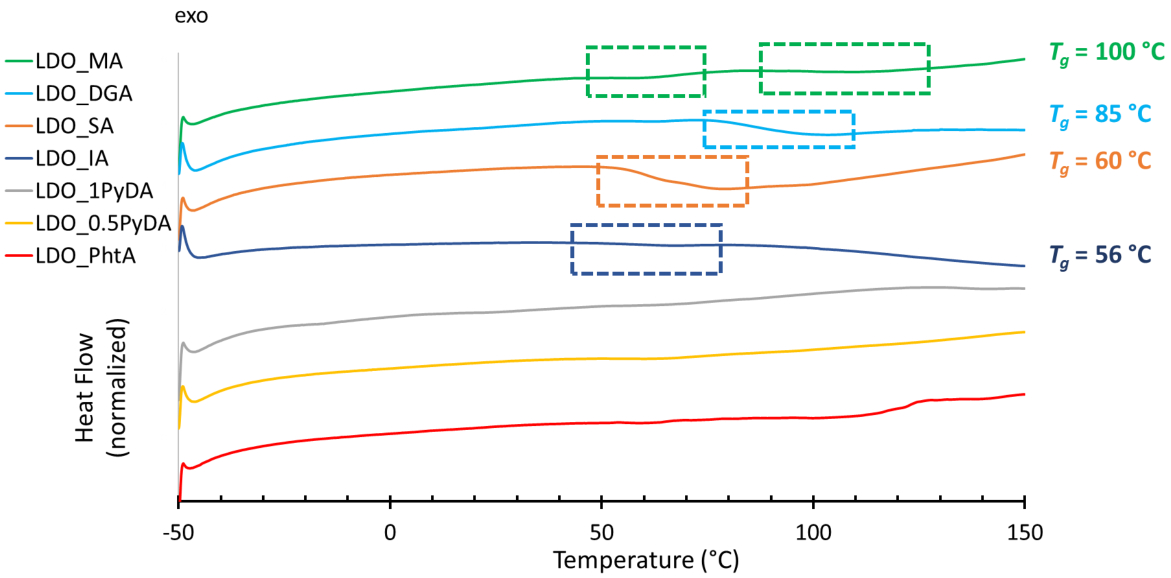


Figure S8. DSC thermograms of all LDO/anhydrides polymers (1:1; 2.5 wt% imidazole); Heating program: from -50 °C to 150 °C; heating rate: 10 °C.min^{-1}

3.2 Thermal stability studies by TGA and DTG analysis

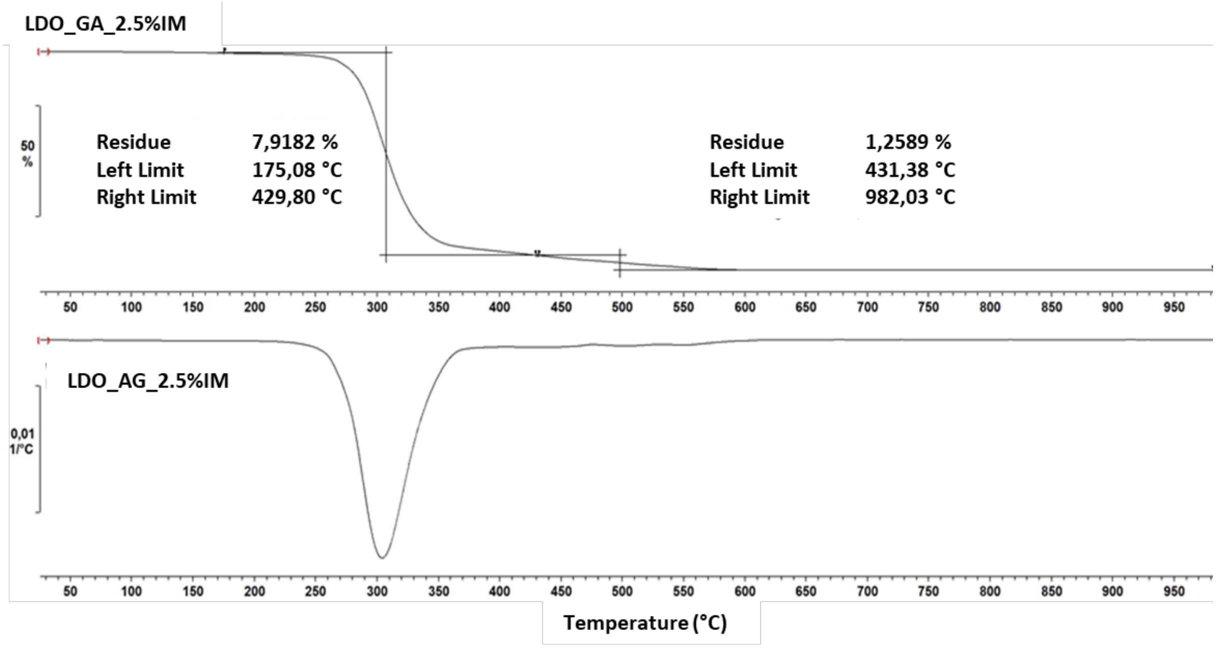


Figure S9. TGA (up) and DTG (down) thermograms of LDO/GA polymer (1:1; 2.5 wt% imidazole); Heating program: from 25 °C to 1000 °C; heating rate: 10 °C.min^{-1}

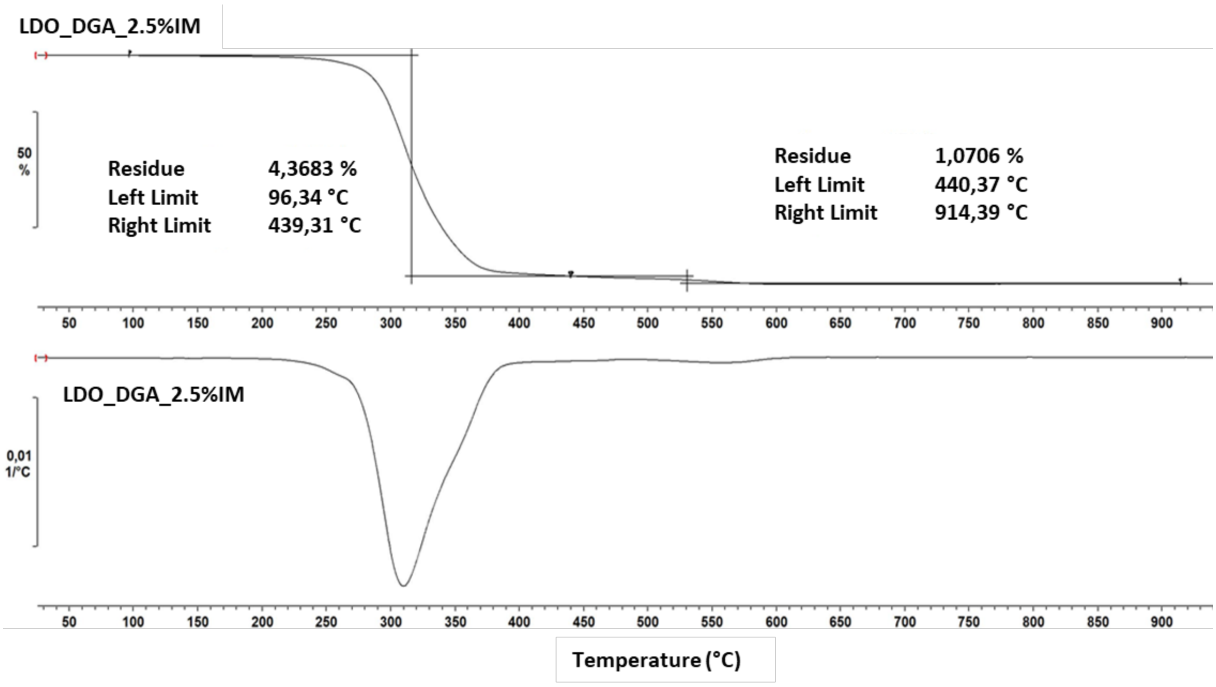


Figure S10. TGA (up) and DTG (down) thermograms of LDO/DGA polymer (1:1; 2.5 wt% imidazole); Heating program: from 25 °C to 1000 °C; heating rate: 10 °C.min^{-1}

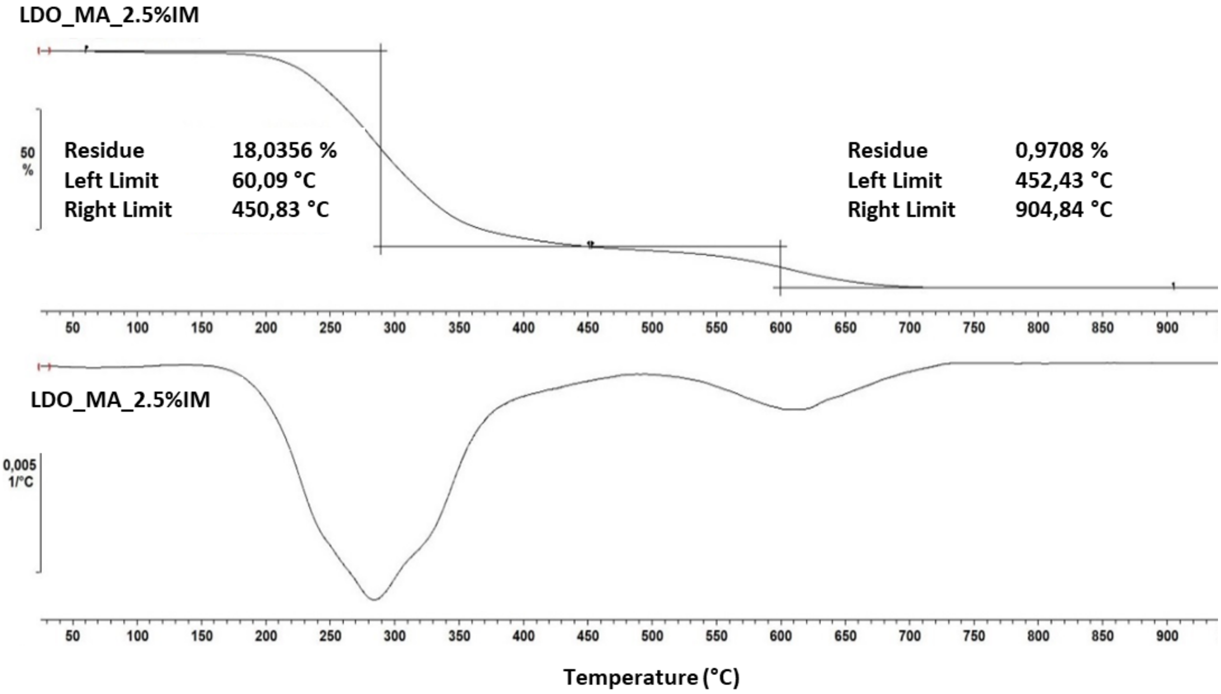


Figure S11. TGA (up) and DTG (down) thermograms of LDO/MA polymer (1:1; 2.5 wt% imidazole); Heating program: from 25 °C to 1000 °C; heating rate: 10 °C.min^{-1}

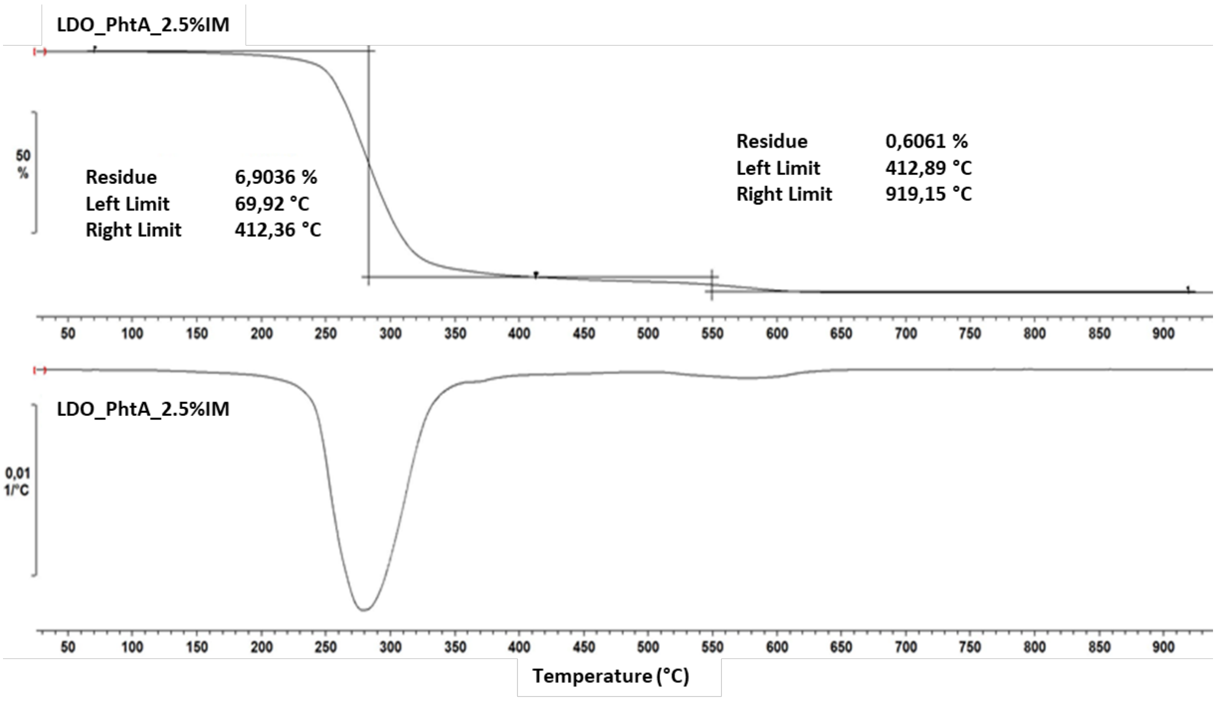


Figure S12. TGA (up) and DTG (down) thermograms of LDO/PhtA polymer (1:1; 2.5 wt% imidazole), Heating program: from 25 °C to 1000 °C; heating rate: 10 °C.min^{-1}

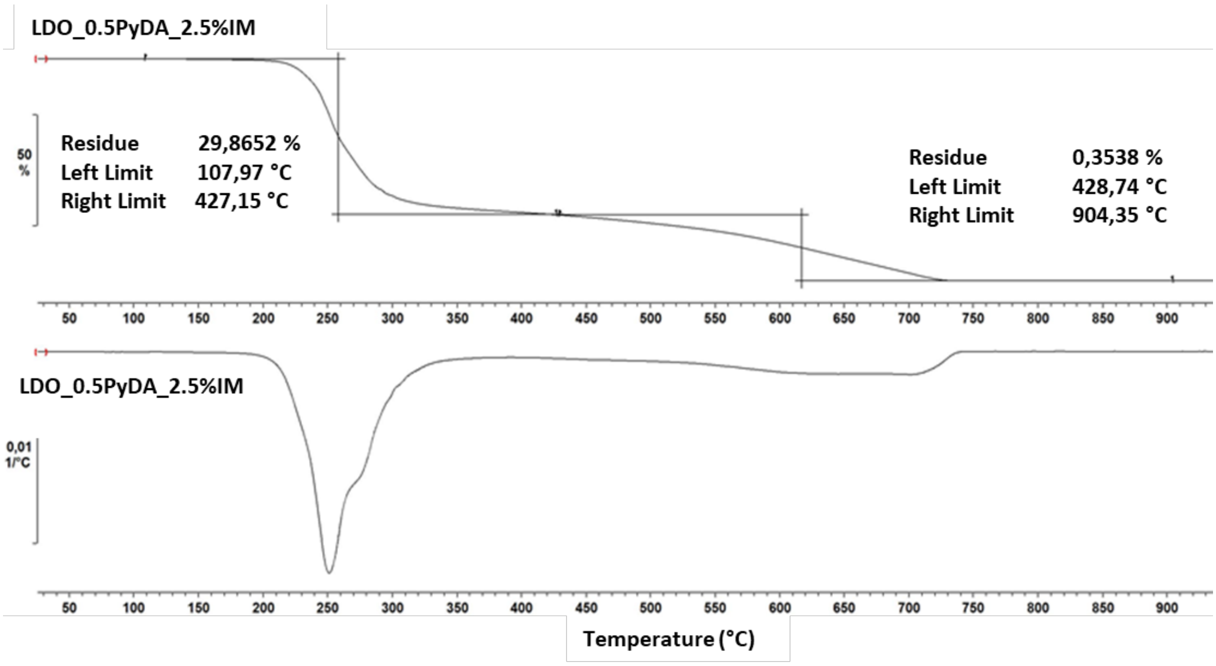


Figure S13. TGA (up) and DTG (down) thermograms of LDO/PyDA polymer (1:0.5; 2.5 wt% imidazole); Heating program: from 25 °C to 1000 °C; heating rate: 10 °C.min^{-1}

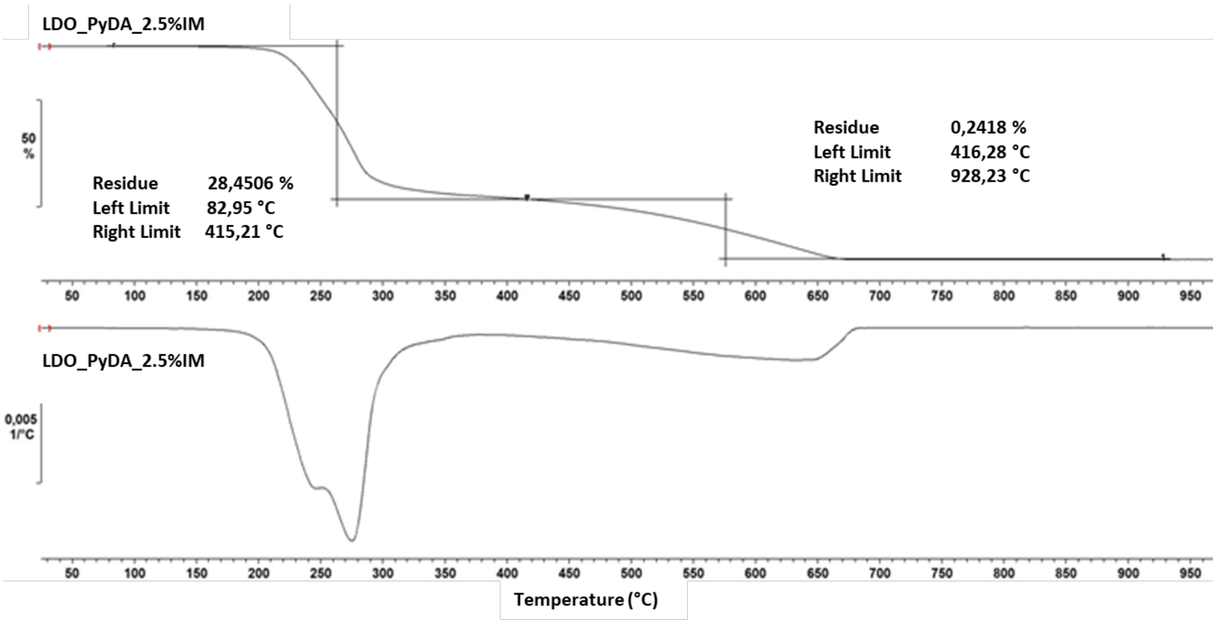


Figure S14. TGA (up) and DTG (down) thermograms of LDO/PyDA polymer (1:1; 2.5 wt% imidazole); Heating program: from 25 °C to 1000 °C; heating rate: 10 °C.min^{-1}

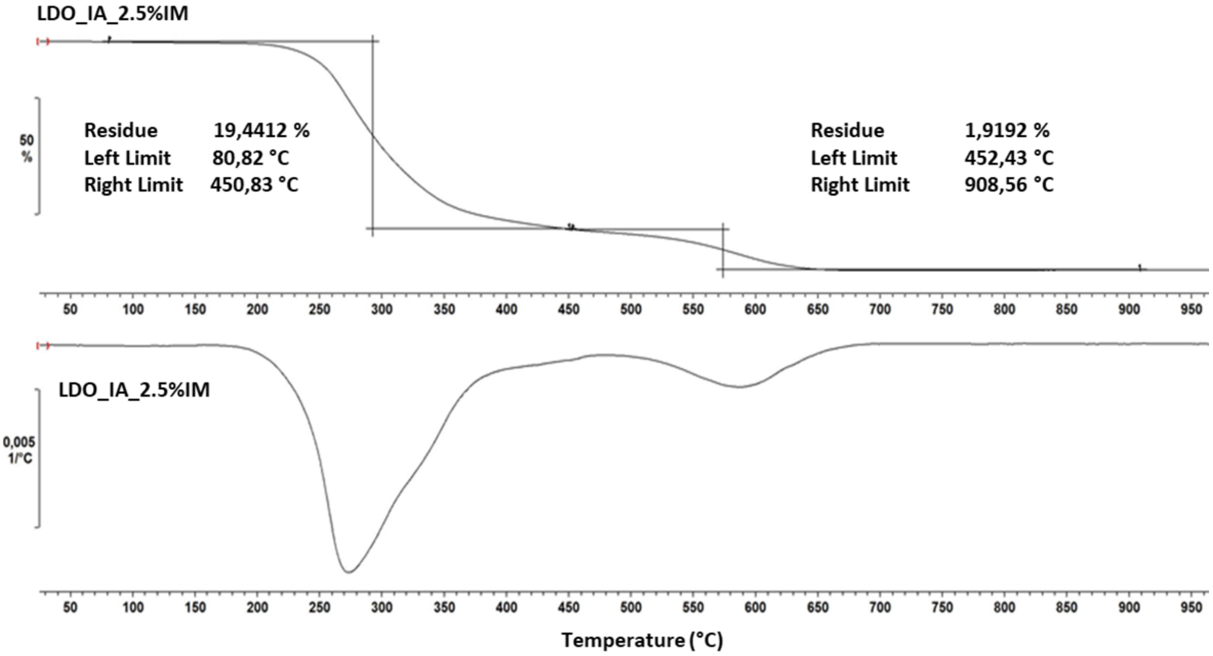


Figure S15. TGA (up) and DTG (down) thermograms of LDO/IA polymer (1:1; 2.5 wt% imidazole); Heating program: from 25 °C to 1000 °C; heating rate: 10 °C.min^{-1}

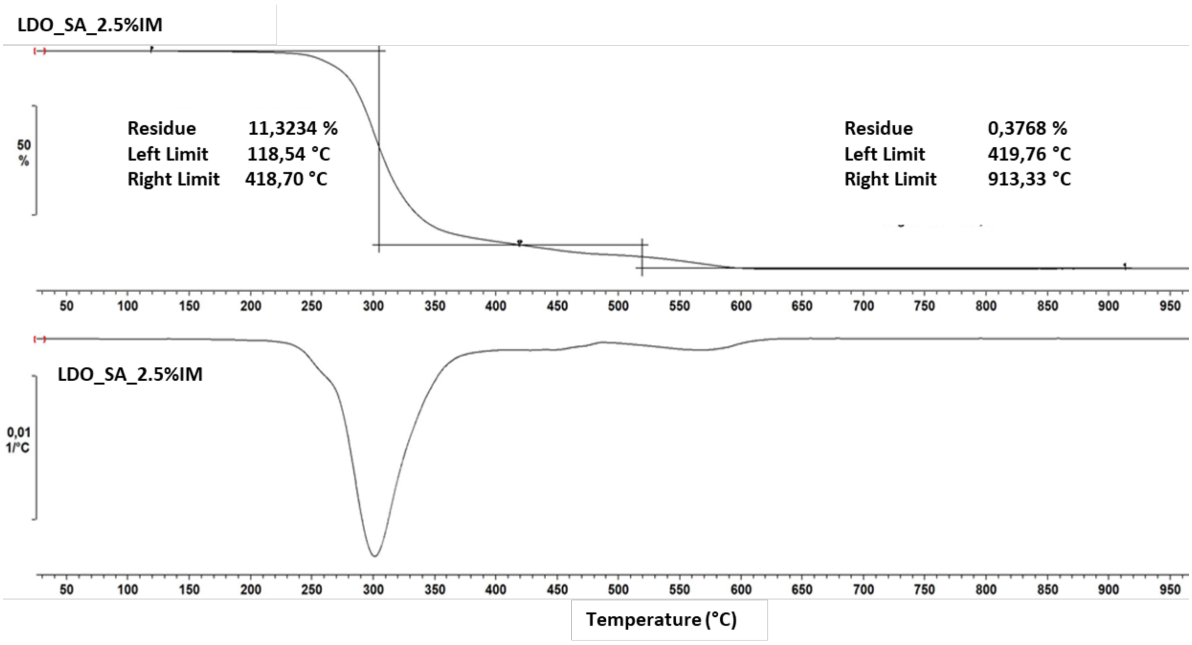


Figure S16. TGA (up) and DTG (down) thermograms of LDO/SA polymer (1:1; 2.5 wt% imidazole); Heating program: from 25 °C to 1000 °C; heating rate: 10 °C.min^{-1}

3.3 FITR analysis

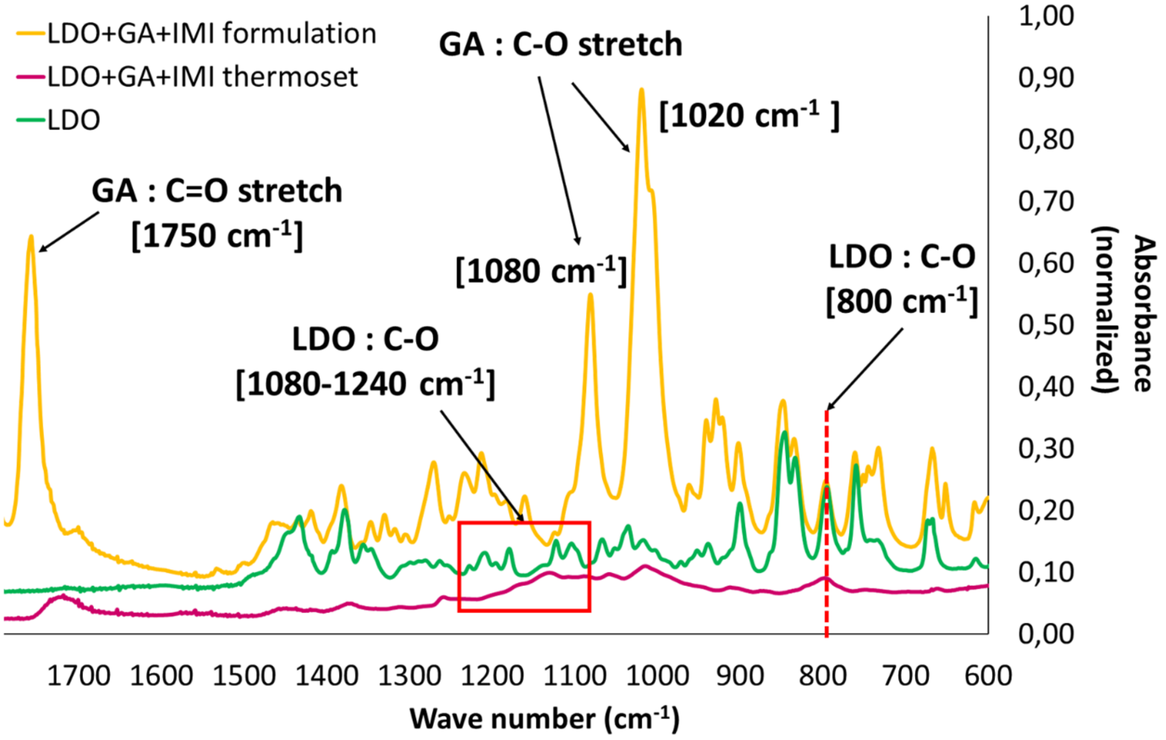


Figure S17. FTIR of the LDO/GA thermoset compared to the synthesized limonene dioxide and the formulation before polymerization

3.4 Swelling

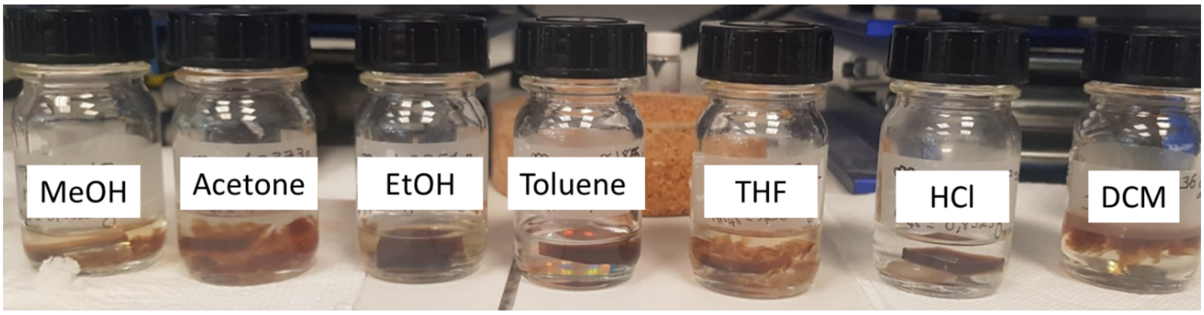


Figure S18. Aspects of LDO/GA polymers immersed in different solvents for 48 h at room temperature.

3.5 Tensile test

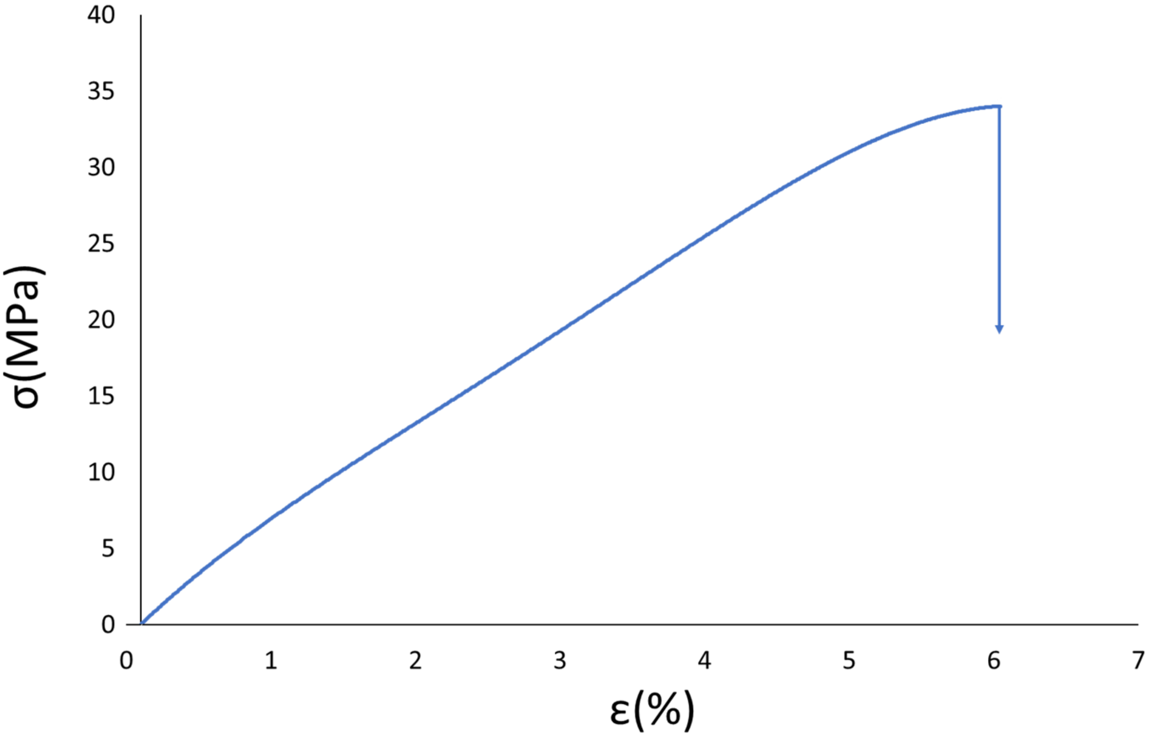


Figure S19. Tensile stress vs. elongation at break curve of LDO/GA specimen

Table S3. Mechanical properties of LDO/GA polymers providing by tensile tests.

Run	σ (MPa)	ε (%)	E (MPa)
1	34	6.04	650
2	37	5.59	812
3	30	4.69	715
Average	**34**	**5.44**	**726**
Standard deviation	**3.5**	**0.69**	**81**

3.6 DMA analysis

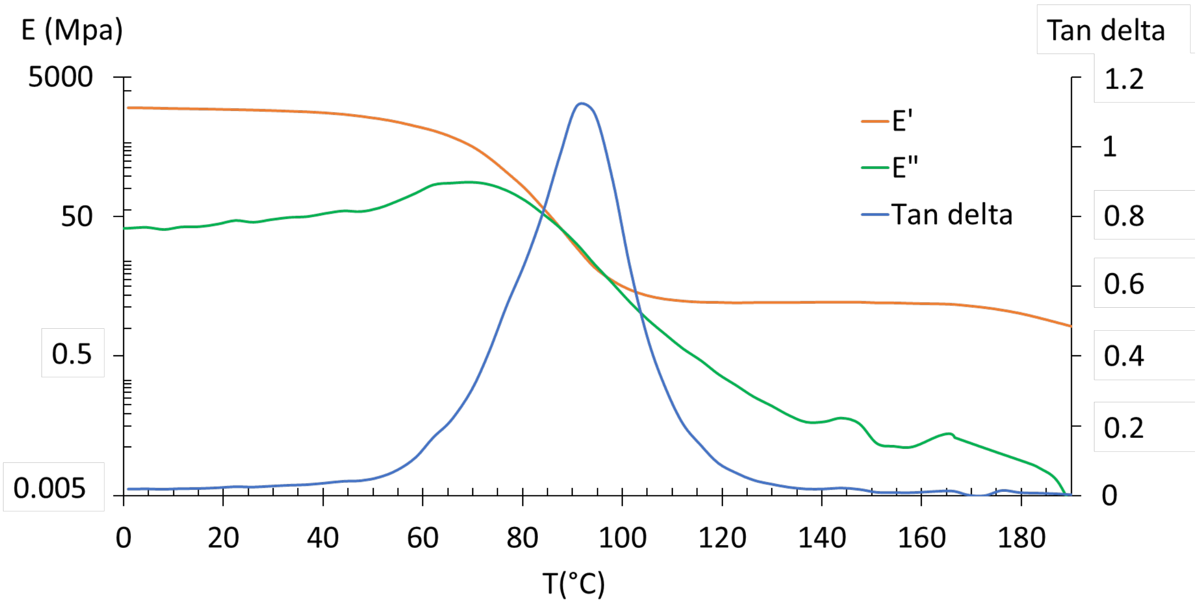


Figure S20. Dynamic mechanical analysis (DMA) analyses of LDO/GA thermoset: evolution of storage modulus (E’), loss modulus (E”) and the damping factor (tan delta) in function of temperature