

PREPARATION OF NEW BIOBASED COATINGS FROM A TRIGLYCIDYL EUGENOL DERIVATIVE THROUGH THIOL-EPOXY CLICK REACTION

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Abstract

A new triglycidyl eugenol derivative (3EPO-EU) was synthesized and characterized by spectroscopic techniques, and used as starting monomer in the preparation of novel bio-based thiol-epoxy thermosets. As thiols, commercially available tetrathiol derived from pentaerythritol (PETMP), a trithiol derived from eugenol (3SH-EU) and the hexathiol derived from squalene (6SH-SQ) were used in the presence of 4-(N,N-dimethylamino)pyridine as the basic catalyst. A flexible diglycidyl ether derived from hexanediol (2EPO-HEX) was also introduced in order to enhance conversion in formulations containing 6SH-SQ. The evolution of the curing was monitored by differential scanning

calorimetry. The materials obtained are rigid at room temperature and showed T_g s up to 103 °C. The thermal stability, thermomechanical and mechanical properties were evaluated and discussed in terms of the structural characteristics of the resulting materials.

Keywords

Biopolymers, crosslinking, renewable resources , thermosets, structure-property relation.

1. Introduction

Epoxy thermosets have been extensively used due to their great number of advantages ranging from excellent thermal resistance, mechanical performance and chemical and environmental stability, among others.^{1,2}

The most popular starting compound in the production of industrial epoxy resins is bisphenol A which is used in the preparation of coatings, adhesives, encapsulants, etc.^{3,4} However, excessive exposure to this compound causes serious damage to health and a lot of research is currently done to find out more convenient alternatives.^{5,6}

Nowadays, there is a great demand for products from renewable sources with the aim of reducing dependence on petrochemical compounds and finding safer alternatives to existing ones. In the last years, many investigations have been focused in the development of greener materials prepared from sustainable, friendly resources with safe behaviour from the point of view of health and environment.^{7,8,9,10} In this respect, many studies have been

performed in the preparation of epoxy thermosets from renewable sources with different structure,^{11,12,13,14} but many of them from vegetable oils.^{15,16,17,18}

Vegetable oils, although produced in huge quantities, cheap and easy to be transformed into pure epoxydated starting materials, have the drawback of their long aliphatic chains that leads to an excessive flexibility and too low T_g of the crosslinked materials, which limits their technological application.^{18,19} For this reason, more rigid structures such as phenols approaching the bisphenol A molecule could be interesting as a green alternative to prepare epoxy thermosets with improved characteristics.²⁰

Eugenol (4-allyl-2-methoxyphenol) is a simple and aromatic compound, which is the main component (80-90%) of clove oil, the essential oil extracted of the clove plant (*Eugenia caryophyllata*). It has two functional groups, OH and allyl that can be further modified to form epoxy compounds with the adequate functionality and for this reason, it seems very attractive as starting material for the preparation of epoxy thermosets. This phenolic compound is a yellowish liquid-oil with its most important application in the medical field because it has great properties as analgesic, antibiotic, antiseptic, anti-oxidant, etc.^{21,22,23,24} It has also been used in perfumery and in manufacturing stabilizers and antioxidants for the plastics industry. As a better advantage, it should be noted that it can be used in foods at low concentrations and therefore is safe as starting material for the preparation of green thermosets.²⁵

Several authors reported on the preparation of epoxy thermosets starting from eugenol based structures. Wang et al.²⁶ prepared a new epoxy

material with a bio-based content of 70.2 %wt from an eugenol derivative cured by 4,4'-diamino diphenyl methane. The new material had a T_g of 114 °C, 40 °C lower than the DGEBA based material. Nevertheless, the new epoxy-eugenol material had higher Young modulus and hardness than DGEBA thermoset.

In another study,²⁷ eugenol was transformed into a diepoxide and cured with methyl tetrahydrophthalic anhydride or with an anhydride derived from rosin (MPA) in the presence of an imidazole as the catalyst. The use of MPA as anhydride allowed to reach T_g s of 155°C and the cured materials exhibited comparable performance to their petrochemical counterparts.

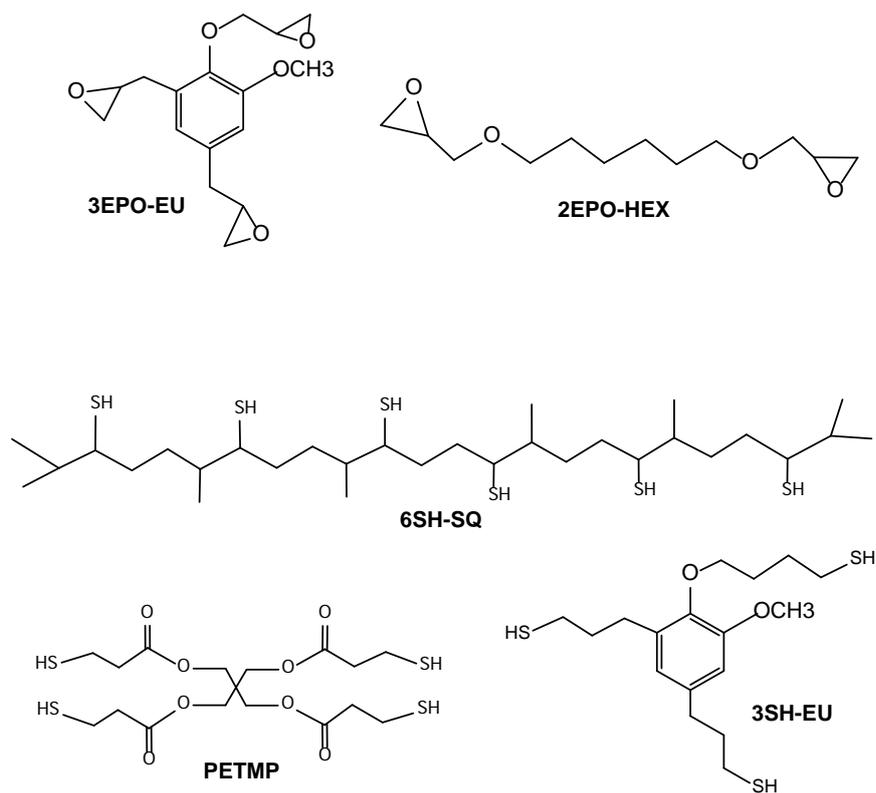
A highly stiff epoxy thermoset derived from eugenol with a triazine core structure and three epoxy groups per molecule was described in the literature.²⁸ This eugenol derivative was cured by using 3,3'-diamino diphenylsulfone. Compared with DGEBA materials cured under the same conditions, the new eugenol-based material led to improved thermomechanical properties (33 °C higher in T_g , 39% higher in Young's modulus and 55% improvement in hardness).

In previous papers, the amine catalyzed thiol-epoxy curing process was reported.^{29,30,31} This reaction follows a *click* pattern with high yield, good regioselectivity in the attack to the epoxide and leads to a polycondensation type polymerization with the formation of a homogeneous network and transparent material appearance. Mechanistic and kinetic studies have been performed to determine the role of the amine added as nucleophile or as a base. Depending on the nature of the amine it can act as a base extracting the

thiol proton forming the corresponding thiolate which is the true nucleophile that attacks to the oxirane. If the amine has better nucleophilic than basic characteristics then the amine can attack to the epoxide forming an alkoxide, which acts as the base that extract the thiol proton forming the thiolate.^{32,33}

In a previous study of our group we put into evidence that thiol-epoxy reaction is highly advantageous in front of thiol-ene processes to obtain crosslinked materials from eugenol derivatives.³⁴ Yoshimura et al. proposed the preparation of networks from triallyl eugenol by thiol-ene processes but the maximum T_g s reached for the materials were not higher than 9.1 °C.⁷ On substituting an allyl by a glycidyl group we increased the T_g in more than 25 °C by the higher efficiency of the thiol-epoxy process compared to the thiol-ene in eugenol substrates.

The present study proposes the preparation of a new eugenol epoxy compound with three glycidyl groups with a compact structure (3EPO-EU), which will later be cured by means of a thiol-epoxy click reaction. According to our experience in thiol-epoxy curing systems a high functionality and rigid structures are needed to reach good thermomechanical characteristics.³⁵ As the thiol curing agent, we synthesized an eugenol derivative (3SH-EU) and we also prepared the hexathiol derived from squalene (6SH-SQ) previously reported.³⁶ We also selected as thiol the commercially available tetrathiol derived from renewable pentaerythritol (PETMP).²⁰ Scheme 1 represents the structure of the starting monomers used in this study.



Scheme 1. Chemical structures of the monomers selected

Through thiol-epoxy curing process, fully bio-based epoxy thermosets with different characteristics have been obtained. It should be mentioned that, depending on the basic catalyst used, the latent character of thiol-epoxy curing allows the formulations to be stored at room temperature for a certain period.³⁷ This fact, together with the easy control of the polymerization reaction, enhances the green character of this type of materials, accordingly to the reduction of the amount of waste material produced.

For the epoxidation of the compound derived from eugenol we followed the concept of green chemistry^{38,39} and the epoxy compound was synthesized using the oxone methodology^{40,41,42} instead of epoxidation by peracid (MCPBA),⁴³ because the former offers many advantages. Oxone is cheaper than MCPBA and the separation and purification processes are much

easier and employs non-toxic organic compounds. MCPBA is non-stoichiometric and acts preferentially in chlorinated solvents. In addition, the thiols were also synthesized by a clean methodology, consisting in the photoinitiated thiol-ene click addition of thioacetic acid to olefins in the absence of any solvent and further saponification by base.³⁶

The study of the thermal curing of different thiol-epoxy formulations was performed by calorimetry and the materials prepared were characterized by thermogravimetry, thermomechanical analysis and mechanical tests. To improve the curing of some formulations and reach their complete curing, the addition of a linear renewable diglycidyl compound derived from 1,6-hexanediol (2EPO-HEX) was tested. This compound acts as flexible chain extender when the compactness of the monomers derived from eugenol and squalene limits the complete reaction that is caused by topological restrictions.

2. Experimental part

2.1. Materials

Eugenol (EU), allyl bromide, thioacetic acid (TAA), 2,2-dimethoxy-2-phenylacetophenone (DMPA), 4-(N,N-dimethylamino)pyridine (DMAP), pentaerythritol tetrakis (3-mercaptopropionate) (PETMP), squalene (SQ) and oxone (potassium peroxomonosulphate) were purchased from Sigma-Aldrich and were used without further purification. 1,6-hexanediol diglycidylether (2EPO-HEX from EPOTEC RD 107 Aditya Birla Chemicals, Thailand. **EE 147 g/eq**) was used as received. Benzyl triethyl ammonium chloride (TEBAC) was purchased from Alfa Aesar. Inorganic salts and bases were purchased from

Scharlab. Methanol from Carlo Erba was used as received. Acetone, ethyl acetate and N,N-dimethylformamide (DMF) from VWR were purified by standard procedures.

2.2. Preparation of starting compounds

2.2.1. Synthesis of the diallyl and triallyl derivatives from eugenol (2A-EU, r2A-EU and 3A-EU)

Diallyl and triallyl eugenol were prepared following a previously reported procedure.⁷ The synthesis includes the allylation of eugenol in basic medium to obtain O-allyl eugenol (2A-EU) and then a Claisen rearrangement on heating to obtain 6-allyleugenol (r2A-EU). This product was allylated and the triallyl eugenol (3A-EU) was obtained (see Scheme 2). The ¹H-NMR spectra of these compounds were coincident with those reported.⁷

2.2.2. Synthesis of triepoxy derivative from eugenol (3EPO-EU)

In a 1000 mL three-necked flask equipped with magnetic stirrer, thermometer and addition funnel, 1 g (4.1 mmol) of 3A-EU was dissolved into 120 mL of acetone and 100 mL of ethyl acetate. To this mixture, 0.2 g (0.8 mmol) of TEBAC, 43.0 g (511.8 mmol) of NaHCO₃ and 60 mL of water were added. The flask was cooled at 5 °C and then 56.7 g of oxone (equivalent to 93.0 mmol of KHSO₅) dissolved in 190 mL of H₂O were added dropwise over 3 h at 5 °C under vigorous stirring. The mixture was kept at room temperature for 48 h. The organic layer was separated and washed with a solution of 20 %wt NaCl in water. After drying with Mg₂SO₄, the solvent was eliminated at vacuum and the residue purified by silica gel chromatography (n-hexane/ethyl acetate (4:6), as eluent). The product 3EPO-EU was a viscous yellow liquid,

50% yield. ^1H NMR (CDCl_3 , δ in ppm), 6.72 m (Ar, 2H), 4.24 and 3.90 m ($-\text{CH}_2-\text{O}-$, 2H), 3.84 s ($\text{CH}_3-\text{O}-$, 3H), 3.34 m (CH of glycidyl ether, 1H), 3.18 and 3.4 m (CH of glycidyl groups attached to phenyl, 2H), 2.93-2.77 m ($-\text{CH}_2-$ of oxirane rings, 6H) and 2.76, 2.68, 2.58 and 2.56 four dd ($-\text{CH}_2-$ of glycidyl groups directly attached to Ph, 4H) (see Figure 1).

^{13}C NMR (CDCl_3 , δ in ppm): 32.6 ($-\text{CH}_2-$), 38.2 ($-\text{CH}_2-$), 44.1 ($-\text{CH}_2-$ oxirane), 46.5 ($-\text{CH}_2-$ oxirane), 46.8 ($-\text{CH}_2-$ oxirane), 50.3 ($-\text{CH}-$ oxirane), 51.6 ($-\text{CH}-$ oxirane), 52.1 ($-\text{CH}-$ oxirane), 55.4 ($-\text{OCH}_3$), 73.5 ($-\text{CH}_2-\text{O}-$), 111.4 (C-3), 122.4 (C-5), 130.6 (C-6), 133.0 (C-4), 144.2 (C-1) and 152.0 (C-2) (see Figure 2).

FT-IR (ATR): 3050, 2996, 2918, 2847, 1589, 1489, 1464, 1430, 1403, 1336, 1290, 1010, 968, 908, 831, 804, 754 cm^{-1}

2.2.3. Synthesis of trithiol compound from triallyl eugenol (3SH-EU)

The synthesis was performed as previously reported by us.³⁴ The synthetic procedure starts from triallyleugenol (3A-EU) that was irradiated with thioacetic acid (TAA) in the presence of DMPA. The thioacetate was saponified with a methanol solution of NaOH.

2.2.4. Synthesis of hexathiol from squalene (6SH-SQ)

The product was prepared following a two-step procedure previously reported, based on the photochemical thiol-ene of thioacetate on squalene in the presence of DMPA and saponification with methanolic NaOH.³⁶

2.3. Preparation of the curing mixtures

Different formulations of the triepoxy derived from eugenol (3EPO-EU) with several thiols as PETMP, 3SH-EU and 6SH-SQ were prepared. The homogeneous mixtures were obtained by mixing with a spatula stoichiometric

amounts of epoxy/S_H groups (1:1), and adding 2 phr (2 parts per hundred of epoxy) of DMAP as basic catalyst. The formulations prepared were named as 3EPO-EU/PETMP, 3EPO-EU/3SH-EU and 3EPO-EU/6SH-SQ. A fourth mixture was prepared named as 3EPO-EU/6SH-SQ/2EPO-HEX which consist of a mixture of 80 %wt of 3EPO-EU and 20 %wt of 1,6-hexanediol diglycidyl ether (2EPO-HEX) with the stoichiometric amount of 6SH-SQ and 2 phr of DMAP. An equivalent formulation with 3SH-EU instead of 6SH-SQ, named as 3EPO-EU/3SH-EU/2EPO-HEX, was also tested but later discarded by its low properties.

2.4. Characterization techniques

¹H NMR and ¹³C NMR spectra were registered in a Varian Gemini 400 spectrometer. CDCl₃ was used as the solvent. For internal calibration the solvent signal corresponding to CDCl₃ was used: δ (¹H) = 7.26 ppm, δ (¹³C) = 77.16 ppm.

The study of the curing was performed by differential scanning calorimetry (DSC) in a Mettler DSC-821e calorimeter calibrated using an indium standard (heat flow calibration) and an indium-lead-zinc standard (temperature calibration). For dynamic studies, a flow of N₂ at 100mL/min was used and the weight of the samples for the analysis was 10 mg. The studies were performed in the temperature range of 30-250°C, with a heating rate of 10 K/min.

The glass transition temperatures (T_gs) of the sample once cured were determined in dynamic scans at 20 °C/min from -20°C to 100°C. The T_gs of the final thermosets were evaluated after two consecutive heating dynamic scans at 20°C/min starting at -20°C in a Mettler DSC-822e device to delete the thermal

history. The T_g value was taken as the middle point in the heat capacity step of the glass transition.

The thermal stability of cured samples was studied by thermogravimetric analysis (TGA), using a Mettler TGA/SDTA 851e thermobalance. All experiments were performed under inert atmosphere (N_2 at 100 mL/min). Pieces of the cured samples with an approximate mass of 8 mg were degraded between 30 and 600 °C at a heating rate of 10 K/min.

A Jasco FTIR spectrometer equipment (resolution of 4 cm^{-1}) with an attenuated-total-reflectance accessory with a diamond crystal (Golden Gate heated single-reflection diamond ATR, Specac-Teknokroma). All the measurements were performed at room temperature. IR was used to follow the diminution of thiol band at 2570 cm^{-1} and the evolution of the curing process of the different formulations. In this case, the spectra were collect before and after thermal process.

Dynamic mechanical thermal analyses (DMTA) were carried out with a TA Instruments DMA Q800 analyzer. The samples were isothermally cured in a mould at 80°C for 1 h with a post curing at 120°C for 30 min with the exception of 3EPO-EU/6SH-SQ and 3EPO-EU/6SH-SQ/2EPO-HEX which was cured at 100°C for 1 h with a post curing at 140°C for 1 h. Three point bending clamp was used on the prismatic rectangular samples ($30 \times 6.5 \times 1.5 \text{ mm}^3$). The apparatus operated dynamically at 5 K/min from 30 to 170°C for deleting the thermal history and then at 3 K/min from 30 to 170°C at a frequency of 1 Hz with and oscillation amplitude of 10 μm .

Young's modulus was determined under flexural conditions at 30°C, with the same clamp and geometry samples, applying a force ramp at constant load rate of 3 N/min, from 0.001 N to 18 N. Three samples of each material were analyzed and the results were averaged. Stress-strain at break tests were performed with the film-tension clamp in force controlled mode. Dog-bone samples were used at a force rate of 1 N/min and the averaged value of at least three different samples were reported.

Microindentation hardness was measured with a Wilson Wolpert 401 MAV device following the ASTM E384-16 standard procedure. For each material at least 10 determinations were made with a confidence level of 95%. The Vickers hardness number (HV) was calculated from the following equation:

$$HV = \frac{1.8544 \cdot F}{d^2} \quad (3)$$

where, F is the load applied to the indenter in kgf (0.025 kgf) and d is the arithmetic mean of the length of the two diagonals of the surface area of the indentation measured after load removal in mm.

3. Results and discussion

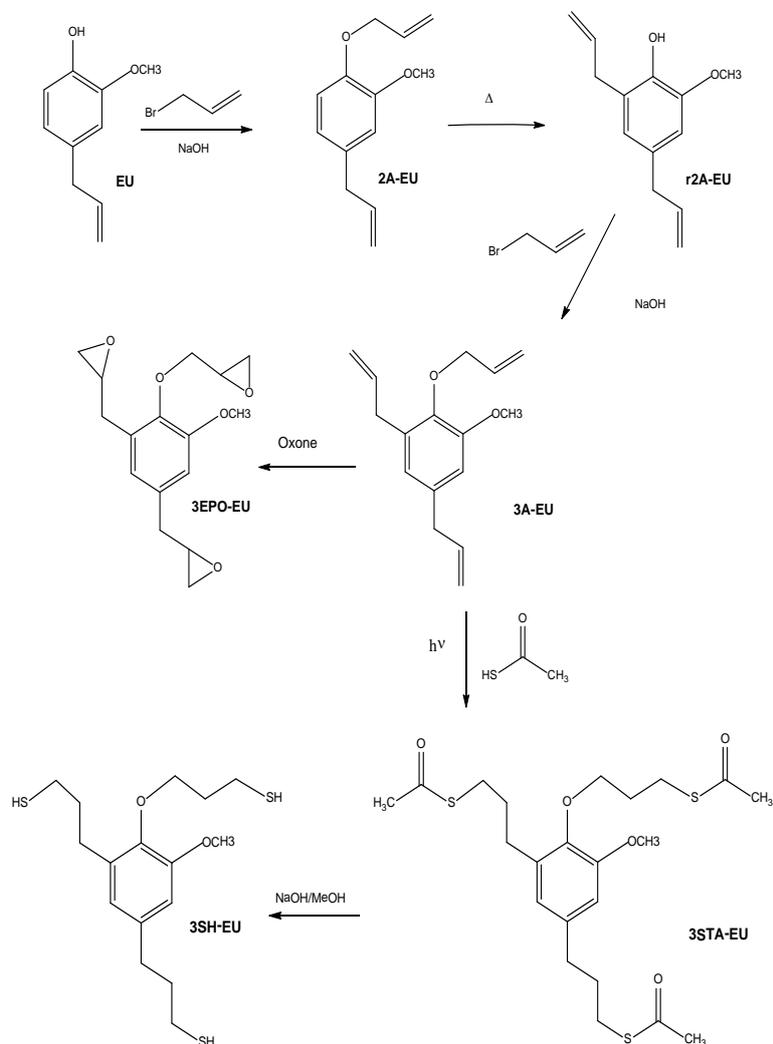
3.1. Synthesis and characterization of the starting monomers

The synthesis of the triepoxy derivative of eugenol was addressed by different synthetic procedures, all of them starting from diallyl phenol (r2A-EU), which was synthesized following a previous paper,⁷ as represented in Scheme 2. The first step consists in the allylation of eugenol and the second is a pericyclic Claisen rearrangement at 200°C with practically quantitative yields.

These products showed a high purity by NMR spectroscopy and no further purification was required.

The first synthetic methodology selected for the preparation of the triglycidyl derivative from r2A-EU was the one inspired in the synthesis of eugenol epoxy derivative proposed by Qin et al.²⁷ These authors started from eugenol, which was acetylated, and then the allyl group epoxidated with m-chloroperbenzoic. The product obtained was finally reacted with epichlorohydrin in the presence of NaOH and the substitution of acetyl group by glycidyl was accomplished with about 60% yield. Although both synthetic steps, epoxidation and glycidation, were well-established procedures, the application of this methodology to the dially derivative (r2A-EU) did not produced the desired 3EPO-EU, but a complex mixture of compounds. The presence of a glycidyl group in *ortho* position to the phenol group, which is the only difference in comparison to the synthesis proposed by Qin,²⁷ could be the responsible of the unexpected side-reactions. Since NaOH catalyses the reaction of the acetate with EPC, the alkoxides formed could attack intramolecularly the epoxy in this *ortho* position or even could lead to oligomeric products by intermolecular attack. As an alternative, we proposed another general synthetic pathway, which is represented in Scheme 2.

This procedure goes through the formation of the triallyl derivative of eugenol, following the methodology proposed by Yoshimura et al.⁷ This methodology allowed the preparation of 3A-EU with excellent yield and purity. ¹H and ¹³C NMR spectra of the di- and triallylic compounds prepared were coincident with those reported in the literature.⁷



Scheme 2. Synthetic pathway for the synthesis of the triglycidyl derivative of eugenol (3EPO-EU) and trithiol (3SH-EU)

The last step in the synthetic procedure was the epoxidation of 3A-EU. The first epoxidation methodology attempted was the classical epoxidation with peracid (MCPBA). The application of this method did not produce the triepoxy compound in good yield but only in small quantity, although a great excess of peracid (9:1 mol/mol) was added and the reaction time was extended for as

long as 10 days. In view of these results, the oxone method^{40,41} was tested. This method can be considered as more environmentally friendly than epoxidation with MCPBA, especially when it was performed in a two-phase system (ethyl acetate/water) using benzyl triethyl ammonium chloride as the phase transfer catalyst (PTC). In these conditions acetone and the formed dimethyldioxirane, which is the true epoxidation agent, are more soluble in the organic phase, which contains the triallyl eugenol derivative, and this method was described to lead to the highest yield of epoxy compound.⁴⁰ By this methodology, we obtained the pure triglycidyl derivative of eugenol (3EPO-EU) in a 50% of yield after purification by column chromatography. Aouf et al.⁴⁴ prepared a tetraglycidyl derivative of gallic acid by allylation and further epoxidation. They also proved the advantages of using the oxone method in front of the epoxidation with m-chloroperbenzoic acid, since a great proportion of peracid was required to get an only moderate yield of the desired epoxy compound. The epoxidated eugenol derivative prepared was characterized by NMR spectroscopy and Figure 1 presents its ¹H NMR spectrum.

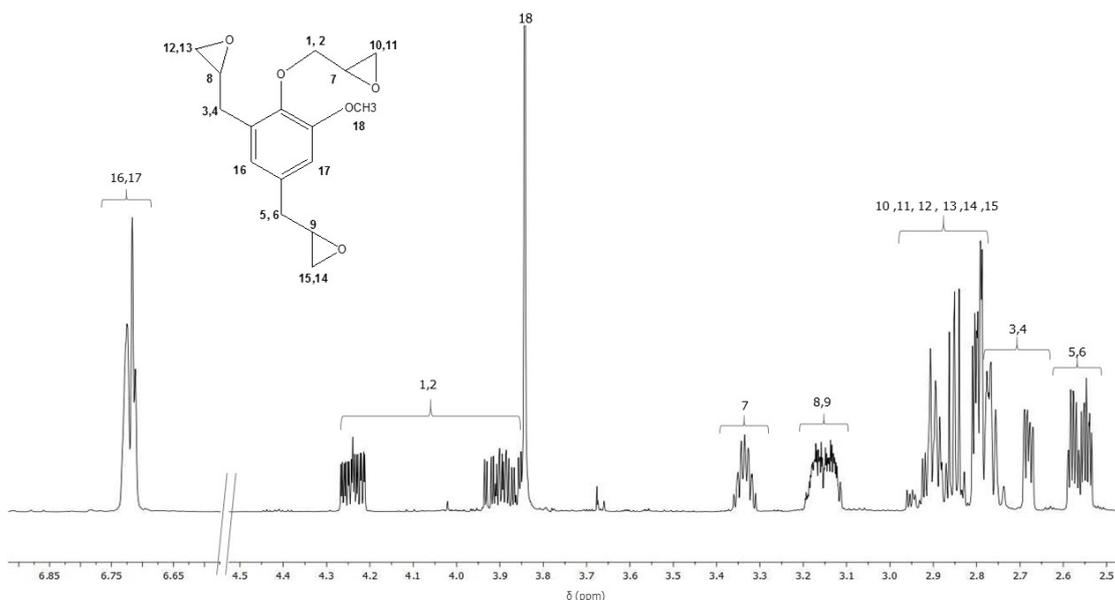


Figure 1. ^1H NMR spectrum of 3EPO-EU in CDCl_3

As we can see, the spectrum is rather complex because of the presence of three different glycidyl groups, two of them directly attached to the aromatic ring, but with different electronic environments and the other, more deshielded because of its attachment to the oxygen atom. Each glycidyl group presents five unequivalent protons due to the presence of the asymmetric carbon that leads to the methylene protons to be diastereotopic among them. Therefore, five different signals are expected for each glycidyl group with a complex coupling pattern. The integration of the signals and the chemical shifts support the structure for 3EPO-EU. Moreover, the purity of the product is put in evidence.

Figure 2 shows the ^{13}C -NMR spectrum of the epoxy derivative with the corresponding assignments, which were mainly done by comparison with similar structures.⁷ The spectrum also shows a great number of signals, because of the total absence of symmetry.

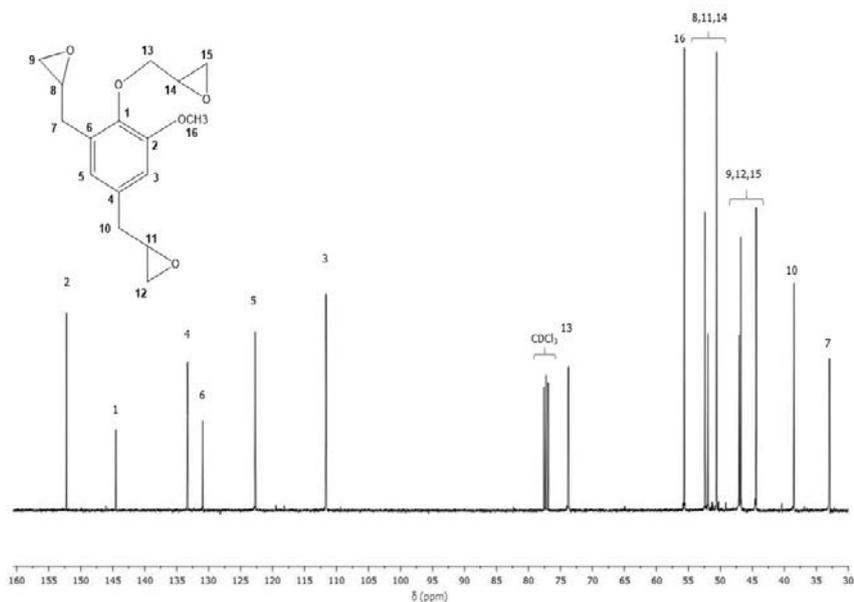


Figure 2. ^{13}C NMR spectrum of 3EPO-EU in CDCl_3

The triallyl derivative of eugenol (3A-EU) was also the starting material for the synthesis of the trithiol derived from eugenol (3SH-EU), which was prepared by a two-step synthetic procedure as represented in Scheme 2. This consist in a first photochemical thiol-ene reaction followed by the saponification of the thioester formed. This compound was described in a previous publication.³⁴ The viscous liquid product was obtained with high yield and purity and its structure confirmed by spectroscopic measurements. The hexathiol derived from squalene (6SH-SQ) was prepared by the same synthetic methodology (thiol-ene/saponification) as reported before.^{36,34}

3.2. Study of the curing process

Calorimetric studies were performed to see the evolution of the curing process for the different mixtures studied. In a first study, stoichiometric mixtures of 3EPO-EU with three thiols (PETMP, 3SH-EU and 6SH-SQ) and 2 phr

of DMAP were cured at 10 °C/min in the calorimeter. The resulting curves are collected in Figure 3.

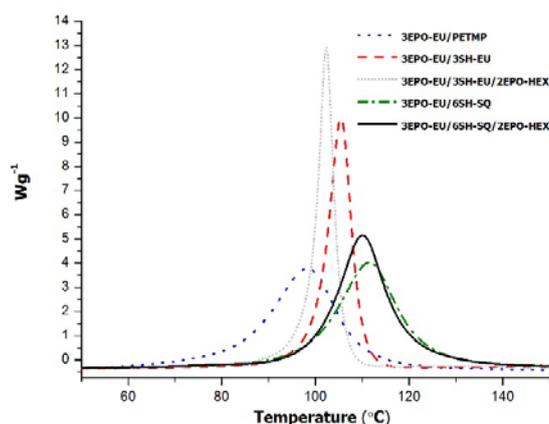


Figure 3. DSC thermograms corresponding to the dynamic curing at 10°C/min of the mixtures eugenol triepoxide/thiols and with a proportion of 2 phr of the DMAP.

As we can see, the mixture containing PETMP begins to react at lower temperatures, indicating its higher reactivity, whereas the thiol derived from squalene is the one that reacts at the highest temperature. The main data obtained from the calorimetric study are collected in Table 1.

Table1. Calorimetric data of the mixture epoxy with thiols using a proportion of DMAP as catalyst.

Sample	$\dot{A}H^a$ (J/g)	$\dot{A}H^b$ (kJ/ee)	T_g^c (°C)
3EPO-EU/ PETMP	518.7	115.0	60
3EPO/3SH-EU	439.9	94.1	70
3EPO/6SH-SQ	333.7	69.9	103
3EPO/3SH-EU/2EPO-HEX	443.8	96.6	47
3EPO/6SH-SQ/2EPO-HEX	430.0	90.0	87

- Enthalpy evolved by gram of sample in a dynamic curing
- Enthalpy by equivalent epoxy of sample in a dynamic curing
- Glass transition temperature of the material after thermal curing

The degree of curing achieved for the formulation is mainly related to the enthalpy released by epoxy equivalent, which was described to be around 130 kJ/ee for thiol-epoxy reaction.^{29,30} From the values of the table, it is inferred

that 6SH-SQ reacts only partially (about 50-60%), since the enthalpy released is about 70 kJ/ee, much less than the one obtained from the curing of 3EPO-EU/PETMP formulations and much lower than the one reported. Also in the case of using 3SH-EU as the thiol, the enthalpy evolved was a little lower than expected. According to that, we investigated if a higher degree of curing could be achieved, by adding a linear flexible diepoxy compound to the formulation to reduce steric and topological restrictions in the network formation. 1,6-Hexanediol diglycidylether (2EPO-HEX) was selected as reactive diluent, since this compound is a derivative of adipic acid, which is a natural product. A 20%wt of 2EPO-HEX and an 80% of 3EPO-EU were mixed and the stoichiometric amount of the selected thiol was added. The curves for 3EPO-EU/3SH-EU/2EPO-HEX and 3EPO-EU/6SH-SQ/2EPO-HEX are also included in Figure 3 and the main data collected in Table 1. As we can see, the curing exotherms are slightly shifted to lower temperatures by adding 2EPO-HEX to the formulation and the reaction occurs more quickly. The curing enthalpies increased but only slightly in case of mixtures with 3SH-EU.

To confirm that the curing process has been completed, FTIR-ATR spectra were registered. Figure 4 shows, as an example, the most significant regions of the spectra before and after curing of the formulation cured with 3SH-EU.

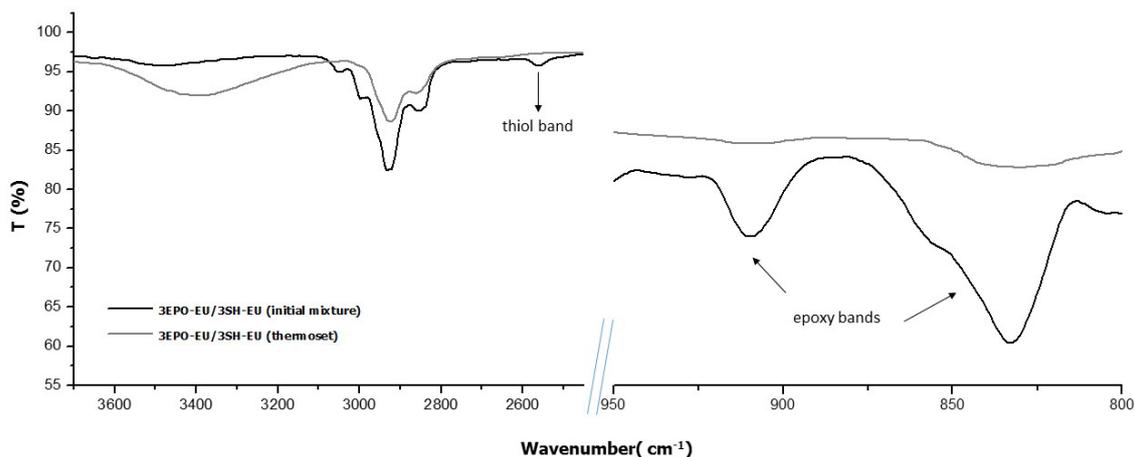


Figure 4. FTIR spectra of a mixture 3EPO-EU/3SH-EU catalyzed by 2 phr of DMAP before and after curing

The initial spectrum shows the typical absorptions of S-H st. at 2570 cm^{-1} and the band at 908 and 831 cm^{-1} corresponding to the epoxy ring. Both absorptions have disappeared completely in the spectrum of the cured material, whereas a new broad absorption at 3500 cm^{-1} appears due to the formation of the β -hydroxy thioether group in the network structure. The small size of the thiol absorption and the partial overlapping of epoxide band with others in the region make difficult the monitoring of the evolution of the curing process.

3.3 Thermal characterization of the thermosets

The T_g of the materials after dynamic curing were determined by DSC and the values are included in Table 1. We can comment that although the 3EPO-EU/6SH-SQ mixture was not completely reacted, the T_g of the material obtained is higher than $100\text{ }^\circ\text{C}$ due to the multifunctionality of the thiol and is also much higher than the materials obtained from PETMP and 3SH-EU as the thiols. In a previous study on the curing of cycloaliphatic epoxy resins with

several thiols, a T_g of 116 °C was reached when using 6SH-SQ as the thiol, which was also much higher than in similar materials prepared from PETMP or 3SH-EU. Despite of the flexible aliphatic structure of the squalene derivative, the high functionality and short distance between reactive groups leads to materials with a tightly crosslinked network structure.

We can also observe that the addition of 2EPO-HEX to the reactive mixture reduces notably the T_g and therefore, an increase in its proportion in the formulation, although possibly beneficial from the point of view of the degree of curing attained, is detrimental for this characteristic. The low T_g of the material derived from 3EPO-EU/3SH-EU/2EPO-HEX led us to discard this material for the following characterization studies.

In a previous study,³⁴ triallyl eugenol (3A-EU) was photocured through thiol-ene reaction with the same thiols selected in the present study and the T_g s of the materials obtained were very low, between 1 and 14 °C. In the same study, the combination of thiol-ene and thiol-epoxy reaction of the diallyl glycidyl eugenol with the same tiols allowed to increase the T_g s up to 28-57 °C, which was attributed to the better behavior of thiol-epoxy processes. In the present study, in which the thiol-ene reaction has been changed to thiol-epoxy, higher T_g s have been reached, confirming that thiol-ene processes in eugenol derivatives had not the expected click characteristics than thiol-epoxy reaction has. Thiol-ene is accompanied by side-reactions like radical-radical coupling that limits the achievement of high crosslinking densities.

The materials prepared were characterized by thermogravimetry to investigate their stability at high temperatures. Figure 5 shows the weight loss

curves against temperature in inert atmosphere and Table 2 collects the main data obtained from these studies.

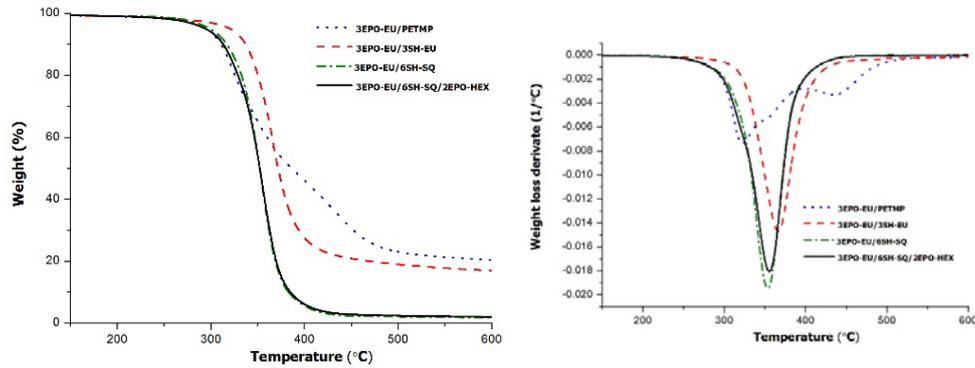


Figure 5. TGA and DTG curves under N₂ atmosphere at 10 K/min of the materials obtained from triglycidyl eugenol with different formulations.

Table 2. Thermal and thermomechanical data of the materials obtained from the different formulations selected.

Sample	TGA			DMTA		
	T _{5%} ^a (°C)	T _{max} ^b (°C)	Residue ^c (%)	T _{tanδ} ^d (°C)	E _r ^e (MPa)	E ^f (MPa)
3EPO-EU/PETMP	295	322	20	76	23.5	1014
3EPO-EU/3SH-EU	320	366	22	86	25.4	1526
3EPO-EU/6SH-SQ	299	353	2	108	28.5	1619
3EPO-EU/6SH-SQ/2EPO-HEX	295	355	2	98	18.6	1187

- Temperature of 5% of weight loss in N₂ atmosphere
- Temperature of the maximum rate of degradation in N₂ atmosphere
- Yield chart after degradation in N₂ atmosphere
- Glass transition temperature determined by DMTA
- Storage modulus in the rubbery state determined at tan δ + 50°C
- Young's modulus at 30°C under flexural conditions

From the values of temperatures of initial weight loss (5%) and the temperature of maximum degradation rate, we can see that the material with a

lower thermal stability is the one obtained from PETMP, probably due to the presence of ester groups that can break by pyrolytic β -elimination processes. It has been reported that ester groups begins to degrade at temperatures above 250 °C but weight loss is influenced by the global network structure.⁴⁵ According to that, the degradation curve and specially the derivative curve of this material show a more complex degradation pattern. The material obtained from 3EPO-EU/3SH-EU formulation presents the highest initial degradation temperature and seems to have the simplest degradation mechanism. This can be explained because of its aromatic character. In contrast, in the previously studied thiol-ene formulations,³⁴ the use of 3SH-EU as thiol led to materials with the worst characteristics. Its eugenol-derived structure can justify the occurrence of side-reactions in the thiol-ene crosslinking, limiting the effectiveness of the process and preventing the formation of highly dense crosslinked structures.

The thermomechanical characteristics of the thermosets prepared were studied by DMTA and Table 2 collects the most significant data extracted. The temperature of the maximum of the α relaxation shows values according to the T_g determined by DSC but a little higher, as expected from this technique. Figure 6 shows the $\tan \delta$ evolution against temperature. The materials obtained from PETMP and 3SH-EU show high and quite narrow curves, which are an indication of homogeneous materials, with the relaxation taking place at moderate temperatures. The materials prepared from 6SH-SQ show a broader relaxation curve at higher temperature evidencing the formation of a more heterogeneous network structure, typical of more densely crosslinked materials.

This difference can be explained by the multifunctionality of the hexathiol and the difficulty of all groups to react (only 50-60 % of conversion). The relaxation of the network occurs at lower temperature and in a narrower range on adding 2EPO-HEX to the formulation, due to the flexibilizing effect of 2EPO-HEX, as expected.

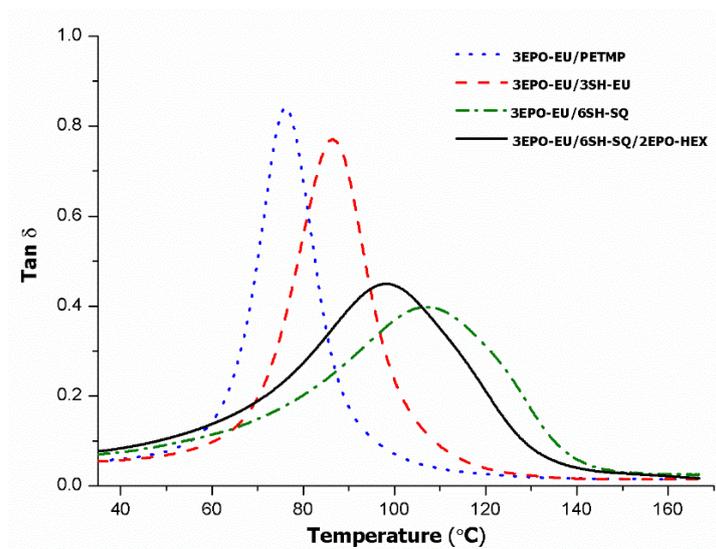


Figure 6. Plot of $\tan \delta$ against temperature for the different materials prepared.

The dependence of the storage modulus against temperature is represented in Figure 7 for all the materials and the main values are listed in Table 2.

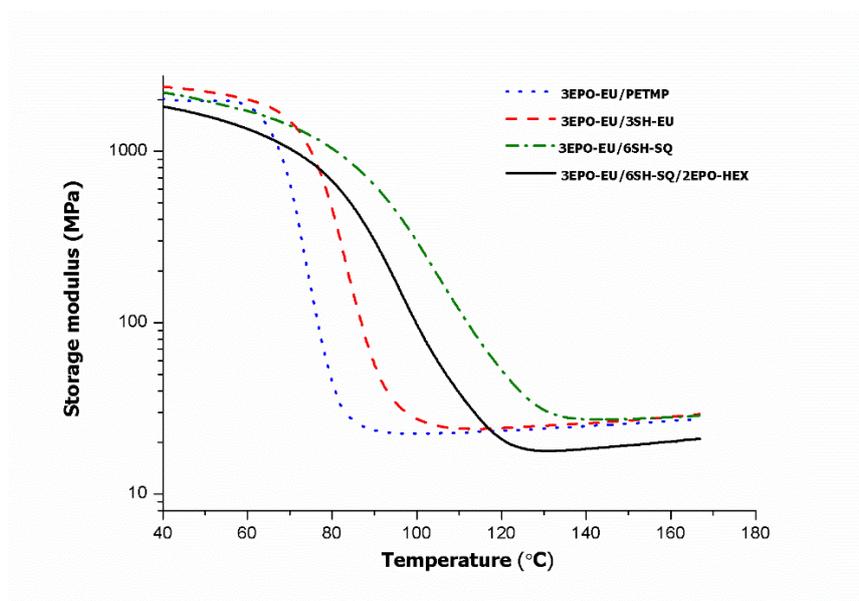


Figure 7. Plot of storage modulus against temperature for the different materials prepared.

From the values of the table, we can see that the Young's moduli of the materials at 30°C, determined under flexural conditions, are higher when the thiol with the **highest functionality and smaller size between reactive groups, which leads to a more compact structure (6SH-SQ)**, was used. **However, this is** quite similar to the value of the material prepared from the thiol with aromatic structure (3SH-EU). The addition of the flexible diglycidyl compound to the formulation with 6SH-SQ leads to a reduction in the modulus, as expected.

The moduli in the rubbery region cannot be rationalised according to the structure and molecular weight between crosslinks because of the concurrence of different factors: functionality and flexibility of the thiol monomers and degree of conversion reached. However, on comparing the materials obtained from 6SH-SQ, we can observe that the addition of the reactive diluent leads to a reduction of this modulus.

Dog-bone samples of the different materials were prepared and studied with the tension clamp in the DMTA to obtain the stress-strain relationships. Table 3 shows the values obtained by this technique together with the values of microindentation hardness measured.

Table 3. Mechanical data of the materials obtained by dual curing by stress-strain at break and microindentation hardness testing. Coefficients of variation less than 8% for stress and strain, and less than 5% for microindentation hardness.

Sample	Strain at break (%)	Stress at break (MPa)	Microindentation hardness ¹ (HV)
3EPO-EU/PETMP	3.0	27.2	12.8
3EPO-EU/3SH-EU	2.2	30.1	14.1
3EPO-EU/6SH-SQ	2.3	50.4	20.3
3EPO-EU/6SH-SQ/2EPO-HEX	4.1	48.5	18.4

¹ Coefficient of variation less than 8% for 3EPO-EU/6SH-SQ/2EPO-HEX.

Results from microindentation hardness are in accordance with the tensile behaviour and their results presented in Table 3. From the values of the table, we can state that the material obtained from 6SH-SQ alone shows low strain at break and the highest stress at break and elastic stiffness, due to the multifunctionality of the thiol and to the smaller size of the structural unit between crosslinks. In addition, the value of microindentation hardness in this material is higher than that determined for the materials obtained from other thiols. The addition of the reactive diluent to the formulation slightly reduces the stress at break but reduces the elastic stiffness and clearly enhances the strain at break, due to the flexibility introduced by the 2EPO-HEX structure, making it a more ductile material. May seem quite unexpected the slight

decrease in microindentation hardness on adding this modifier, but this result is in accordance with the similar yield behaviour of both materials. It is also worth noting that microindentation hardness values for the sample 3EPO-EU/6SH-SQ/2EPO-HEX were more difficult to obtain due to their higher ductile nature, hence the higher deviation in the results. A partial plastic deformation occurred in some parts of the indentation mark, which allowed some elastic recovery to take place along the sides, causing the face of the mark to curve inwards and form a star-shaped indentation. However, as the elastic recovery in the direction of the diagonals is very small (because of intense stress concentration) the measurement of diagonal lengths gives valid hardness values but with greater deviation.

Finally, the material prepared from PETMP shows the lower mechanical performance of all the thermosets prepared in terms of stress at break and Young's modulus (see Table 2). Because this product is commercially available, the material obtained could have broad application where the mechanical requirements were not so high.

The materials prepared from 3EPO-EU by the thiol-epoxy crosslinking process shows better mechanical performance than similar materials obtained by thiol-ene or dual thiol-ene/thiol-epoxy processes.³⁴ This confirms the goodness of the thermal thiol-epoxy reaction in front of the radical thiol-ene process, when applied to eugenol derivatives.

4. Conclusions

A triepoxy compound derived from eugenol has been obtained by a four step procedure that included allylation, Claisen rearrangement and epoxidation by oxone. The structure and purity of this compound was confirmed by ^1H - and ^{13}C -NMR spectroscopy.

The curing of this compound was performed by thiol-epoxy click reaction using three different thiols derived from renewable resources in the presence of a base as catalyst. When the hexathiol derived from squalene was used, an uncomplete reaction was detected. The addition of a reactive diluent as 1,6-hexanediol diglycidylether allowed a higher curing degree to be attained because of the reduction of steric and topological constrains.

The thermosets obtained showed T_g values higher than room temperature, and the maximum value was reached in case of the material obtained from the squalene thiol derivative, with a T_g higher than 100 °C. This material also displayed a good mechanical performance, with the highest Young's modulus and stress at break. The addition of the diglycidylic flexible derivative, 2EPO-HEX, reduced the T_g value and the Young modulus, but does not affect much to the stress at break and microhardness.

The thermomechanical data displayed by the thermosets prepared confirms the goodness of the thiol-epoxy process in the preparation of thermosets from eugenol and the possibility of preparation of fully bio-based thermosets with good characteristics. These characteristics also show the adequacy of the triglycidyl eugenol derivative as epoxy monomer for the preparation of biobased thermosets. The adequate selection of the structure of

thiols and epoxy monomers allows preparing biobased materials with tuned properties.

5. Acknowledgments

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