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Limonene dioxide as a building block for 100% bio-based thermosets

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Limonene dioxide as a building block for 100% bio-based thermosets†

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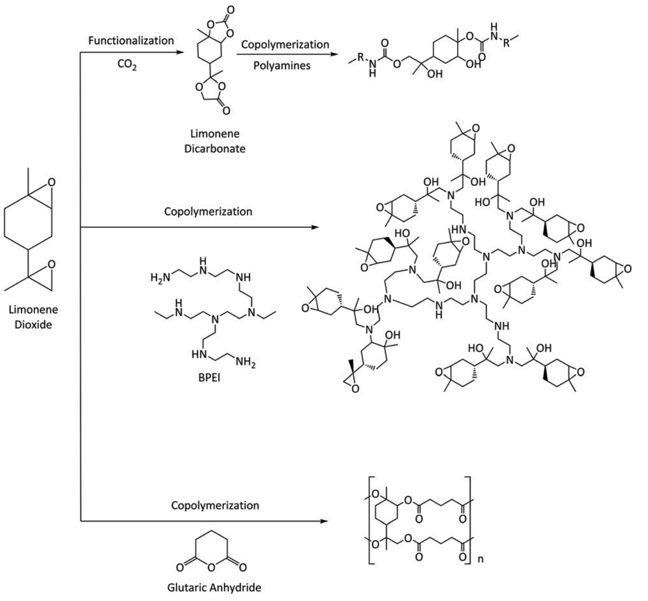
This study valorises the benign epoxidation of (*R*)-(+)-limonene to generate novel bio-resourced limonene dioxide monomers. Without additional steps of separation or functionalization, the racemic limonene dioxide was cured with glutaric and dimethylglutaric anhydrides leading to thermosets with a high T_g (~98 °C) and good mechanical properties (σ = 27 MPa; ε = 3.5%; *E* = 1150 MPa; *E*′ = 1650 MPa, Shore *D* = 78).

Recent studies showed the use of monoterpenes as a versatile class of compounds, offering more than 1500 renewable molecules with potential biological and chemical use.[1] Some of these cyclic monoterpenes have great potential to be used as monomers and therefore to generate thermoplastic or thermosetting polymers. Among them, the by-products of the citrus industry, (*R*)-(+)-limonene for instance, are waste products generated after the juicing process, producing about 90% by-products from fresh fruit. More than 13.6 million tons of orange peel waste are produced every year, leading to reportedly more than 60 000 tons of (*R*)-(+)-limonene, mainly obtained by extraction.[2,3] Recently, it has been largely studied for its potential use as a chemical feedstock and building block for the polymer industry, which is still reliant on petroleum-derived products and processes.[4]

(*R*)-(+)-Limonene is a monocyclic terpene made of two isoprene units and has two carbon double bonds that could be functionalized by a variety of chemical reactions. Its epoxidation for instance leads to oxygen-rich epoxides that display less toxicity than common commercial monomers, mainly based on bisphenol A, and they are versatile building blocks for the polymer industry.[5] Following our interest in bio-based polymers[6] and green chemical processes,[7] we got interested in the valorisation of (*R*)-limonene and more specifically of its oxide derivatives. Whereas the primary epoxidation product of limonene, 1,2-limonene oxide, has been studied as a key monomer for various polymers,[8–12] limonene dioxide (LDO) has been used and transformed to polymers only recently (Scheme 1).[13–16] Koschek *et al.* studied the ring-opening polymerization and polyaddition of LDO in the presence of amines to gain insight into the reactivity of LDO's endocyclic and terminal epoxide groups.[13] Claverie *et al.* examined the reactivity of LDO in the presence of petroleum based primary and secondary amines and obtained thermosets with a storage modulus of 1 GPa at room temperature and a glass transition temperature (T_g) of 70 °C (Scheme 1, (2)).[14] Limonene dioxide can be functionalized to obtain new monomers. Mülhaupt *et al.* monitored the catalytic carbonation of LDO with CO_2 to obtain a novel cyclic limonene dicarbonate and then polymerized it with different oil-based diamines to produce linear non-



Scheme 1 Representation of the functionalization or copolymerization strategies of limonene dioxide.

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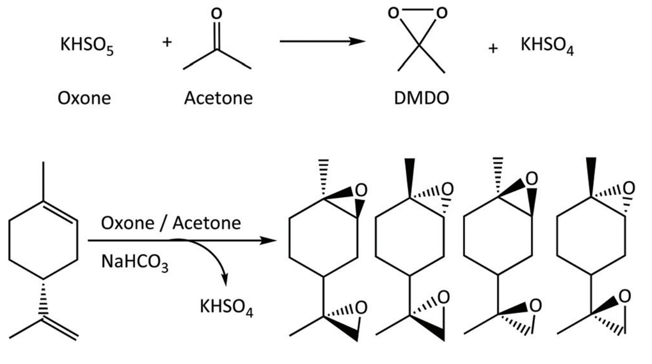
isocyanate oligo- and polyurethanes (Scheme 1, (1)).[15] To the best of our knowledge, there is no example reporting a direct copolymerization of the LDO monomer with bio-based anhydrides. Hence, for the first time this study reports the successful anionic copolymerization of racemic limonene dioxide to produce 100% biobased thermosets by direct crosslinking with carboxylic anhydrides. This kind of renewable thermosetting resin can find several potential applications as sustainable and eco-friendly coatings, food packaging, and structural matrices, among others.

In line with our main goal to conduct the most benign synthesis of limonene dioxide (LDO) from commercial (*R*)-limonene, we selected dimethyldioxirane (DMDO), generated using Oxone® and acetone at room temperature. Oxone is an available, cheap and stable salt (potassium peroxymonosulfate) and acetone acts as both a ketone source and solvent.[17] The *in situ* generated dimethyldioxirane (DMDO) from Oxone® and acetone was thus used to perform the total epoxidation of (*R*)-(+)-limonene following the method of Kaliaguine *et al.*[17] in order to obtain a mixture of its four diepoxides as shown in Scheme 2. According to these authors, the reaction is successful at room temperature with an optimal limonene/Oxone ratio of 1 : 2.6. Nevertheless, in the present study, limonene is fully converted into LDO with a limonene/Oxone ratio of 1 : 2.8. The LDO isomers were analyzed by ^{1}H NMR, FTIR and GC-FID (Fig. S1 and S2†). Typical peaks of LDO's epoxides can be noticed at ~2.5 ppm for the external cyclic epoxide and at ~3 ppm for the internal one in the ^{1}H NMR spectrum. C–O stretching signals can be observed around 840 cm^{-1} and between 1080–1240 cm^{-1} in the FTIR spectrum.[18] Furthermore, no signals of the internal double bond (at 5.5 ppm in ^{1}H NMR and 880 cm^{-1} in FTIR) or the external double bond (at ~4.7 ppm in ^{1}H NMR and 1650 cm^{-1} in FTIR) are present. The ^{1}H NMR spectrum confirms also the presence of four diastereoisomers from the peaks at 1.23 ppm (internal methyl).[13] The synthesized LDO's purity, determined by GC-FID, is superior to 96% (Fig. S2†).

Limonene dioxide was reacted using different nucleophilic molecules. The mechanism of the reaction is a living anionic copolymerization.[19,20] Epoxides can be activated using imidazole and its derivatives, tertiary amines, or Lewis acids. Imidazole (IMI) was chosen considering its high efficiency to initiate the epoxy ring opening polymerization.[21]



Scheme 2 Epoxidation of (*R*)-(+)-limonene with *in situ* generated DMDO from Oxone/acetone.

Firstly, the reactivity of different formulations with the initiator amount from 0 to 5 wt% was studied by DSC analysis (Fig. S3 and Table S1†). The first selected hardener was glutaric anhydride (GA), a biobased molecule, and the ratio of LDO/GA was chosen to be stoichiometric. The amount of imidazole giving the best results (regarding reactivity but also glass transition, Table S1 and Fig. S6†) was 2.5 wt%.[22] This amount corroborates with the literature results which indicate that the best polymerization reactivity is obtained with between 2 and 3 wt% of the initiator.[12] Once the initiator amount was fixed (2.5 wt%), formulations were prepared with a LDO/GA ratio from 1 : 0.5 to 1 : 3, increasing by 0.5.

The analysis results are presented in Table S2 and Fig. S4.† The highest enthalpy of reaction, ~584 J g^{-1}, is provided by the molar stoichiometry LDO/GA formulation (run 2, Table S2,† implying two epoxide functions for one anhydride function, Scheme S1†) and not the functional stoichiometry one (run 4 Table S2,† implying one epoxide for one anhydride, Scheme S1†). After this study, other potential hardeners were tested: glycerol (Gly), 2,2-dimethylglutaric anhydride (DGA), maleic anhydride (MA), phthalic anhydride (PhtA), pyromellitic dianhydride (PyDA), itaconic anhydride (IA) and succinic anhydride (SA). All of them are biobased except for pyromellitic dianhydride.[23] The LDO reactivity towards these hardeners using a stoichiometric ratio and 2.5 wt% IM was analyzed by DSC. All the formulations except for that with glycerol led to solid polymers. Thus, the formulation with glycerol was dropped from further studies and from Table 1. The LDO reactivity towards DGA is similar to that towards GA in terms of reaction interval and temperature of reaction peak, but it has a lower enthalpy of ~441 J g^{-1}, instead of 584 J g^{-1}. For LDO/MA (run 3), the enthalpy of reaction is also high, ~410 J g^{-1}, and the reaction starts at a lower temperature, at around 44 °C. PyDA (runs 5 and 6) is very reactive towards LDO. With the given stoichiometric ratio (run 6), the reaction starts at room temperature during the mixture preparation. The mixture

Table 1 Reaction enthalpy, interval, temperature of the reaction peak (T_{peak}), glass transition and degradation temperature of LDO/anhydride systems

Run	Anhydride	*A* (eq.)	ΔH (J g^{-1})	T_{peak} (°C)	Reaction interval	T_{g} (°C)	$T_{5\%}$ (°C)
1	GA	1	584	155	85–195	98	271
2	DGA	1	441	154	79–195	85	271
3	MA	1	410	95	44–198	100	212
4	PhtA	1	205	121	52–186	nd	241
5	PyDA	0.5	146	93	42–138	nd	228
6	PyDA	1	—	—	—	nd	222
7	IA	1	218	124	52–157	56	231
8	SA	1	268	123	67–172	60	261

Heating program: heating rate = 10 °C min^{-1}; to get ΔH, T_{peak}, and reaction interval: 25 to 210 °C; to get T_{g}: −50 to 150 °C; to get $T_{5\%}$: 25 to 1000 °C.

becomes viscous quickly which explains the missing value of enthalpy in Table 1. When the amount of PyDA is decreased (run 5), the reaction starts less quickly but is still fast (42 °C). Pyromellitic dianhydride seems to be a good candidate for copolymerization with limonene dioxide but due to its high melting point and reactivity, the copolymerization cannot be optimized in bulk. A solvent polymerization should be more indicated for this system. PhtA, SA and IA (runs 4, 7 and 8) show the lowest enthalpies of reaction with LDO, almost half of the values of precedent systems.

All the different formulations (the LDO/GA and LDO/hardener systems) were then cured in an oven using a curing and post-curing program determined by DSC analysis. The T_g (Fig. S7 and S8†) and the degradation temperature (Fig. S9–16†) of the polymerized systems were evaluated by DSC and TGA; the obtained results are summarized in Table S2† and Table 1.

In the series LDO/GA (Table S2 and Fig. S7, S9†), T_g increases with the decrease of GA amount until the stoichiometric ratio where it reaches 98 °C (which confirms that in terms of enthalpy this ratio is the best for the elaboration of LDO-based thermosets). The most promising results in terms of T_g and $T_{5\%}$ are given by the LDO/GA and LDO/DGA systems (runs 1 and 2, Table 1). The LDO/MA (run 3, Table 1) system leads to the highest $T_g \sim 100$ °C, but also to the lowest $T_{5\%}$; so, this formulation should be optimized before further tests (the optimized curing program for the LDO/GA formulation does not suit the LDO/MA system).

All the characterization studies were, thus, carried out on LDO/GA, the reference system, as it presented the best results. The thermosets of LDO/GA (LDO + AG + IMI) were analyzed by FTIR and compared with the synthesized LDO (Fig. 1). The –C–O–C– symmetric and asymmetric stretching vibrations in the FTIR spectrum were observed from 800 to 1200 cm^{-1}.[24] According to the study of Claverie *et al.*,[14] the symmetric and asymmetric stretching vibrations of the 8,9-epoxide group are observed from peaks at 800 cm^{-1} and those of the 1,2-epoxide group from 1000 to 1250 cm^{-1}. In our case, in contrast to them, external and internal epoxide groups disappeared partially during the polymerization compared to a neat LDO monomer. This difference, compared to that obtained by Claverie *et al.*,[14] could be explained by the functionality of the comonomers. In our case, the LDO/GA ratio is stoichiometric for the molarity but not for the functionality (which leads to the unreacted epoxy function) unlike the results obtained by Claverie *et al.* where the LDO/amine ratio is functionally stoichiometric. The C═O vibration (1750 cm^{-1}) as for the C–O vibrations (1080 and 1020 cm^{-1}) of GA completely disappeared which confirms that all the anhydride functions reacted (Fig. S17†).

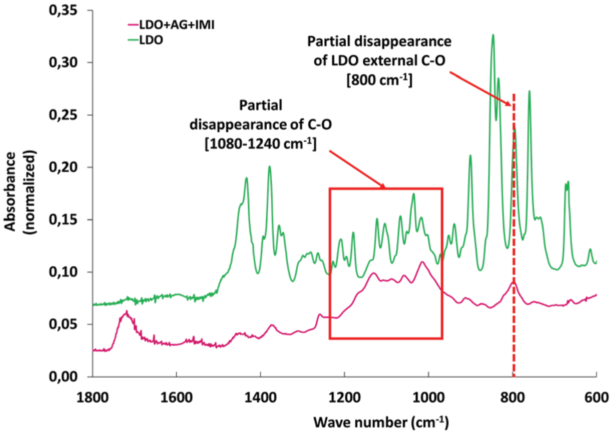


Fig. 1 FTIR analysis of a neatly synthesized LDO and a polymerized LDO/GA system.

Polymers of LDO/GA were immersed in methanol, ethanol, acetone, toluene, THF, dichloromethane, and a solution of 1 M HCl for 48 hours at room temperature. The swelling ratios in these different solvents are given in Table 2. The swelling is low in ethanol, toluene and HCl, and we can notice that it decreases in the following order of the type of solvent: protic polar > aprotic polar > aprotic apolar. The cured samples started to disaggregate in methanol, acetone, THF and DCM within 48 h but never solubilized (Fig. S18†). These results confirm the presence of a crosslinked network (Scheme S1†).

This also demonstrates that more than one epoxide of some LDO monomers has reacted during the copolymerization. However, the fact that the material started to fall apart in some solvents highlights the reversibility of the ester links. As all the epoxy rings of the LDO were not involved in the copolymerization reaction, the network was less dense which permitted a better impregnation of the solvent in the polymer. Thus, dynamic exchange reactions (which enable thermoset disintegration under mild conditions) occurred.[25–28]

The mechanical properties of the LDO/GA materials were studied by uniaxial tensile tests. The results obtained with the LDO/GA specimens are presented in Table S3 and Fig. S19.† The tensile stress at break is 34 ± 3.5 MPa, the elongation at break is 5.44 ± 0.69% and Young's modulus is 726 ± 81 MPa. The high Young's modulus and small strain at break indicate a rigid material.[29] Regarding the tensile properties (Table 3), the obtained results are slightly lower than those expected for unsaturated polyester thermosets[30–32] but similar to fully bio-based epoxy thermosets.[33–37]

Shore hardness is a measure of the resistance of a material to the penetration of a spring-loaded needle-like indenter. The measure goes between 0 and 100 and a higher number represents a harder material. Tests on LDO/GA materials led to reproducible results; the Shore SD hardness corresponds to 78 ± 1, which is expected for polyester thermosets.[32]

Table 2 Swelling ratio of the LDO/GA polymer according to the solvent after 48h

	MeOH	EtOH	Ac.	Tol.	THF	DCM	HCl (1 M)
S (%)	—	12	—	8	—	—	0.8

Table 3 Main properties of LDO/GA polymers compared to other systems reported in the literature: LDO/amine; LDO dimethacrylate; polyester and epoxy thermosets

	LDO copolymerization		LDO functionalization	Common thermosets		
	LDO/GA	Schutz (ref. 14)	Barh (ref. 15)	Polyester (ref. 32)	DGEBA (ref. 33)	Fully biobased epoxy (ref. 33–37)
T_g (°C)	98	70	60	—	143	63–204
σ (MPa)	34	—	21	40	52	23–57
ε (%)	5.44	—	2	5.1	4.8	4.3–258
E (GPa)	0.73	—	2.7	1.1	2.5	0.15–2.6
E' (Gpa)	1.65	0.6	—	—	1.6	1.1–2.6
υ (mol. L^{-1})	0.29	0.1	—	—	0.6	0.4–3.5

A typical DMA experiment was conducted to measure E', E'' and tan δ as a function of temperature. The modulus E' accounts for the elastic response of the material and the loss modulus E'' represents the viscous response. The DMA analysis of the LDO/GA thermoset is presented in Fig. S20.† At room temperature, the polymer is in the glassy state and the storage modulus is 1.65 GPa. Beyond δ which is observed at ~90 °C (which corroborates the result in Table 1), the polymer is in the rubbery state and the storage modulus is about 3 MPa. The crosslink density is therefore 0.29 mol L^{-1} which is higher than that obtained for the LDO/amine thermoset.[14]

All the results presented in Table 3 therefore demonstrate that the performances obtained for the LDO/GA thermoset are comparable to or even higher than those obtained for copolymerization with the amine system, directly[14] or following a functionalization[15] (except for the Young's modulus). The LDO/GA thermosets' properties are in the range of those of fully biobased epoxy thermosets.[33–37] The advantage of limonene dioxide is that its synthesis starts from a building block (limonene), a product from waste peel citrus. It, thus, contributes to food waste reduction by recycling. This system is a proof of concept and further studies will be dedicated to optimize LDO thermosets properties and compete with radical polymerization systems[16] or DGEBA thermosets.[33]

Conclusions

We have therefore succeeded in the unprecedented preparation of a 100% bio-based polymer, starting from a diepoxide monomer based on limonene. The amounts of initiator and co-monomers were optimized to reach the optimal copolymerization process. At a stoichiometric molar ratio, the copolymerization of LDO with glutaric and maleic anhydrides led to excellent reactivities and fully biobased polymers with high glass transition temperatures (up to 100 °C) and degradation temperatures (up to 270 °C). The results with LDO/GA are superior to those obtained with a direct copolymerized LDO/amine system so far.[14,15] The characterization of LDO/GA polymers highlights the presence of a crosslinked network (no melting, solvent resistance, similar mechanical properties to epoxy resins or thermoset polyesters) but not fully converted (some residual epoxy bonds available in FTIR, low storage modulus in the rubbery state in DMA) as the functionality ratio is not stoichiometric. Furthermore, the LDO/AG thermoset was found to disaggregate in some solvents which demonstrates the reversibility, and thus, the recycling potential of the polymer. Further studies will concern the selective reactivity of a trans-LDO to try to potentially reach a higher crosslinked fully biobased thermoset.

Author contributions

Conceptualization, A. M., S. O. and V. M.; investigations, E. L., V. K., S. L. and P. M.; writing—original draft preparation, E. L.; writing—review and editing, E. L., A. M., S. O. and V. M.; supervision, A. M., S. O. and V. M.

Conflicts of interest

There are no conflicts to declare.

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