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A Biosourced Epoxy Resin for Adhesive Thermoset Applications

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Abstract: Biobased epoxy-derived raw materials will be essential for future coating and adhesive designs in industry. Here, a facile approach is reported towards the incorporation of limonene into an epoxy-functionalized polycarbonate and its crosslinking with a polyamine curing agent to obtain a thermoset material. For the first time, a solvent-borne adhesive with excellent film-forming, mechanical and adhesion strength properties is described.

Introduction

Many companies are trying to develop polymers which are more sustainable than the currently used ones as the environmental footprint of industrial products must be improved in the next 25 years not only in Europe but also worldwide. The replacement of petroleum-based raw materials by biosourced feedstock is considered to be crucial in this context paving the way for greener consumer plastics and materials.

Solvent-borne epoxy resins dominate the coatings and adhesive markets, especially in those cases where high chemical and mechanical resistance are required. The global forecasted market for epoxy resins (including paints and coatings, adhesives, construction, electrics and electronics, transportation and other sectors)¹ is estimated to be USD 764 million by 2022. Several reports advocate the use of low carbon footprint polymers to move to a more sustainable plastic production and market.²⁻⁴ However, for the moment the development of more sustainable epoxy thermosets has received comparatively little attention. Mija *et al.*⁵ were the first to report a fully biobased thermoset composed of limonene dioxide and several biosourced anhydrides. Although there has been some recent development on the use of renewable epoxy derivatives,⁶⁻⁸ most of the examples focused on the utilization of vegetable oils such as linseed oil, soybean and castor oil among other,⁹⁻¹¹ and carbohydrates including isosorbide and itaconic acid.^{12,13} In many of these cases, the alternative epoxy resins offer inferior thermal and mechanical performance due to the presence of long alkyl chains in the cured polymer. Furthermore, the low reactivity of the epoxy groups may

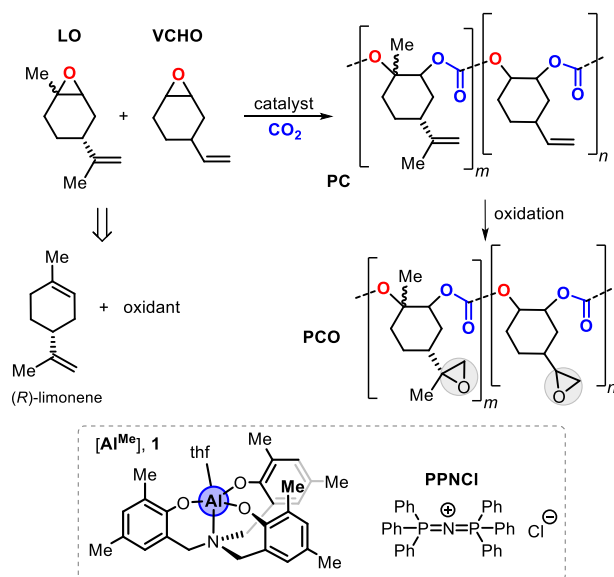
affect the final resin properties due to the presence of unreacted functional groups.¹⁴ Moreover, a huge disadvantage of these known epoxy based resins is that they typically are obtained through complex synthesis and purification processes that will inevitably affect the financial competitiveness.¹⁵

Consequently, industrial applications of such biobased resins have not been reported up to now despite the clear need for biobased product development. Notwithstanding, some promising results towards new adhesive and coating technologies have emerged. Gomez-Lopez *et al.*¹⁶ recently reported an overview on poly(hydroxyurethane) polymers derived from biobased poly(cyclic carbonate)s and synthetic diamines. The polycarbonate precursor can react with both aliphatic and cyclic amines, and with highly reactive melamines (such as hexamethoxy methyl melamine (HMMM) to produce solvent-based and solvent-free thermosets.

In order to expedite the use of (partially) biobased thermosets, new approaches that contemplate on easy-to-access bio-feedstock delivering useful alternative epoxy resins that can potentially replace classical bis-phenol A diglycidyl ether (DGEBA) based ones are needed. In this regard, we envisioned that starting materials derived from limonene^{6,17-20} would provide a suitable starting point for advanced polymer development as limonene is relatively cheap, accessible and amenable to post-modifications. Combined with the previously disclosed catalytic conversion of limonene oxide (LO) and CO₂,²¹⁻²⁴ a new terpolymeric polycarbonate (PC) polymer architecture was thus prepared and studied by combining two functional epoxy monomers (LO and vinyl cyclohexene oxide, VCHO). Post-synthetic oxidation led in a straightforward way to a PC with two different epoxy groups (abbreviated as PCO) that were subsequently used in thermoset development (Scheme 1). PCO treated with a polyoxypropylenediamine hardener was examined in the preparation of new thermosets as well as different combinations of PCO with commercial DGEBA for comparison of the adhesion properties. The importance of the current study is the achievement of superior sticking of the biosourced epoxy thermoset when compared to the petroleum-based one, showing

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the potential of these terpene based biopolymers as sustainable alternatives with a favorable carbon footprint.²⁵



Scheme 1. Synthetic route for the preparation of biobased PCO from LO and VCHO through PC. The binary catalyst comprises of Al-complex [AlMe]₃ 1 and PPNCI. In both cases the oxidant stands for 3-chlorobenzoic peroxycarboxylic acid (mCPBA). The *m:n* ratio of the repeating units in PCO is approximately 10:1 as determined by ¹H NMR.

Results and Discussion

The new, versatile thermoset material is easily prepared by mixing the biobased solid resin (PCO), dissolved in a small amount of solvent, with a commercially available amine curing agent (free of solvent). The presence of 2 wt % of catalyst proved to be beneficial to reduce the curing time and to promote the crosslinking at room temperature (r.t.), which is a very important aspect for coatings and adhesive applications. Thus, according to the twelve principles of green chemistry,²⁶ the present work provides impetus concerning the use of a renewable feedstock and using catalysis to prepare the biobased resin and accelerating the curing process of the thermoset resin thereby reducing the reaction time, temperature and thus the energy demand.

In search of a perfect binder, the molecular weight and the thermal properties of the epoxy resin play an important role. High molecular weight will provide good film stability, whereas the glass transition (T_g) and the decomposition temperatures (T_d) will affect the flexibility of the polymer at room temperature and its use at high temperatures, respectively. PCO is obtained in only three steps as shown in the Scheme 1, in high yield (~90%) and with an M_n of 4.17 kDa and polydispersity \mathcal{D} of 1.41 (see the Supporting Information, SI). The conversion of limonene to LO has been described elsewhere.²¹ Previous studies identified conditions for chemoselective oxidation of the pendent double bonds of poly(limonene)carbonate (a PC with 100% limonene-based repeat units), yielding the oxidized PLCO with a maximum T_g of 135 °C and high $T_d^{5\%}$ of 224 °C.²³ Therefore, similar oxidation conditions (using mCPBA, 0 °C; see the SI) were successfully

used to convert PC into PCO, which had a T_g of 132 °C and a T_d^{max} of 250 °C.

PCO has a lower reactivity than the generally used DGEBA resin and, therefore, a reactive amine was necessary, and we chose a low molecular weight curing agent, viz. polyoxypropylenediamine (400 g/mol, hereafter denoted as “Jeff” following its commercial tradename Jeffamine). When PCO is combined with this curing agent, it is possible to obtain good films after deposition of the mixture in a Teflon mold (see Scheme 2). The small amount of solvent used (2 mL/g of PCO resin) is compliant with VOC regulations.^{27,28} Films are quickly formed after thermal curing at high temperatures (1 h at 120 °C, and 2 h at 150 °C), and longer times were required at r.t. (24 h for drying to touch and 7 days for complete thermoset curing). From these findings, we inferred that PCO behaves like the classical DGEBA reagent at r.t. upon reacting with diamines. For the polymer characterization, the films were obtained in two ways (see for the experimental details in the SI).

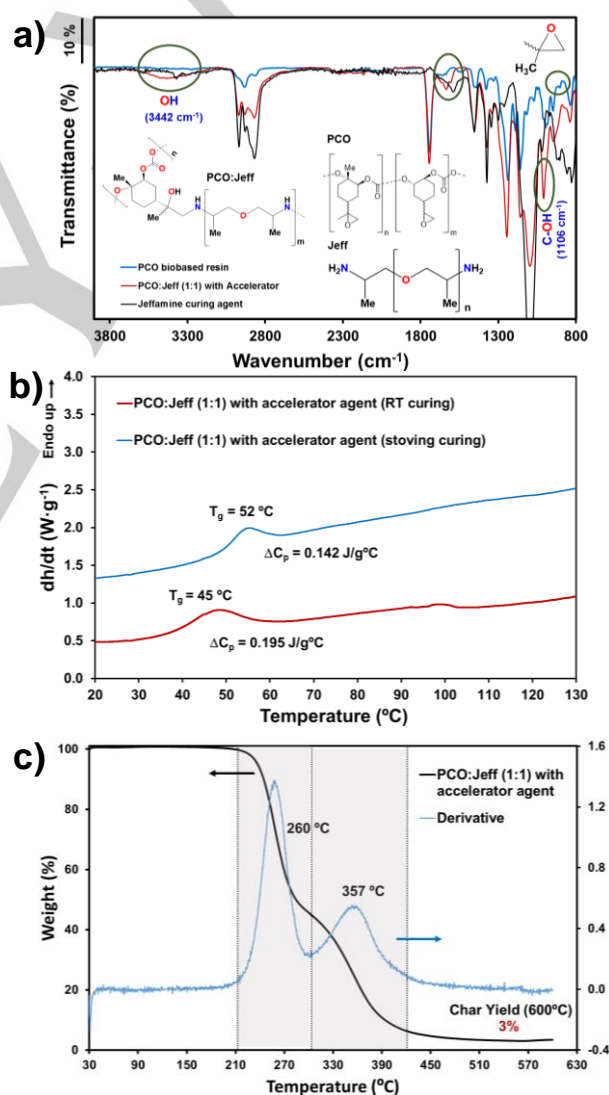


Figure 1. (a) FTIR spectra of biobased epoxy PCO, the hardener (Jeff) and thermoset after curing (PCO:Jeff 1:1 combination). (b) DSC analysis of PCO:Jeff (1:1) with accelerator agent and cured at r.t. and at 120 °C for 2h (stoving conditions). The second heating curve is provided. (c) Thermogravimetry of PCO:Jeff (1:1) with accelerator agent.

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As can be observed in Scheme 2A, the thermoset preparation is user-friendly. For large amount of epoxy resin dispersions with the Jeff hardener, a cowles disperser is necessary to previously homogenize the solid biobased PCO in the solvent, following by the addition of the hardener. However, to prepare smaller amounts simple magnetic stirring of the solid epoxy-based PCO in xylene was enough to obtain a homogeneous mixture (Scheme 2B). The solvent choice was based on the good solubility and compatibility of common epoxy compounds used for solvent-borne formulations. However, it is important to emphasize that xylene was only used to dissolve the solid PCO. Although it is not considered as a green solvent, among hydrocarbons it is not classified as hazardous as other typical solvents such as pentane, hexane and benzene,²⁹ and xylene remains still the most used solvent in solvent-borne coating formulations.

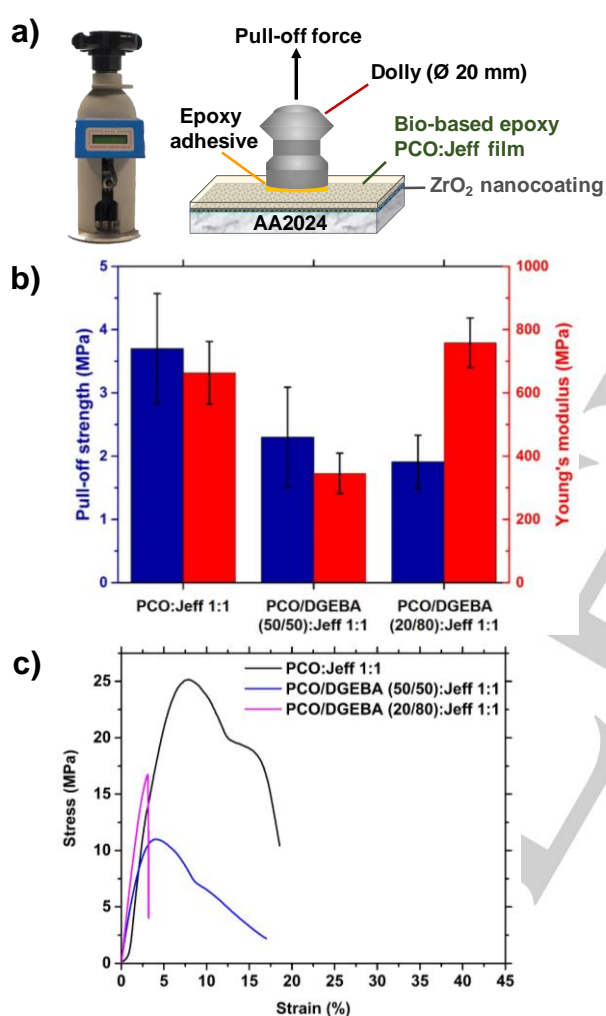


Figure 2. (a) Pull-off test experimental setup; (b) pull-off force and Young's modulus for the three epoxy thermosets studied in this work; and (c) representative stress-strain curves for each system.

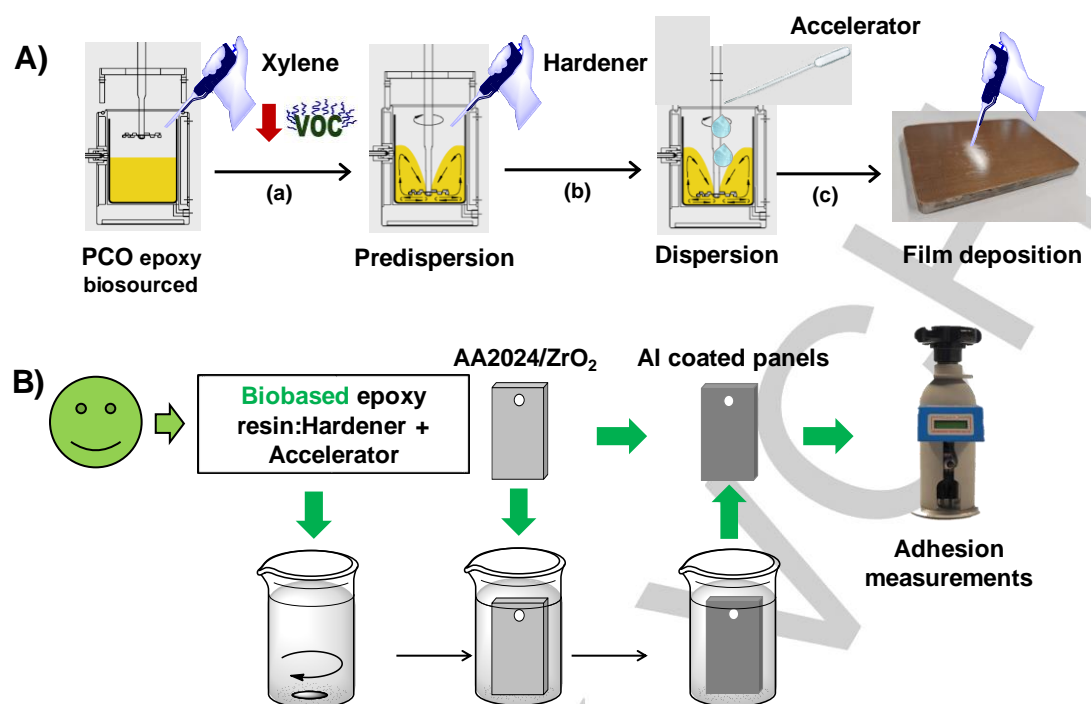
Different polymer compositions were prepared and analyzed by IR spectroscopy. Apart from the pure components PCO and DGEBA, also 1:1 and a 1:4 blends were examined and compared against each other (Figure 1a, and S1 in the SI). As can be seen

in Figure 1a, the main absorption bands for PCO are at 2850-2928 cm^{-1} (aliphatic C-H), 1743 cm^{-1} (carbonate group), 1100-1250 cm^{-1} (C-O-C) and 903 cm^{-1} for the oxirane rings. After reaction with Jeff, which has characteristic absorptions for the primary amine (3368 and 1586 cm^{-1}) and ether bonds (1092 cm^{-1}), a thermoset cured polymer was obtained. A clear difference compared to the separate components PCO and Jeff is the presence of new absorption bands at 3442 cm^{-1} (OH) and 1106 cm^{-1} (C-OH stretching) as a result of the nucleophilic ring-opening by the amine reagent. Additional evidence that the envisioned curing process had occurred is the (partial) disappearance of the epoxy absorption band at 903 cm^{-1} and the primary amine groups of the hardener at 1586 cm^{-1} (Figure 1a).

Interestingly, the addition of 2 wt % of an accelerator agent (*i.e.*, 2,4,6-tris(dimethylaminomethyl) phenol, also known as accelerator 960-1) helped to increase the reactivity of PCO and its reaction with Jeff at low temperature without losing the thermal properties of the thermoset material (Figure 1b). The heat capacity released per gram of sample (ΔC_p) was similar for samples either cured at room temperature or obtained by stoving conditions. The low T_g of about 50 °C for the 1:1 blend of PCO:Jeff is advantageous when compared to the PCO biobased and the commercial DGEBA prepolymers ($T_g = 132$ °C and 100 °C, respectively), as working at much higher temperatures can lead to loss of chemical resistance. In adhesive technology, the epoxy compound is recommended to be applied above its T_g , as it makes the adhesion bond more shock and vibration resistant. Moreover, the epoxy resin is also less likely to damage fragile components as a result of its lower rigidity. The reported T_g is based on 100 % conversion (full cure). DSC curves of PCO:Jeff with and without accelerator are displayed in Figure S2a (SI) for comparison.

The decomposition of 1:1 PCO:Jeff occurs in two steps, at 260 °C and 357 °C (Figure 1c) and, as expected, it is independent of the inclusion of the accelerator reagent (Figure S2b, SI). When PCO is mixed with the DGEBA resin, a good compatibility in xylene solvent and good thermal stability are also achieved after cross-linking with Jeff curing agent (Figure S3, SI). Moreover, the addition of 50 wt % and 80 wt % of DGEBA resin enhances the overall reactivity with the hardener (high values of ΔC_p) and causes the T_g to decrease below 10 °C (Figure S3a, SI). The decomposition temperatures, however, are not too much different from the one obtained with a 1:1 PCO:Jeff thermoset, being 366 °C and 364 °C for mixtures PCO/DGEBA (50/50):Jeff (1:1) and PCO/DGEBA (20/80):Jeff (1:1), respectively (Figure S3b, SI).

Pull-off adhesion tests were carried out using the experimental set up depicted in Figure 2a and using the UNE-EN-ISO 4624 standard. The substrate chosen for these tests was AA2024, a structural aluminium alloy with good mechanical properties, slightly passivated with a nanometric layer of ZrO_2 .^{30,31} The pull-off force of each thermoset system is shown in Figure 2b and the values are listed in Table 1. As all tested samples presented adhesive type failure with aluminium substrates, the measured strength refers to the adhesion between the commercial epoxy adhesive used for such purpose, and the biobased epoxy film. The highest values were obtained for the 1:1 PCO:Jeff sample (3.70 ± 0.87 MPa), which also has the highest tensile strength (26.3 ± 1.3 MPa) and elongation at break (20.8 ± 9.7 %), see Figure 2c. The adhesion for the DGEBA-free



Scheme 2. A) Illustration of PCO dispersion in xylene, followed by a pre-dispersion with the hardener component (a), and subsequently, homogenization of all compounds under mechanical mixing (b), and, finally, the deposition of the bicomponent epoxy resin in a Teflon mold to cure (c). B) Picture for the preparation of small amounts of biobased epoxy solid resin with polyamine adduct for the deposition in aluminum plates previously passivated with zirconium oxide, for further adhesion measurements.

formulation is comparable to other DGEBA-based epoxy coatings and surpasses that of other partially biobased epoxy systems.³² It is also similar to the adhesion behavior observed for other Zr-treated substrates with epoxy coatings.³³

Contrary, when a high content of DGEBA is present in the epoxy composition, the strength-strain curve corresponds to a fragile material with the Young's modulus being very high and having low elongation at break (Figure 2c). In other words, the presence of the PCO biobased resin helps to palliate the brittle behavior of DGEBA-containing polymers due to its high molecular weight and less constrained chemical structure (Scheme 1). This is clearly evidenced when comparing our thermoset with similar biobased thermosets made from limonene-derived small organic molecules. For instance, Mija et al.⁵ were able to obtain a high elastic modulus (726 ± 81 MPa) and tensile strength (34 ± 3.5 MPa) for a fully biobased thermoset, which was prepared from limonene dioxide (LDO) and glutaric acid (GA). However, the elongation at break ($5.44 \pm 0.69\%$) was much lower than that found for the 1:1 PCO:Jeff thermoset (20.8 ± 9.7 MPa). The highest elongation at rupture is an attractive characteristic in comparison to the typically breakable behavior of low molecular weight bio-based epoxies and DGEBA-based commercial epoxies,³⁴ providing an opportunity to extend the scope of adhesives including flexible surfaces, as will be demonstrated in the following paragraph.

Additionally, qualitative pull-off tests were performed by securing a loading of a PCO:Jeff 1:1 composition onto different substrates with two types of architectures, being either flat or porous (Figure 3). The preparation of the films was similar to the previous samples, while keeping the temperature carefully with below 100 °C during the curing process. This was to avoid issues

that may rise because of the presence of thermoplastics, as model substrates, that have low heating deflection temperatures. As illustrated in Figures 3a-e, the coatings are homogenous and able to stick to the dolly accessory (Figures 3h-l). Polystyrene foam (Figure 3f) and polypropylene mesh (Figure 3g) absorb the liquid, as expected. However, after two layer applications, the samples become yellowish and both the foam and the mesh adhere to the dolly (Figures 3m-n). After the detaching assay, the novel biobased thermoset proved to be rather versatile exhibiting cohesive, adhesive and glue failures (Figures 3o-u) depending on the type of substrate.

Table 1. Elastic modulus, maximum tensile strength, elongation at break and adhesion force measured for the three thermoset films studied in the present work.^[a]

Material	Y (MPa)	σ^{\max}	ϵ^R	Adhesion Force (MPa) ^[b]
		(MPa)	(%)	
A	663.5 ± 98.9	26.3 ± 1.3	20.8 ± 9.7	3.70 ± 0.87
B	345.6 ± 63.8	10.2 ± 1.1	16.9 ± 5.8	2.30 ± 0.79
C	758.5 ± 78.4	17.8 ± 1.3	3.3 ± 0.2	1.91 ± 0.42

[a] For more experimental details, see the ESI†. A = PCO:Jeff 1:1, B = PCO+DGEBA (50/50):Jeff 1:1, and C = PCO+DGEBA (20/80):Jeff 1:1. Y represents the elastic modulus, σ^{\max} is the maximum tensile strength, ϵ^R is the elongation at rupture. [b] Values correspond to rupture type -Y: Cohesive failure (adhesion > cohesion).

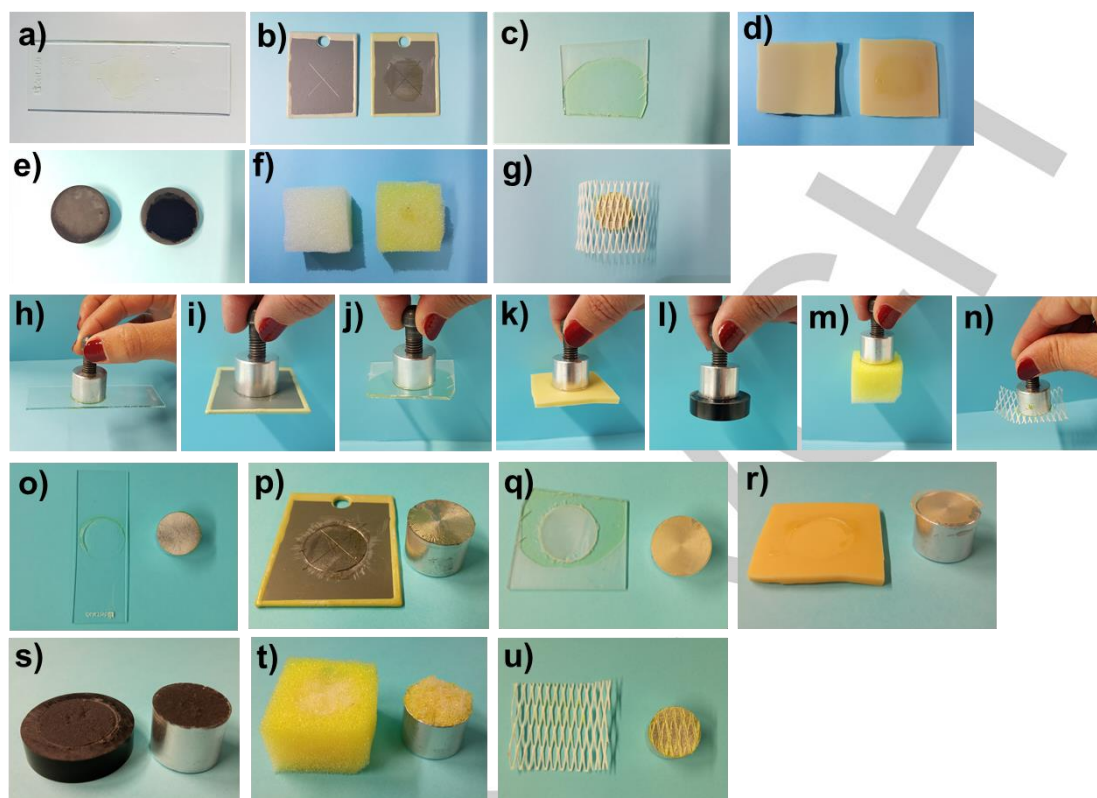


Figure 3. Photographs of PCO:Jeff 1:1 based films deposited onto different substrates and after applying a curing process: a) glass slide; b) coated metallic panel; c) LDPE sheet; d) vulcanized rubber; e) epoxy disk; f) polystyrene foam; and g) polypropylene mesh. (h-n) Photographs of samples stuck to the dolly fixture. (o-u) Photographs of samples and dolly detached after the pull-off test.

Taken together, the good adhesion force and mechanical performance of the 1:1 PCO:Jeff blend, the new biobased epoxy resin PCO represents a promising and interesting alternative to the classical synthetic adhesives used in industry.

Conclusion

This work has clearly demonstrated that a high quality thermoset adhesive can be obtained from a new biobased epoxy resin (PCO) prepared in few steps from a readily available terpene feedstock. The good film forming properties of the new biobased thermoset at room temperature and under stoving conditions, combined with the excellent thermal properties allowed to explore it in solvent-based adhesive applications. The adhesive strength and a lower degree of brittleness further add to the relative mechanical properties, compared to classical formulations based on DGEBA. Moreover, formulations of pure PCO:Jeff 1:1 have been shown to stick to a broad range of substrates (glass, metal and plastics) with flat and complex architectures.

The (partial) replacement of fossil-fuel derived DGEBA by biobased PCO is important in the context of developing polymer applications for adhesive and coating materials with a lower carbon footprint. Obviously, a balance between the chemical properties and scalability for biobased epoxies remain key aspects for commercial exploitation. Therefore, despite the

potential described herein, more investigation is required to examine the chemical/solvent resistance of PCO-derived thermosets.

Experimental Section

Synthesis of terpolymeric poly(carbonate) (PC)

A mixture of *cis/trans* (4*R*)-1-methyl-4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptane (LO) (16.4 g, 17.7 mL, 1 equiv, 108 mmol) and 3-vinyl-7-oxabicyclo[4.1.0]heptane (VCHO) (1.34 g, 0.1 equiv, 10.8 mmol) was azeotropically distilled with 2 mL of dry toluene prior to addition into a Teflon vessel equipped with a cross-shaped magnetic stirring bar containing the catalyst [Al^{Me}]₃ (651 mg, 95 wt. %, 0.0111 equiv, 1.20 mmol), bis(triphenylphosphine)iminium chloride (PPNCl, 344 mg, 0.00556 equiv, 600 μmol) and a further 3 mL of dry toluene. The teflon vessel was placed in a 45 mL stainless steel reactor and purged three times with 5 bar of CO₂. Finally, the pressure was stabilized at 15 bar of CO₂ at room temperature (r.t.). After placing the reactor in a metal heating block, the reactor was heated to an inside temperature of 45 °C (55 °C outside temperature) for 68 h at 600 rpm. The reaction was stopped by cooling down the reactor to r.t. and depressurization. The crude was dissolved in dichloromethane (DCM) and a sample was taken for ¹H NMR analysis. Around 68% conversion of limonene oxide (LO) and full conversion of the vinyl epoxide was observed under these conditions. The crude was concentrated to around 40 mL, transferred to an addition funnel and poured into a flask containing acidic methanol (400 mL MeOH + 40 mL 12 M HCl). A sticky,

yellow solid was formed that could not be filtered. Instead the liquid was removed by decantation and the remaining solid was washed with some MeOH. Afterwards the solid was dried in a rotational evaporator to give a yellow foam with a yield of 62% (14.2 g). The experimental conditions and the complete synthesis of PC is provided in Scheme S1 (SI). $^1\text{H NMR}$ (300 MHz, chloroform- d) δ 5.88–5.65 (bs, 0.1H), 5.09 (d, J = 19.5 Hz, 1H), 4.94–4.85 (m, 0.1H), 4.85–4.59 (m, 2H), 2.53–2.30 (m, 1H), 2.30–2.12 (m, 1H), 1.98–1.80 (m, 2H), 1.80–1.67 (m, 4H), 1.67–1.53 (m, 2H), 1.53–1.43 (m, 2H), 1.43–1.27 (m, 1H) ppm. M_n = 3.85 kDa, M_w = 5.33 kDa, D = 1.38. T_g = 74.5°C; T_d^5 = 223°C; T_d^{max} = 242°C. Further details are provided in the SI.

Synthesis of biobased poly(limonene carbonate)epoxy (PCO)

In a typical procedure, PC (12.5 g, 1 equiv, 56.3 mmol) was dissolved in DCM (200 mL) and the flask placed in a water bath. 3-Chlorobenzoperoxoic acid (*m*CPBA, 17.1 g, 77 wt. %, 1.30 equiv, 73.2 mmol) was added portion-wise as a solid. Stirring was continued for 20 h at 25°C. The formed suspension was filtered and then 120 mL of a saturated aqueous Na_2SO_3 solution was added under vigorous stirring for 30 min to quench the excess of *m*CPBA. The phases were separated and saturated NaHCO_3 solution was added to the organic phase under vigorous stirring. After phase separation, the organic phase was washed with brine, dried over MgSO_4 and all volatiles were removed under vacuum. The polymer was additionally purified by precipitating it from MeOH/DCM. The solid was then dried under vacuum to provide the desired compound as a white solid (12.4 g, 92%). The epoxidation level obtained was 96% as determined by signal integration. $^1\text{H NMR}$ (300 MHz, chloroform- d) δ 5.21–4.97 (m, 1H), 4.97–4.85 (m, 0.2H), 4.85–4.74 (m, 0.2H), 2.87–2.71 (m, 0.5H), 2.71–2.49 (m, 3H), 2.49–2.16 (m, 1H), 2.04–1.80 (m, 2H), 1.80–1.52 (m, 8H), 1.52–1.44 (m, 3H), 1.34–1.15 (m, 5H) ppm; M_n = 4.17 kDa, M_w = 5.88 kDa, D = 1.41. T_g = 132°C; T_d^5 = 223°C; T_d^{max} = 250°C. Further details are provided in the SI.

Further experimental details, including the experimental set-up for the film-making and manipulation are described in the Supporting Information.

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Conflict of Interest

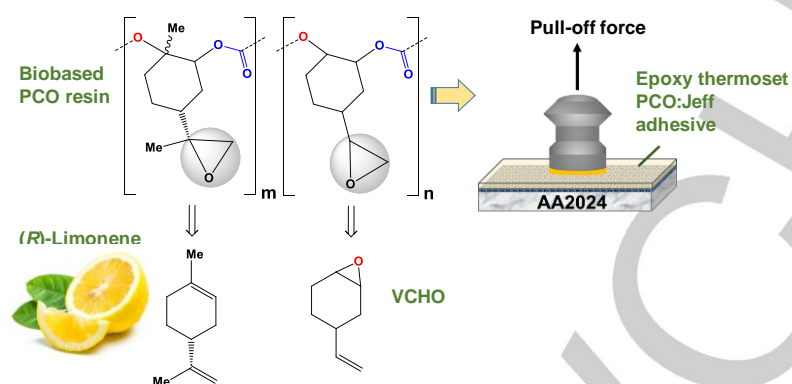
Results presented in this work is part of a European Patent (EP21383139.9), which owners are UPC, ICIQ and ICREA research centers.

Keywords: adhesives • biobased epoxies • limonene • polycarbonate • thermosets

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[1] Markets and Markets Research Private Ltd., Flexible Epoxy Resin Market by Type, 2021.

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Bio-glued: A biobased epoxy-resin derived from a poly(limonene carbonate) terpolymer (PCO) is reported together with its treatment with polyoxypropylenediamine (Jeff) as a curing agent. The cured polymer shows attractive adhesive properties and a lower degree of brittleness compared against the use of a fossil fuel based epoxy demonstrating thus good potential as a bio-substitute.

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