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DUAL-CURED THERMOSETS BASED ON EUGENOL DERIVATIVES AND THIOL CHEMISTRY

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Prof. Remzi Becer

Tarragona, August 17th2023

Dear Prof. Becer:

With this, I submit our manuscript entitled "*Dual-cured thermosets based on eugenol derivatives and thiol chemistry*" to be considered for publication in European Polymer Journal.

Recently, great attention has been paid to using bio-based monomers to prepare materials with good characteristics. This is still one of the critical points as the alternative to petrol-based ones. Moreover, dual-curing methodologies, based on click reactions, have been recently implemented in many fabrication technologies since it facilitates processing.

The present manuscript is of significant interest, from our point of view, since the preparation of these sustainable thermosets has been done by including: a) the use of bio-based monomers chemically modified through green methodologies, b) the adoption of dual curing through click-type reactions to implement more efficient manufacturing processes, avoiding waste generation during fabrication. This work combines two click reactions in the dual curing process: thio-Michael addition and thiol-epoxy. Both occur under thermal conditions, but the thiol-epoxy reaction only starts at high temperatures, which allows the obtention of stable intermediate materials. By changing the composition of the formulations, viscous or gelled intermediate materials have been obtained.

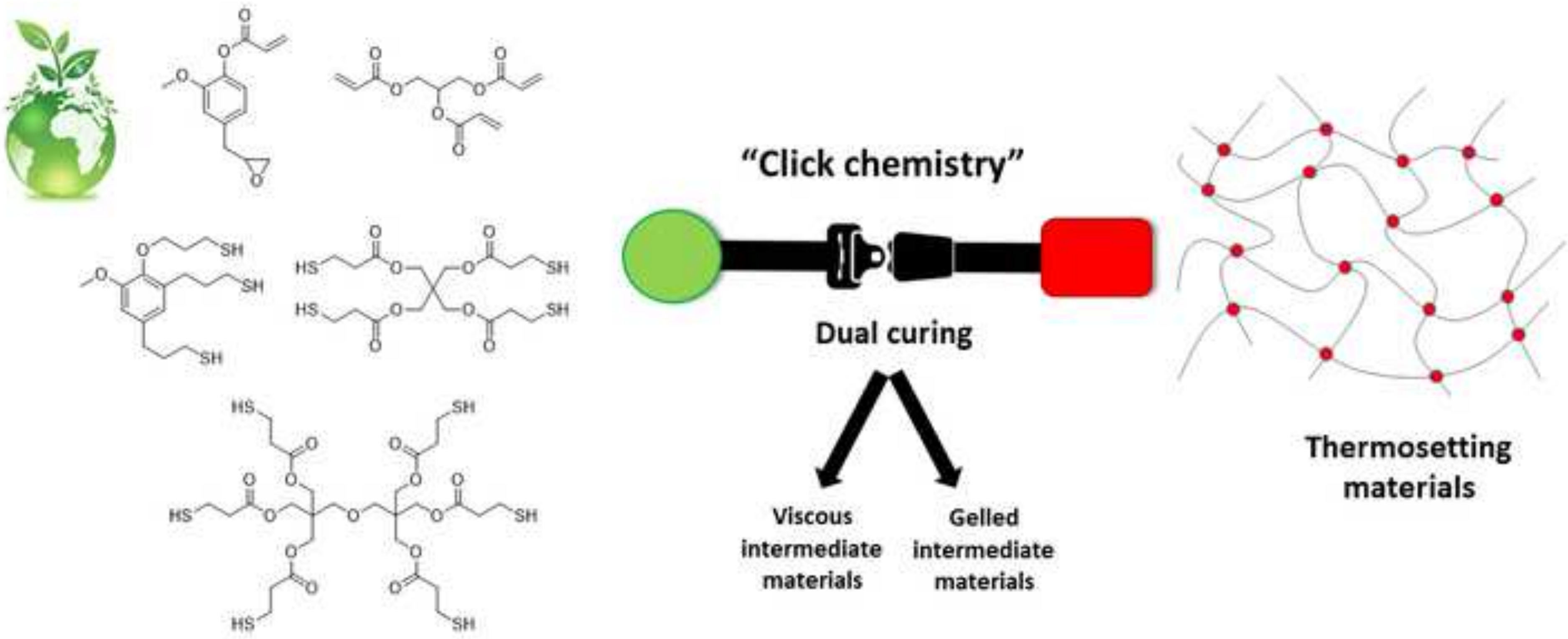
We thank you for considering our submission.

Looking forward to your reply, I send my best regards.

Prof. Angels Serra

Highlights

- Eugenol has been used as the bio-based monomer
- A new thermal dual-curing procedure has been implemented
- Thio-Michael and thiol-epoxy were the two click reactions used in the curing process
- The change in the formulation allows for obtaining viscous and gelled intermediate materials


"Click chemistry"
Dual curing
Viscous intermediate materials
Gelled intermediate materials
Thermosetting materials

DUAL-CURED THERMOSETS BASED ON EUGENOL DERIVATIVES AND THIOL CHEMISTRY

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KEYWORDS: biobased, eugenol, dual-curing, thio-Michael, thermosets

Abstracts

This paper aims to increase sustainability in thermosetting polymeric fields using bio-based monomers and environmentally friendly processing technologies based on dual-curing. Eugenol has been transformed into acrylate epoxy eugenol (AEEU) that can participate in thio-Michael additions and thiol-epoxy reactions. These reactions constitute the first and second steps of the sequential dual-curing process. A basic catalyst has been added to favor the kinetics of the curing process. We have selected three thiols with functionalities 3, 4, and 6, the first is derived from eugenol, and the others are derived from pentaerythritol, all can be obtained from renewable resources. To tailor and improve the intermediate material characteristics in the dual-curing process, we have added the triacrylate of glycerol. By changing its proportion, a liquid or a rubbery solid can be obtained as an intermediate, which allows a significant number of application technologies. Rheology, DSC, and FTIR were used to follow the evolution of both curing steps and to confirm the sequential character of the dual-curing. The thermal

characteristics of intermediate and final materials have been evaluated by TGA and DMTA. Tensile tests at break were performed to evaluate the mechanical properties.

1. INTRODUCTION

Eugenol is a natural antimicrobial and analgesic compound used as a fragrance and flavoring additive in the cosmetics and food industry. Moreover, it has interesting pharmacologic properties such as antioxidant, antispasmodic, antidepressant, and anticarcinogenic, etc [1,2]. The particular structure and commercial availability of eugenol have turned the natural product into an exciting feedstock for building bio-based polymers that can substitute petrol-based ones in a more environmentally friendly manner.

There are many publications on the use of eugenol in the synthesis of thermosets [3-8].The chemistries implied in their preparation are quite varied because of the functionality of the eugenol molecule with a phenol and an allyl group that can be further modified. Thiol-ene reactions, taking advantage of the allyl group, and the possibility to transform the phenol into the allyl ether, have been proposed in the preparation of adhesives [9]. Moreover, homopolymerization of acrylic derivatives have been explored in the preparation of dental materials [10]. Also, bisbenzoxazines [11] and bismaleimides [12] were prepared and polymerized obtaining high-performance thermosets. However, most of the thermosetting derivatives of eugenol are based on the chemistry of the epoxy groups, introduced in the phenol function as glycidyl ether [13], by epoxidation of the allyl group [5,8,14] or both [15,16].

Dual curing is a practical and versatile methodology to prepare thermosets by combining two different polymerization processes simultaneously or sequentially, which can be activated by different stimuli such as temperature or UV light or by applying different reaction conditions. When the functionality of the monomers is adequate, this process leads to thermosets and can be applied in multi-stage or advanced fabrication technologies [17]. For the sequential dual curing, the control of the polymerization sequence is relevant. It is advantageous in front of the

B-stage process since the control of the first and second steps is based on the composition of the formulation and not to tight time-temperature conditions. Thus, in sequential dual curing, the reactions involved in both stages must be well controlled; for this reason, click reactions are preferred. According to the formulation's composition, the intermediate material's characteristics can be tailored as desired. It can be a conformable solid or a viscous liquid, depending on the application of this material in the following fabrication steps. In this way, higher flexibility can be reached during the fabrication of the devices, which usually leads to less waste material and reduces the processing energy costs, making this process more environmentally friendly.

There are a great number of click reactions used in the synthesis of thermosets such as nucleophilic attack to epoxides [18,19], Michael addition [20,21], photoinitiated thiol-ene and thiol-ine additions [22,23], thiol-isocyanate addition [24], Diels-Alder and azide-ine cycloadditions [25,26], as the more extended. The most relevant characteristic of click reactions in the dual-curing procedure is their orthogonality [27]. This allows both polymerization reactions to occur independently with a temporal control and well-defined and predictable characteristics of the intermediate material. Moreover, the possibility of being performed in an air atmosphere without solvents and soft conditions is also advantageous technologically.

In previous work in our group, we applied a dual-cured methodology for preparing thermosets based on eugenol derivatives [28]. We combined a UV-initiated thiol-ene with a thermal thiol-epoxy starting from diallyl epoxy eugenol and various thiol derivatives. Although the first thiol-ene process was UV-initiated and the second thiol-epoxy was thermal, we could not observe a clean sequential character since the first thiol-ene process did not reach completion, and the photochemical and thermal processes partially overlapped. This was attributed to stabilized allyl-benzylic radicals forming in the eugenol structure with low reactivity.

In the present work, we synthesized epoxy eugenol acrylate (AEEU) to react with multifunctional thiols with different structures and functionalities. The dual-curing process is constituted by a thio-Michael addition occurring at low temperatures followed by a thiol-epoxy reaction in the second step at higher temperatures. It is worth commenting that thermal triggering is more convenient for thick and complex-shaped samples because it is more uniform than photoinitiation, and vitrification of the final material, which can occur in photopolymerized samples, is avoided. Since AEEU is monofunctional in the thio-Michael reaction and the aim is to reach a networked structure during the first step, different proportions of the triacrylate of glycerol have been added. By selecting the proper proportion of this glycerol derivative, the characteristics of the intermediate material, viscous or rubbery, have been tailored. The fact that the multifunctional thiol monomer participates in both polymerization reactions hinders exudation or bleeding. The intermediate and final materials have been characterized by thermal, mechanical and thermomechanical analysis, and the gelation time during the first or second step by rheology.

2. EXPERIMENTAL SECTION

2.1. Materials

Eugenol (EU, 99%), *m*-chloroperbenzoic acid (MCPBA, 70-75%), sodium bicarbonate ($NaHCO_3$, 99%), glycerol (Gly, 98%), 1-methyl imidazole (1MI, 99%), and sodium chloride (NaCl, 99%) were purchased from Thermo Scientific. Acryloyl chloride (≥97%), *candida antarctica* lipase B (CALB), methyl acrylate (MA, 98%), allyl bromide (97 %), thioacetic acid (TAA), 2,2-dimethoxy-2-phenylacetophenone (DMPA), and oxone were obtained from Sigma Aldrich. Triethylamine (TEA), *tert*-butanol (*t*BuOH), methyl *tert*-butyl ether (M*t*BE) and sodium disulfite ($Na_2S_2O_5$) were purchased from Scharlau, and triethyl benzyl ammonium chloride (TEBAC, 99%) from Alfa Aesar. Pentaerythritol tetrakis (3-mercapto propionate) (S4, 98%, 122.17 g/eq) and dipentaerythritol hexakis (3-mercapto propionate) (S6, 98%, 130.5 g/eq) were kindly supplied from Bruno Bock

Thiochemicals and used as received. All chemicals were used without any purification except CALB that was put in a desiccator under vacuum overnight with anhydrous $MgSO_4$.

2.2. Synthesis of eugenol acrylate (AEU)

EU (10.0 g, 61 mmol) and TEA (13 mL, 71.4 mmol) were dissolved in 30 mL of anhydrous dichloromethane (DCM) under inert conditions. The solution was cooled down to 0-5 °C and stirred for 30 min before adding dropwise acryloyl chloride (5.9 mL, 71.4 mmol) dissolved in 10 mL of dry DCM. The reaction was allowed to proceed for 24 h at room temperature. Then, the reaction was vacuum filtered and washed once with HCl 1M (100 mL), twice with saturated $NaHCO_3$ solution (100 mL), and finally with saturated NaCl solution (100 mL). The organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed in a rotary evaporator to afford AEEU as a yellowish viscous oil (12.6 g, 95%). ^{1}H NMR ($CDCl_3$, δ in ppm): 6.99 (d, 1H); 6.79 (m, 2H); 6.61 (dd, 1H); 6.35 (dd, 1H); 6.00 (dd, 1H); 5.99 (m, 1H); 5.11 (m, 2H); 3.81 (s, 3H); 3.39 (d, 2H) (see Figure S1). ^{13}C NMR ($CDCl_3$, δ in ppm): 164.29, 150.95, 139.09, 137.82, 137.07, 132.42, 127.70, 122.53, 120.71, 116.18, 112.81, 55.88, 40.12 (see Figure S2).

2.3. Synthesis of acrylate epoxy eugenol (AEEU)

The synthesis of AEEU was performed in two different ways. Here, we described the one using oxone as a reagent. The other one can be seen in the SI. AEU (1 g, 4.60 mmol), acetone (47.0 mL, 0.64 mol), H_2O (25 mL), ethyl acetate (50 mL), TEBAC (0.21 g, 0.92 mmol), and $NaHCO_3$ (16.9 g, 0.20 mol) were added in a 500 mL three-necked flask and stirred for 5 minutes and cooled down to 0-5 °C. Then, oxone (22.5 g, 73.3 mmol) in portions of 7.15 g diluted in 50 mL of H_2O was added every day for 2 days. The mixture was allowed to react another day at 0-5 °C. Then, the organic product was extracted with diethyl ether (3 x 100 mL), and the organic layer was washed with H_2O twice, dried over anhydrous $MgSO_4$, and the solvent removed in the rotary evaporator obtaining AEEU as a yellowish solid (0.86 g, 80%). Melting point was 62.2 °C (by DSC). ^{1}H NMR ($CDCl_3$, δ in ppm): 7.01 (d, 1H); 6.85 (m, 2H); 6.60 (dd, 1H); 6.35 (dd, 1H); 6.00 (dd, 1H);

3.82 (s, 3H); 3.16 (m, 1H); 2.85 (d, 2H); 2.81 (dd, 1H); 2.56 (dd, 1H) (Figure 1). ^{13}C NMR ($CDCl_3$, δ in ppm): 164.22, 151.04, 138.32, 136.32, 132.53, 127.63, 122.70, 121.12, 113.27, 55.93, 52.34, 46.84, 38.69 (Figure 2). FTIR (ATR): 1737 cm^{-1} (C=O acrylate); 1636 cm^{-1} (C=C acrylate); 1600 cm^{-1} (aromatics); 825 cm^{-1} (epoxide) (Figure S3).

2.4. Synthesis of glycerol triacrylate (GTA)

The synthesis of GTA was performed in two different ways. Here, the one using CALB is described while the other route is described in the SI. In a 250 mL two-necked round bottom flask equipped with a magnetic stirrer and a Soxhlet system with glass wool, activated 4 Å molecular sieves, and a condenser, glycerol (1 g, 10.9 mmol) was mixed with 80 mL of M*t*BE/*t*BuOH (1:1 v/v). Then, MA (14.7 mL, 0.2 mol) was added, the mixture heated until reflux, and the Soxhlet drained 4 times. Next, CALB (200 mg, 20% w/w to Gly) was added, and the mixture was kept for 24 h at reflux. Afterward, the mixture was vacuum filtered and washed twice with 1 M NaOH solution. The organic phase was dried with anhydrous $MgSO_4$ and filtered, and the solvent and the excess of MA were removed in a rotary evaporator yielding GTA as a brownish viscous oil (30%). ^{1}H NMR ($CDCl_3$, δ in ppm): 6.45 (dd, 1H); 6.15 (dd, 1H); 5.88 (dd, 1H); 4.27 (m, 4H); 4.18 (m, 1H) (Figure S4). ^{13}C NMR ($CDCl_3$, δ in ppm): 165.55, 165.13, 131.94, 131.74, 127.75, 127.68, 69.16, 62.33 (Figure S5).

2.5. Synthesis of the triallyl derivative of eugenol (DAllylEU)

DAllylEU was prepared by a reported procedure [9]. The synthesis went through the allylation of eugenol in a basic medium to obtain O-allyl eugenol (OAllylAEU) (Figure S6 and S7). By heating the previous product, a Claisen rearrangement led to 6-allyleugenol (6-AllylAEU) (Figure S8 and S9). This product was finally allylated to obtain the 6-allyl O-allyl eugenol (DAllylEU) (see supporting information).

^{1}H NMR ($CDCl_3$, δ in ppm): 6.7 s (Ar, 2H), 6.05 m (-CH=,1H), 5.90 m (-CH=, 2H), 5.34 dd (CH_2=, 1H), 5.19 dd (CH_2=, 1H), 5.15-5.0 m (CH_2=, 4H), 4.46 d (-CH_2-O-, 2H), 3.87 s (CH_3-O-, 3H), 3.38 d (-CH_2-Ar, 2H), 3.31 d (-CH_2-Ar, 2H) (Figure S10).

^{13}C NMR ($CDCl_3$, δ in ppm): 152.6, 144.1, 137.5, 137.3, 135.7, 134.5, 133.7, 121.7, 117.0, 115.8, 115.5, 110.5, 73.7, 55.7, 40.1 and 34.3 (Figure S11).

FTIR (ATR): 3072, 3018, 2901, 2825, 1637, 1583, 1510, 1451, 1418, 1256, 1230, 1141, 1026, 986, 907, 804 and 752 cm^{-1}.

2.6. Synthesis of the trithiol derivative of eugenol (3SHEU)

2.6.1. Photochemical thiol-ene reaction (SAcEU)

The synthesis followed a reported procedure [28]. A mixture of 5 g (20.5 mmol) of DAllylEU, 22.2 g (291.6 mmol) of TAA and 0.1290 g (0.50 mmol) of DMPA were photoirradiated with a UV lamp at 356 nm for 1 h. The product obtained was dissolved in $CHCl_3$, extracted with a saturated NaOH solution, washed with water, and dried over anhydrous $MgSO_4$. The solvent was eliminated on a rotary evaporator. The product obtained was a viscous liquid with 96 % yield.

^{1}H NMR ($CDCl_3$, δ in ppm): 6.52 s and 6.50 s (Ar, 2H), 3.91 t (-CH_2-O-, 2H), 3.80 s (CH_3-O-, 3H), 3.10 (-CH_2-S-, 2H), 2.85 m (-CH_2-Ar, 4H), 2.56 m (-CH_2-S-, 4H), 2.31 s (CH_3-CO-S-, 9H), 1.99 m (-CH_2-CH_2-CH_2-O-, 2H), 1.8 m (-CH_2-CH_2-CH_2-Ar, 4H) (Figure S12).

^{13}C NMR ($CDCl_3$, δ in ppm): 195.7, 195.6, 195.5, 152.3, 143.9, 136.6, 134.5, 121.4, 110.3, 70.0, 55.5, 34.5, 31.0, 30.5, 30.3, 30.2, 29.1, 28.7, 28.4 and 25.8. (Figure S13).

FTIR (ATR): 2930, 2825, 1680, 1587, 1505, 1460, 1424, 1355, 1260, 1232, 1135, 1010, 950, 800 and 607 cm^{-1}.

2.6.2. Hydrolysis of SAcEU (3SHEU)

9.31 g (19.7 mmol) of SAcEU were dispersed in 100 mL of methanol in a flask with magnetic stirring and then 1.70 g (42.5 mmol) of pulverized NaOH were added. The mixture was heated to reflux temperature under inert atmosphere for 5.5 h. The solution was cooled and the solvent was removed. The product obtained was dissolved in HCl acidic water solution and extracted with $CHCl_3$. Then washed with distilled water and dried over anhydrous $MgSO_4$. The product obtained was a pale-yellow viscous liquid with 84 % yield.

^{1}H NMR ($CDCl_3$, δ in ppm): 6.56 s (Ar, 2H), 3.98 t (-CH_2-O-, 2H), 3.82 s (CH_3-O, 3H), 2.77 q (-CH_2-S-, 2H), 2.61 m (-CH_2-S-, 4H), 2.51 q (-CH_2-Ar, 4H), 2.1 m (-CH_2-CH_2-CH_2-O-, 2H), 1.85 m (-CH_2-CH_2-CH_2-Ar, 4H), 1.5 t (-SH, 1H), 1.35 t (-SH, 1H) and 1.33 t (-SH, 1H) (Figure S14).

^{13}C NMR ($CDCl_3$, δ in ppm): 152.2, 143.9, 136.7, 134.6, 121.5, 110.2, 70.3, 55.5, 35.3, 34.6, 34.3, 34.0, 28.5, 24.1, 23.8 and 21.2 (Figure S15).

FTIR (ATR): 2930, 2825, 2580, 1587, 1503, 1460, 1430, 1260, 1230, 1150, 1090, 1010, 950 and 830 cm^{-1}.

2.7. Preparation of the formulations

In a 20 mL vial, a certain amount of AEEU was added and melted at 70 °C for 10 minutes. Then, the corresponding amount of GTA was added and manually mixed with the melted AEEU. Later, the stoichiometric amount (SH:acrylate+epoxy = 1:1) of the corresponding thiol was added, followed by the addition of 5% mol/eq of thiol of 1MI. Finally, the mixture was vigorously stirred in an ice bath, poured into Teflon molds of 30 x 5 x 1.5 mm^3 dimensions and cured in an oven at 35 °C for 1 h (first curing step), 80 °C for 1h, 120 °C for 2 h and 150 °C for 1 h (second curing step). The materials were coded as polyX_Y, where X indicates the thiol used and Y is ascribed to the gelation of the intermediate material. As an example, polyS4_gel is a material in which S4 was used as the crosslinker and the intermediate material of the dual curing was gelled due to the fact that the gelation occurred in the first curing step. Table 1 shows the composition of the different formulations studied.

Table 1. Molar composition of the formulations prepared and acrylates ratio

Formulation	AEEU (% mol)	GTA (% mol)	3SHEU (% mol)	S4 (% mol)	S6 (% mol)	1MI (% mol to SH)	nGTA/nAEEU
poly3SHEU_gel	38.6	17.8	43.6	-	-	5	0.461
poly3SHEU_nogel	53.9	5.0	41.1	-	-	5	0.092
polyS4_gel	43.4	20.0	-	36.6	-	5	0.461
polyS4_nogel	60.2	5.6	-	34.2	-	5	0.092
polyS6_gel	49.4	22.7	-	-	27.9	5	0.459
polyS6_nogel	68.9	6.4	-	-	26.2	5	0.093

2.8. Characterization techniques

^{1}H NMR and ^{13}C NMR spectra were recorded using a Varian VNMR-S400 NMR spectrometer. $CDCl_3$ was used as a solvent. All chemical shifts are given in δ in part per million (ppm) using the signals of the solvent as internal standard (^{1}H NMR: $CDCl_3$ = 7.26 ppm; ^{13}C NMR: $CDCl_3$ = 77.16 ppm).

A Mettler DSC-3+ differential scanning calorimeter (DSC) was employed to study the curing process. It was calibrated using indium (heat flow calibration) and zinc (temperature calibration) standards. Samples of 8-10 mg were used and analyzed in aluminum pans with pierced lids in N_2 atmosphere with gas flow of 50 cm^3/min. Temperatures between -80 °C and 250 °C were scanned with a heating rate of 10 °C/min to characterize the curing process. The T_gs of the intermediate and final materials were determined with a heating rate of 20 °C/min. The reaction enthalpy (Δh) was obtained by integration of the the calorimetric heat flow signal (dh/dt) using a straight baseline using the STARe software.

FTIR spectra were recorded in a Jasco FT/IR-680 Plus with an attenuated total reflection accessory with thermal control and a diamond crystal (Golden Gate Heated Single Reflection Diamond ATR, Specac-Teknokroma) to confirm that the complete curing of the samples was achieved. Real-time spectra were collected in absorbance mode in the wavelength range 4000 to 600 cm^{-1} with a resolution of 4 cm^{-1}. 20 scans were taken and averaged for each spectrum. The disappearance of the absorbance peak at 1636 cm^{-1} corresponding to the stretching of the C=C bond of acrylates as well as the decrease of the thiol (S-H) peak at 2570 cm^{-1} were used to confirm that the first step of the curing was complete. The peak at 915 cm^{-1} corresponding to the epoxy group and the appearance of a peak at 3500 cm^{-1} related to the formation of OH groups by the thiol-epoxy reaction were used to confirm the completion of the second stage [29].

Thermomechanical properties were determined with a DMA Q800 (TA Instruments) using a film tension clamp. The samples (with dimensions of 30 x 5 x 1.5 mm^3) were tested with an amplitude of 10 µm and a frequency of 1 Hz in the temperature range from -30 °C to 200 °C with a heating rate of 2 °C/min.

TGA analyses were performed using a Mettler Toledo TGA2 thermobalance. Cured samples of about 10 mg were heated between 30 and 600 °C at a heating rate of 10 °C/min in nitrogen atmosphere with a gas flow of 50 cm^3/min.

The gelation time was determined using a rheometer ARES-G2 (TA Instruments) equipped with an electrical heated plate device (EHP) and 20 mm parallel plate geometry. The strain was set at 0. 05 % and the frequencies at 0.5, 1.75 and 3 Hz. Gel point was determined as the crossover of storage modulus (G') with the loss modulus (G'') at the three different frequencies. The procedure intends to simulate the curing in the oven: 35 °C for 1 h, temperature ramp from 35 to 80 °C at 3 °C /min, and 30 min at 80 °C.

The fully cured materials were tested in tensile until break using the DMA in static mode with 3 N/min of force ramp at 20 °c and applying 0.01 N as preload force.

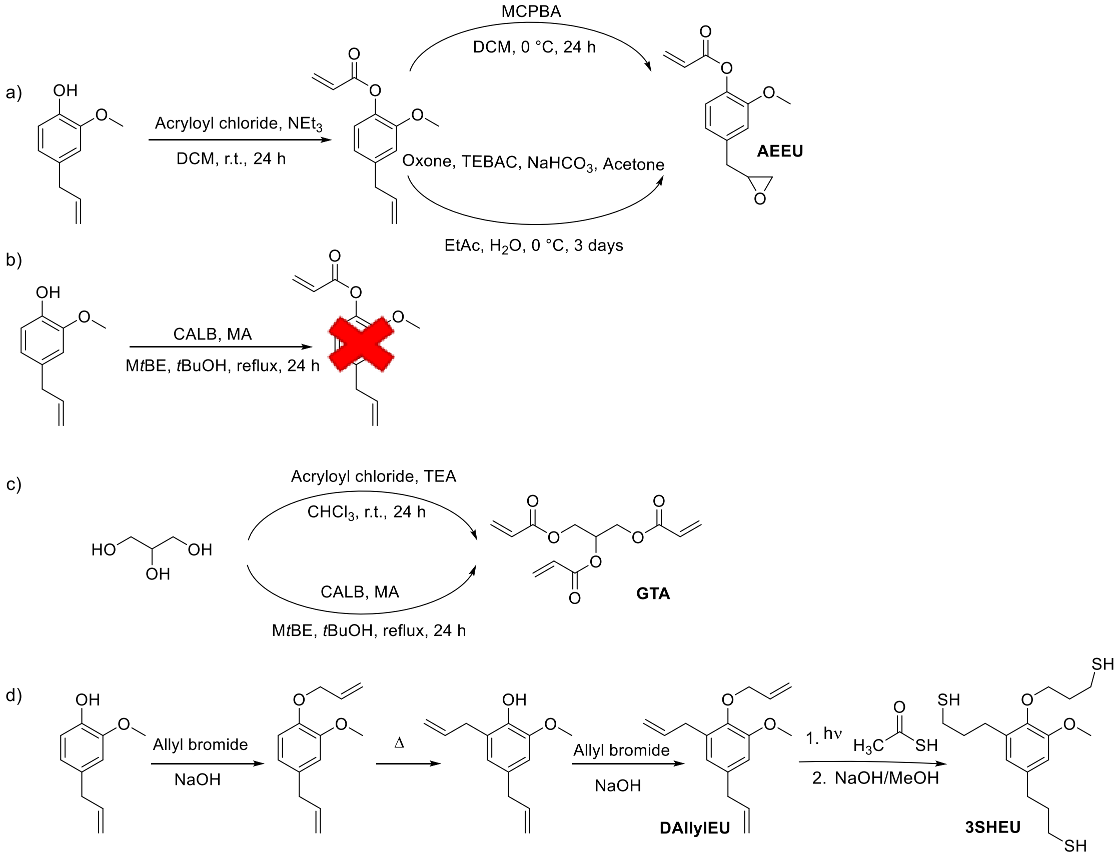
3. Results and discussion

3.1. Synthesis of the starting monomers

The epoxy acrylate of eugenol (AEEU) was synthesized *via* a high-yielding two-step procedure. The first step was the acylation reaction with acryloyl chloride in the presence of TEA, and the second was the epoxidation of the allylic group (Scheme 1a). The literature offers the alternative of using acrylic acid and dicyclohexyl carbodiimide (DCC) in the presence of a base. However, it was reported that this procedure yields only 30 % of the product and therefore it was not used [30]. As a more sustainable alternative to preparing eugenol acrylate, we tried the enzymatic esterification with CALB of eugenol with methyl acrylate following a reported procedure [31], but the desired product was not obtained (Scheme 1b). The reason for that is the phenolic character of the substrate since it is reported that the enzymatic reaction works only well with primary and secondary alcohols.

The quality of AEU was confirmed by ^{1}H NMR spectroscopy (see Figure S1) by the appearance of the acrylic protons between 6.61 and 6.00 ppm, whereas a carbonyl signal appears in the ^{13}C NMR spectrum at 164.29 ppm (see Figure S2).

The further epoxidation of the allyl group was done with MCPBA at 0 °C for 24 h, with a yield of 96 %. As a greener alternative, we tried to use Oxone to perform the epoxidation of the allyl group [32]. In this case, a biphasic system with TEBAC as a phase transfer catalyst was used, obtaining good yields of the desired product after 3 days (80%), demonstrating the possibility to synthesize AEEU more sustainably. The completion of the reaction was confirmed by the vanishment of the allyl signals between 6.00 and 5.11 ppm and the appearance of the epoxydic signals between 3.16 and 2.56 ppm in the ^{1}H NMR spectrum shown in Figure 1 and at 52.34 and 46.84 ppm in the ^{13}C NMR shown Figure 2. Both spectra confirm the purity of the product obtained. Moreover, FTIR spectroscopy presented the characteristic absorptions of the ester moiety, the stretching of the acrylate C=C bond, and the epoxy group at 1740, 1637, and 825 cm^{-1}, respectively.



Scheme 1. Synthetic routes to AEEU starting from eugenol (a, b), GTA starting from glycerol (c), and 3SHEU from eugenol.

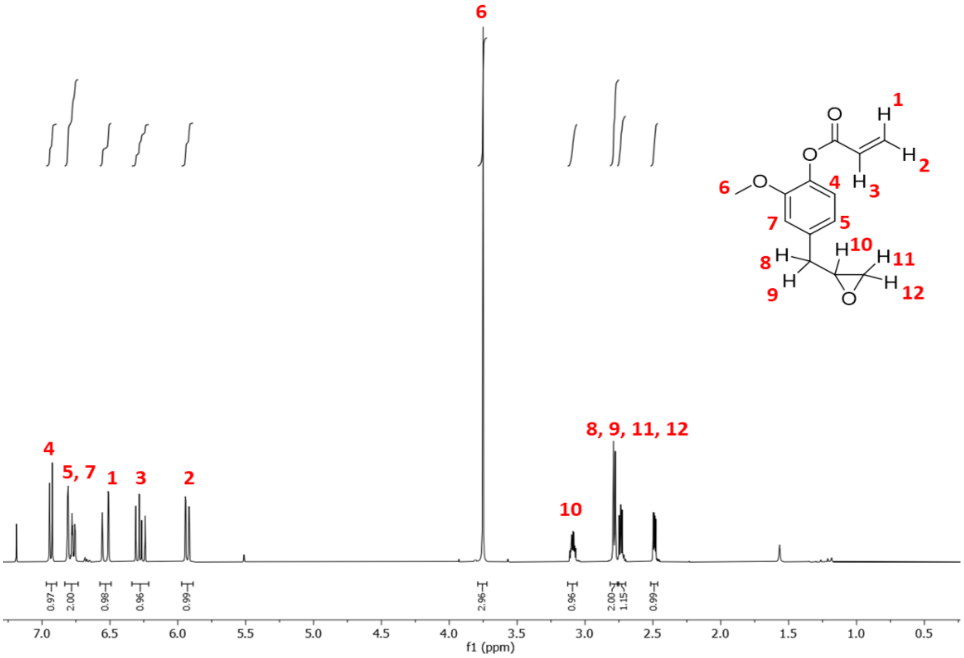


Figure 1. ^{1}H NMR spectrum of AEEU in $CDCl_3$

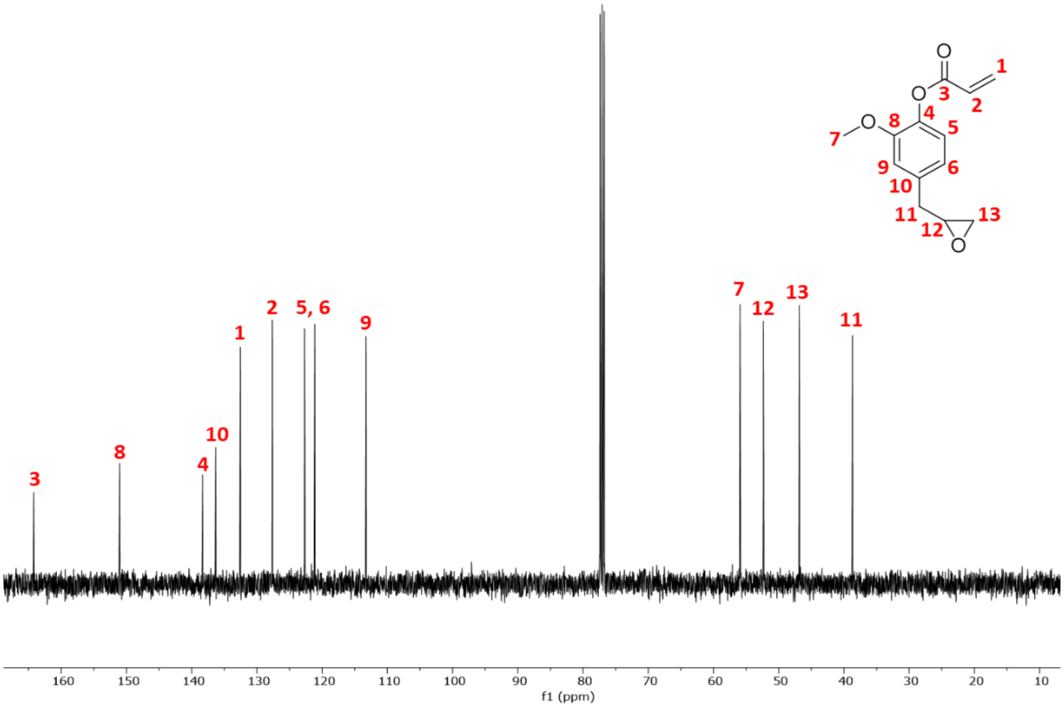


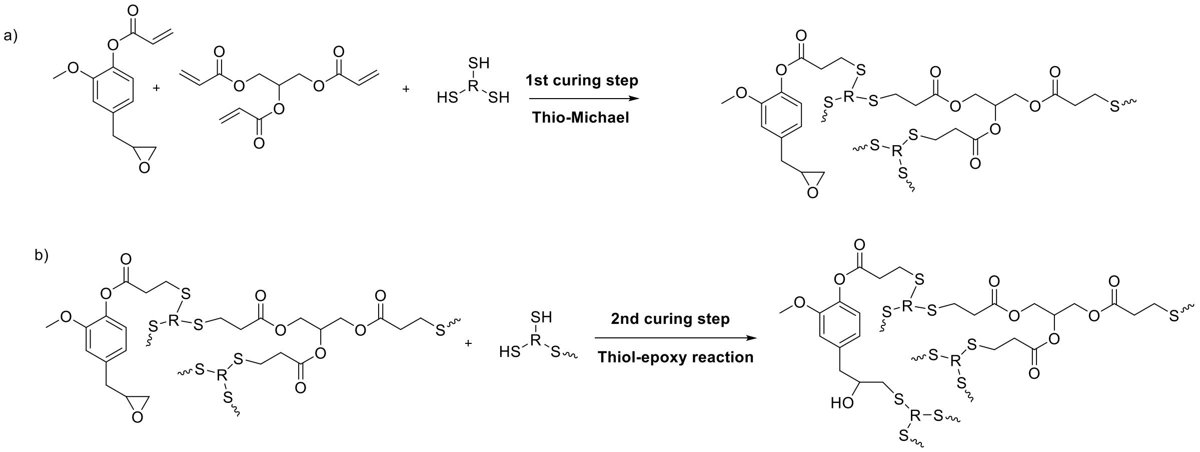
Figure 2. ^{13}C NMR spectrum of AEEU in $CDCl_3$

To synthesize GTA, the first approach tested was using acryloyl chloride and TEA in $CHCl_3$ as a solvent due to its higher polarity than DCM (Scheme 1c). The product was obtained in good yields (94 %). The structure and purity were confirmed by ^{1}H NMR by the appearance of the signals of the double bonds between 6.45 and 5.88 ppm (Figure S4) and the four signals between 127 and 133 ppm in its ^{13}C NMR spectrum (Figure S5). Despite this, the enzymatic CALB methodology could be used to acrylate the primary and secondary alcohols after 2 days of reaction in relatively low yields (30%) but proving that GTA can also be obtained in a green way.

The preparation of 3SHEU was performed as described in previous papers [28,33]. As seen in Scheme 1d, the process consists of a first allylation followed by a thermal Claisen rearrangement and a second allylation of the formed phenolic group, obtaining the triallyl derivative of eugenol. By a photoinitiated thiol-ene reaction with thioacetic acid and further saponification, 3SHEU was obtained and characterized by NMR spectroscopy. The spectra of intermediates and final materials are collected in the SI (Figures S6-S15). All spectra show the high purity of the corresponding products.

3.2. Study of the dual curing of the formulations

The curing procedure by the dual curing methodology includes, as the first step, the thio-Michael addition and the thiol-epoxy reaction as the second one. All formulations include 1-MI as the base catalyst that favors the nucleophilic character of the thiol by forming thiolate groups. Both reactions are represented in Scheme 2. Since in the thio-Michael addition, AEEU acts as a monofunctional monomer, the addition of a multifunctional acrylate is needed to get a network or an oligomeric product, depending if the intermediate material is gelled or not. In our case, we selected triacrylate derived from glycerol because of its bio-based character and its compact structure. As thiols, the trifunctional derivative of eugenol has been selected, and the tetra and hexa functional derivatives of pentaerythritol were also tested. These last thiols were commercially available, but they could be also synthesized from bio-based pentaerythritol [34].



Scheme 2. Chemical processes occurring in the first and second steps of the dual curing.

From both reactions, the thio-Michael addition is the most favored from the kinetics point of view, and it begins at room temperature during the first curing step. However, to ensure that this reaction has been completed, the curing mixture was maintained at 35 °C in an oven for 1 h. Once the thio-Michael reaction has been completed, the thiol-epoxy reaction can proceed at higher temperatures. Thus, the curing mixture was then cured in an oven using the following curing schedule: 80 °C for 1h, 120 °C for 2 h, and 150 °C for 1 h. We could prove by FTIR that in these conditions, the first and the second step were completed and well-differentiated. For example, Figure 3 shows the FTIR spectra of the intermediate and final material recorded for the polyS6_gel formulation.

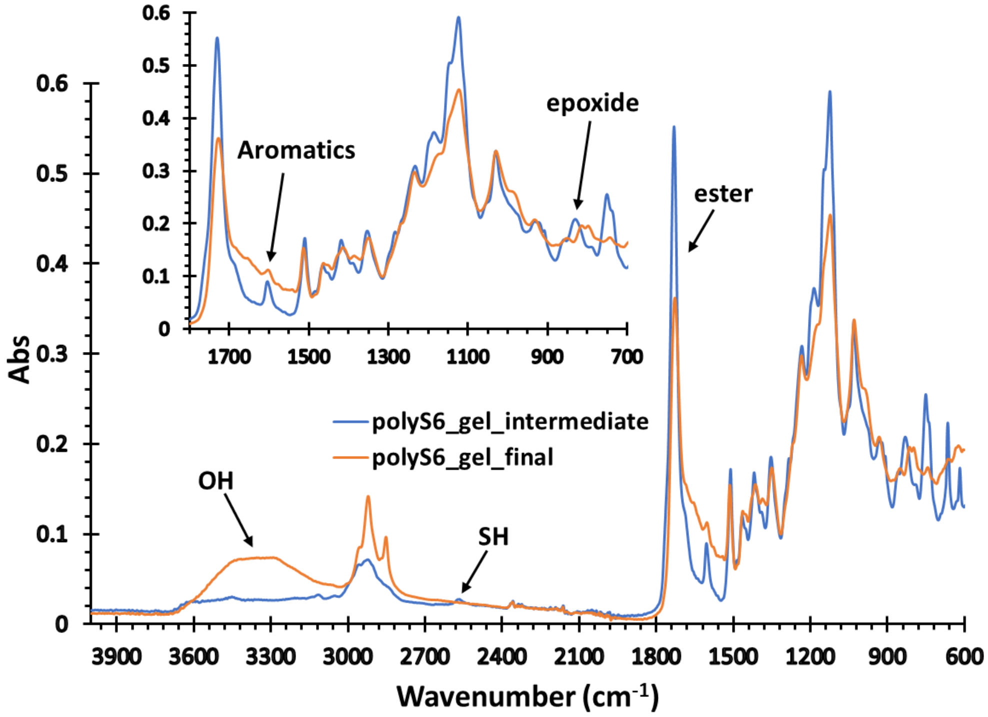


Figure 3. FTIR spectra of the intermediate and final materials obtained in the curing of the polyS6_gel formulation.

Dual curing can be applied to advanced manufacturing processes mainly due to the possibility of tailoring the characteristics of the intermediate material. Thus, the intermediate can be a viscous liquid, and in this case, it can be used as a coating or an adhesive, or it can be a moldable solid that can be further processed to lead to complex shapes, as we could demonstrate in previous works in this topic [17,28,29,35]. The tailoring of these characteristics is done by the composition of the formulation, being the proportion of GTA, the one that defines if the formulation gels during the first or the second step. It is worth noting that no free monomers are left after the first step is completed since AEEU participates in both processes as the thiols do. It means no dripping or exudation of monomers will occur during the storage of the intermediate material.

The use of the Flory-Stockmayer equation (Eq. 1) allows the calculation of the amount of GTA necessary to gel [36,37]. The theoretical conversion of the acrylate groups at the gel point α_{gel} during the thio-Michael reaction can be calculated by Eq. 1, assuming an ideal random step-wise reaction.

$$\alpha_{gel}^{theor} = \sqrt{\frac{r}{(f_1-1)\cdot(f_2-1)}} \qquad \text{(Eq. 1)}$$

where r is the thiol/acrylate equivalent ratio, f_1 the acrylate monomer functionality and f_2 the thiol functionality. Since the functionality of the thiols tested are 3, 4 or 6, we obtained three different values of α_{gel}, each one for each thiol.

By this equation, the critical molar ratio nGTA/nAEEU = 0.287 was obtained as the lowest to achieve gelation at complete conversion of acrylate moieties. Thus, two different possibilities were studied: a) a molar ratio nGTA/nAEEU = 0.46, in which gelation will occur before full conversion to obtain a solid-like intermediate material, and b) a molar ratio nGTA/nAEEU = 0.09, where gelation will not occur in the first step and a viscous-like intermediate material will be obtained.

Rheological measurements confirmed that gelation occurs in the first or second curing step, according to the formulation composition. The formulation is transformed into a solid-like material in the gelation, and the storage modulus (G’, solid contribution) becomes higher than the loss modulus (G’’, liquid contribution). Figure 4 represents the storage and loss moduli evolution with temperature for all the formulations prepared herein.

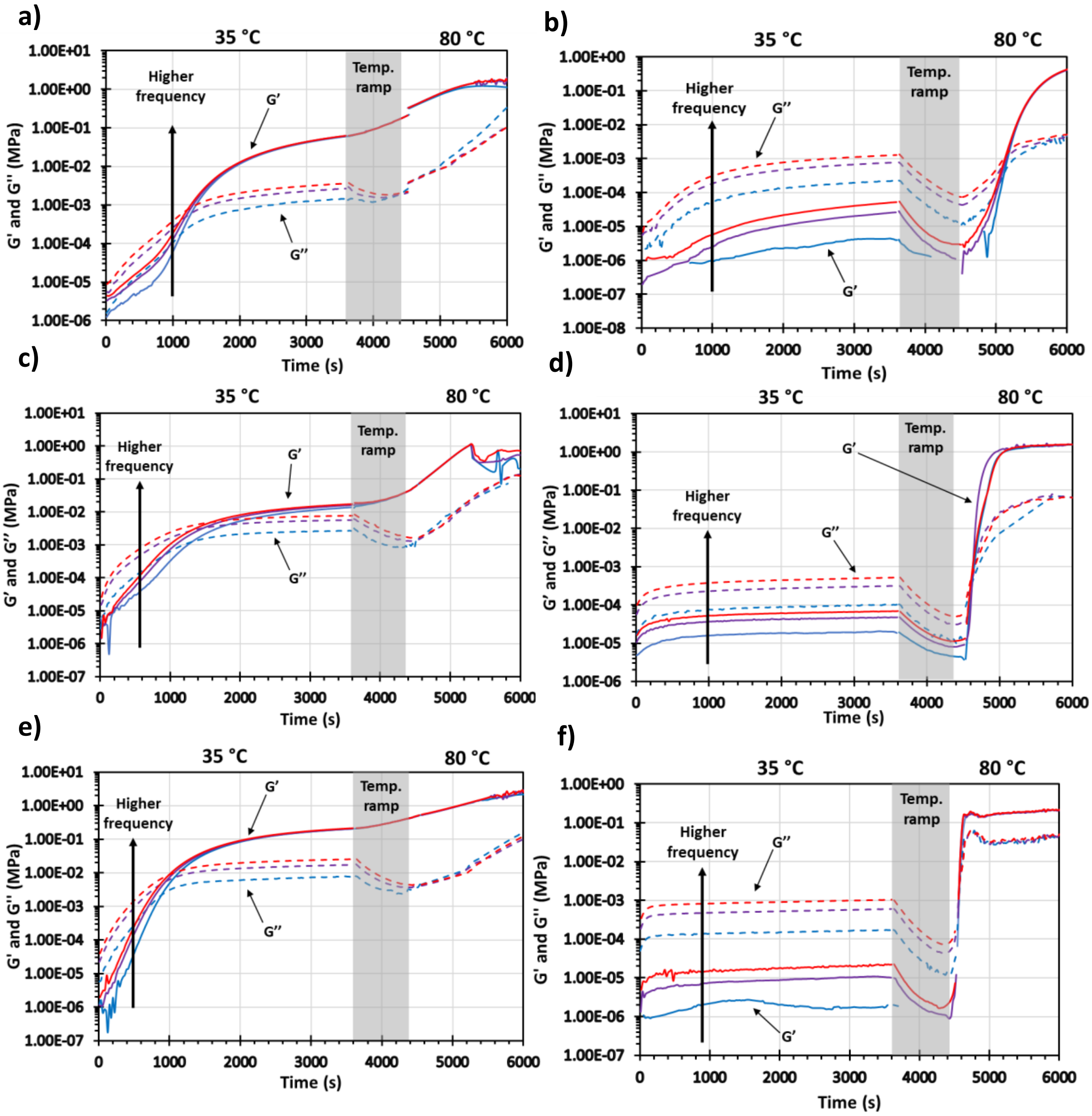


Figure 4. Evolution of storage modulus (G') and loss modulus (G'') vs. time at different frequencies (0.5 Hz, 1.75 Hz and 3 Hz) for a) poly3SHEU_gel, b) poly3SHEU_nogel, c) polyS4_gel, d) polyS4_nogel, e) polyS6_gel, and f) polyS6_nogel during 1 h at 35 °C and 30 min at 80 °C.

As we can see in Figure 4 when the amount of GTA is low (polyX_no gel samples), the gelation cannot occur in the first step at 35 °C where thio-Michael addition is the only reactive process and G'' is higher than G', as corresponds to a liquid-like behavior. G' overpass G'' when the temperature increases to 80 °C when the gelation occurs as a result of a thiol epoxy process. Contrarily, in formulations with a higher proportion of GTA (polyX_gel samples) already in the first curing stage at 35 °C the gelation can be observed, indicating that the functionality of the acrylate mixture is enough to reach a networked structure during thio-Michael addition. The same trends are observed for polyS4 and polyS6 materials. If we compare the times needed to get the gelation during the first step in (polyX_gel samples) , we can see that the time is shorter in the case of polyS6_gel, according to the higher functionality of the thiol, which allows reaching the gel point at a lower conversion of acrylate. When comparing the rheological curves of (polySH3EU_gel samples) with (polyS4_gel samples) we see that is slightly faster in the former. Since the functionality is lower in (polySH3EU_gel samples), the explanation can be found in a more rapid reaction of SH3EU in the thio-Michael addition. This can be related to the lower viscosity of this formulation.

DSC was used to confirm the sequentiality of the curing process. Since the thio-Michael addition begins at room temperature, we could not measure the enthalpy released during the first curing step. Thus, the DSC curves of all the materials after the first curing step were recorded. Figure 5 presents the DSC curves for all the formulations studied. Table 2 collects the enthalpy released in the second step and the T_g of the intermediate and final materials. The enthalpy released by the epoxy equivalent is between 120 and 129 kJ, which agrees with previously published data [38]. Moreover, the curing exotherm begins at a temperature not below 75 °C. This confirms that the dual-curing process is sequential and that both steps occur independently.

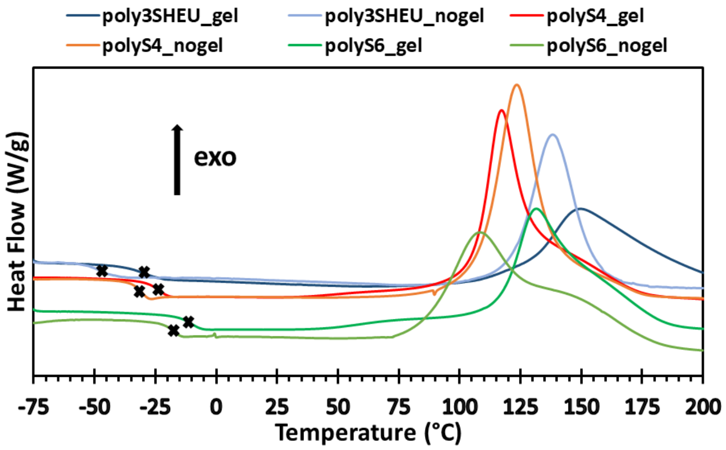


Figure 5. DSC curves at 10 °/min of the curing of all the intermediate materials prepared.

Table 2. Main calorimetric and thermogravimetric data obtained for all formulations

Formulation	ΔH^a (kJ/ee)	$T_g{}^b$ interm (°C)	$T_g{}^b$ final (°C)	$T_{2\%}{}^c$ (°C)	$T_{max}{}^d$ (°C)	Char yield^e (%)
poly3SHEU_gel	120.4	-27.9	33.0	228	360	15.7
poly3SHEU_nogel	122.3	-42.3	37.0	220	363	16.3
polyS4_gel	126.5	-22.7	23.4	240	342	15.0
polyS4_nogel	128.9	-30.9	31.8	247	329	14.9
polyS6_gel	123.8	-9.8	39.3	250	346	14.5
polyS6_nogel	120.3	-17.3	45.1	235	330	15.3

a. Enthalpy released in the thiol-epoxy reaction by epoxy equivalent.

b. Glass transition temperatures of the intermediate and final materials.

c. Temperature of 2 % of weight loss.

d. Temperature of the maximum rate of degradation.

e. Char residue at 600 °C.

Looking at the T_gs determined for all the intermediate materials, we can see that they are well below room temperature, indicating their rubbery or fluid-like characteristics for gelled and non-gelled materials. As expected, the non-gelled materials have lower T_gs than the gelled ones. However, the contrary behavior is observed for the final materials. The materials with a lower proportion of GTA have higher T_g values. This can be explained by the flexibility introduced in the network by the GTA structure, and the flexible moieties originated through the thio-Michael addition. Moreover, the higher proportion of GTA requires more thiol in the formulation, which imparts a higher flexibility. A parallel behavior of the evolution of the T_gs on changing the formulation composition was observed in previous studies.[29,39]

The highest T_gs of the cured materials were obtained from S6 due to its higher functionality, increasing the crosslinking density. Although the functionality of S4 is higher than that of SH3EU, the rigidity of its aromatic ring in the eugenol derivative reduces the network's flexibility and mobility, leading to higher T_g values.

3.3. Thermal characterization of the materials

Thermogravimetry was used to evaluate the thermal stability of the fully cured materials. Figure 6 shows the weight loss evolution with temperature and the derivative curves. The main data extracted can be seen in Table 2.

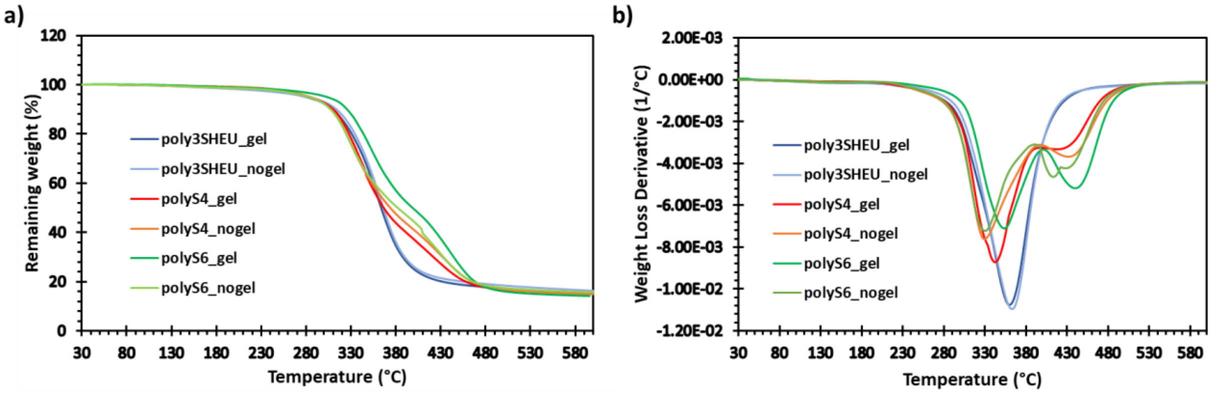


Figure 6. TGA (a) and DTG (b) curves for the dual-cured thermosets prepared in N_2 atmosphere.

The DTG curves show that the degradation process occurs in two steps, except for poly3SHEU formulations. Since a significant proportion of ester groups are present in the network structure, the β-elimination process can happen to a great extent. The first degradation step can be attributed to this process, whereas the second can be attributed to the complete network degradation.

From the values collected in Table 2, no significant differences in the initial degradation among all the materials can be observed, and all the values are higher than 220 °C. There are also no significant differences in the char residues at 600 °C. However, the temperatures of the faster degradation rates are higher for poly3SHEU materials, showing only one degradation step.

The thermomechanical properties of the fully cured materials were determined by DMA. Figure 7 shows the evolution of storage moduli and tan δ against temperature. The main data extracted from these studies are presented in Table 3.

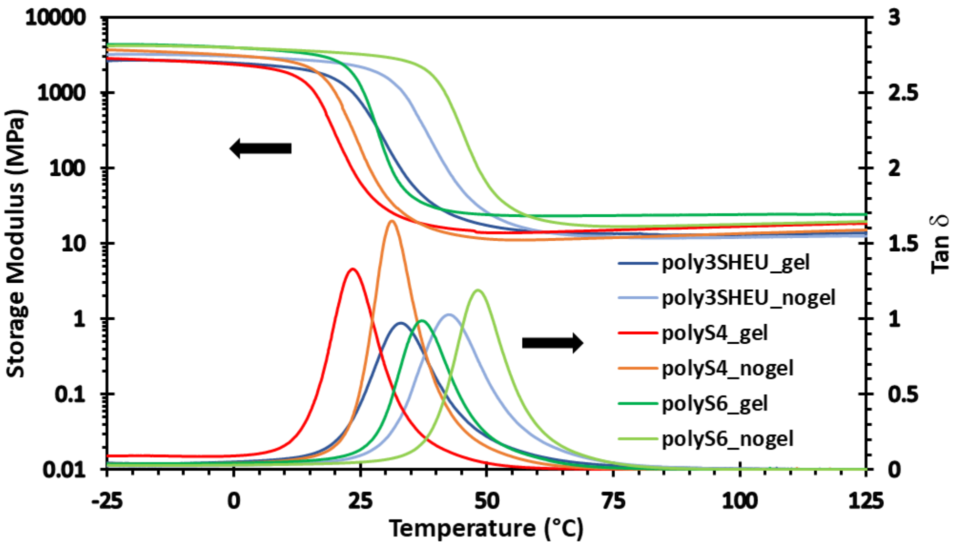


Figure 7. Evolution of tan δ and storage modulus against temperature for all the fully cured materials.

Table 3. Main thermomechanical and mechanical data obtained for all the fully cured materials

Formulation	$T_{\tan\delta}$^{a} (°C)	E'_{glassy}^{b} (MPa)	$E'_{rubbery}$^{c} (MPa)	FWHM^{d} (°C)	σ_{break} (MPa)	ε_{break} (%)	Tensile modulus (MPa)
poly3SHEU_gel	32.9	2602	14.5	15.5	3.1±0.5	12.1±1.0	150±12
poly3SHEU_nogel	42.4	2977	12.9	16.2	4.5±1.1	2.4±0.4	754±75
polyS4_gel	23.5	3000	18.7	11.8	3.7±0.3	32.3±3.6	32.4±6.3
polyS4_nogel	31.3	3761	15.3	11.7	3.9±1.7	23.0±3.5	78.5±18.6
polyS6_gel	37.2	4000	24.3	12.2	4.2±0.2	6.4±0.4	648±82
polyS6_nogel	48.2	4050	19.6	11.9	4.0±0.5	1.6±0.7	1354±125

a. Temperature of the maximum of tan δ peak at 1 Hz.

b. Glassy storage modulus at T_g – 50 °C determined by DMA.

c. Rubbery storage modulus at T_g + 50 °C determined by DMA.

d. Full width at half maximum of the tan δ peak.

In Figure 7, we can see that the tan δ curves are monomodal and relatively narrow, with similar and low FWHM values, indicating the high homogeneity of the material due to the click character of the thio-Michael and thiol-epoxy reactions. The T_g values (considered as the temperature of the maximum of tan δ peak) agree well with the T_gs measured by DSC following the same trend as explained before. The damping capacities (maximum of the tan δ peak) are higher in those materials that gel in the second step of curing due to their lower crosslinking density. Storage moduli increase with the functionality of the thiol selected in both glassy and rubbery states. The storage moduli in the glassy state are slightly higher in those materials that gel in the second step of curing, whereas the storage moduli in the rubbery state are somewhat lower. This is due to the GTA added. In polyX_gel, its amount is higher, increasing the crosslinking density (increasing E' in the rubbery state) but introducing more flexibility in the network due to its aliphatic structure and the higher proportion of flexible thiols needed. Contrarily, in polyX_nogel, the ratio of GTA is lower, reducing the crosslinking density and the flexibility of the network structure.

3.4. Mechanical characterization of the materials

The mechanical characterization of the final materials was done in tensile in the DMA (in static mode) using the tension clamp at 20 °C. Figure 8 presents the stress-strain curves, and the main parameters extracted are presented in Table 3.

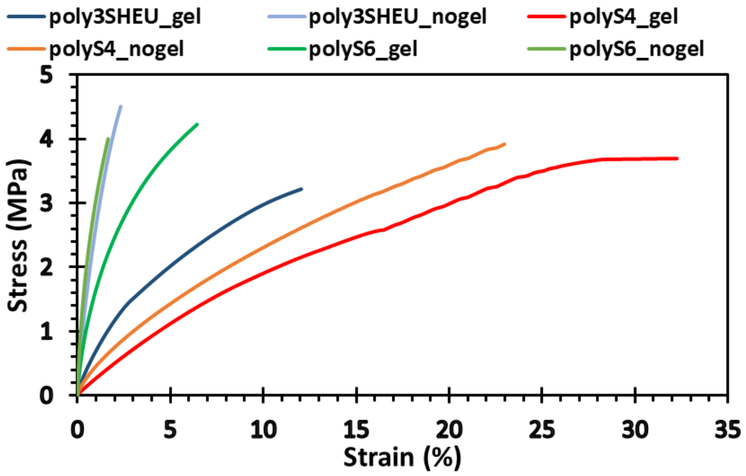


Figure 8. Stress-strain curves for the thermosets obtained.

The behavior observed in the tensile tests reflects two different factors. The first one is the network structure at the testing temperature (20 °C), being samples poly3SHEU_nogel and polyS6_nogel in the glassy state but all the other in the transition zone. This fact explains the higher rigidity (higher tensile modulus) and fragility (lower $\varepsilon_{\mathrm{break}}$) of poly3SHEU_nogel and polyS6_nogel samples, the high ductility of S4 materials (almost totally relaxed at 20 °C) and the similar stress at break values of around 5 MPa. The second factor to consider is the ratio of GTA. The materials that gel in the first curing step, with a higher ratio of GTA, are more ductile that their counterparts with a lower ratio. This is due to the higher aliphatic character that allows an easier deformation without breaking.

4. Conclusions

A sequential dual-curing procedure using bio-based monomers as starting compounds has been implemented. Eugenol was transformed into acrylate epoxy eugenol, which was reacted with thiols of different functionalities: 3, 4, and 6. The trithiol used was also obtained from eugenol. The curing process consisted of a first step of thio-Michael addition and a second thiol-epoxy reaction catalyzed by 1-methylimidazole.

The addition of different ratios of the triacrylate of glycerol allowed to modify the characteristics of the intermediate materials. Low proportions of this compound led to a viscous intermediate material, whereas higher proportions led to rubbery solids since the gelation occurred during the first steps.

The fully cured materials were thermally stable until temperatures higher than 200 °C and showed T_gs in the 23 to 45 °C range. The materials with a higher proportion of the triacrylate showed lower T_gs and storage moduli in the glassy state but higher in the rubbery state due to their higher crosslinking densities.

The aliphatic moieties of the network structure enhance the flexibility and deformation ability of the prepared thermosets and this fact was confirmed with the thermomechanical and the mechanical characterization of the samples.

ASSOCIATED CONTENT

Supporting Information

Alternative synthesis of monomers, structural characterization of the synthesized products, FTIR spectra and rheological curves.

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Authors Contributions

Adrià Roig conducted the experimental part, all the mechanical studies and wrote the original draft. Xavier Ramis, Silvia De la Flor and Àngels Serra validated the studies, made conceptualization, supervised the work and reviewed and edited the final manuscript.

Notes

The authors declare no competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

The raw data required to reproduce these findings cannot be shared at this time due to technical limitations. Please, contact us in case you need some specific data.

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Declaration of interests

☐The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☒The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Supplementary Material