European Polymer Journal 206 (2024) 112782

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Eugenol-based dual-cured materials with multiple dynamic exchangeable bonds

Adrià Roig [a], Xavier Ramis [b], Silvia De la Flor [c,*], Àngels Serra [a,*]

[a] Universitat Rovira i Virgili, Department of Analytical and Organic Chemistry, C/ Marcel·lí Domingo 1, Edif. N4, 43007, Tarragona, Spain
[b] Universitat Politècnica de Catalunya, Thermodynamics Laboratory ETSEIB, Av. Diagonal 647 08028, Barcelona, Spain
[c] Universitat Rovira i Virgili, Department of Mechanical Engineering, Av. Països Catalans 26 43007, Tarragona, Spain

ARTICLE INFO

Keywords:
Biobased
Eugenol
Dual-curing
Covalent adaptable networks
Recyclability

ABSTRACT

In the present work, the preparation of sustainable thermosets has been approached simultaneously from three different points of view: 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, and c) inclusion of interchangeable groups in the network, to enable the reuse and recycling of the material at the end of its useful life and avoid waste generation.

The first goal has been approached by synthesizing in a greener way an acrylate-epoxy derivative of eugenol (AEEU) and a glycerol triacrylate (GTA), both biobased resources. Then, the second approach was addressed by using biobased cystamine as a crosslinker to obtain materials through a dual-curing procedure based on a first “click” aza-Michael reaction and a second “click” epoxy-amine reaction. Intermediate and final materials could be prepared with different tailorable properties by controlling the molar ratio of the AEEU and GTA. By using DSC and rheology, we could evaluate the sequentiality and the gelation of the curing process. Finally, the covalent adaptable networks (CANs) prepared contained three different types of dynamic bonds (disulfide, esters, and β-aminoesters) and their thermomechanical properties were tested by DMA revealing T_gs above room temperature from 47 to 70 °C. Bending tests at break were performed to evaluate the mechanical properties reaching values up to 90 MPa of stress at break and 7 % of deformation. Stress relaxation tests showed that all materials could relax the stress at relatively low temperatures (120 °C) in less than 21 min. The associative and dissociative behavior of these materials was investigated through rheology revealing a clear drop of the modulus at high temperatures and frequencies when cystamine was used as a crosslinker. Moreover, their reprocessability was tested obtaining homogeneous samples with no significant changes in their chemical and thermal properties highlighting the great potential and wide range of possibilities in many different fields of these CANs.

1. Introduction

In a world where the depletion of fossil fuel reserves concerns the population, the need to search for alternative routes to overcome it stands out as a significant and critical challenge. The polymer industry is one of the technological fields where replacing petrol-based resources is still in the early stages. For this reason, researchers are developing polymers from natural resources such as vegetable oils, terpenes, terpenoids, carbohydrates, or lignin [1,2]. Among all of them, lignin derivatives like vanillin or eugenol are being widely used as building blocks for biobased polymeric structures [3–5].

In the field of polymers, the recyclability of thermosetting materials is struggling society. Thermosets have excellent mechanical performance and chemical resistance and are, therefore, very durable materials, but the 3D crosslinked network inhibits the reprocessability or reshaping, resulting in amounts of polymeric waste that end up in landfills and cause major environmental issues. For this reason, the introduction of dynamic bonds able to undergo reversible reactions upon applying a certain stimulus in the chemical structure of the polymers has raised up as a promising solution to avoid the generation of trash [6]. Thus, these materials, covalent adaptable networks (CANs), behave as thermosetting materials at low temperatures maintaining their good mechanical properties, but when an external stimulus is applied, they can flow and therefore, be reshaped thanks to these

---

* Corresponding authors.
E-mail addresses: silvia.delaflor@urv.cat (S. De la Flor), angels.serra@urv.cat (À. Serra).

https://doi.org/10.1016/j.eurpolymj.2024.112782
Received 12 December 2023; Received in revised form 3 January 2024; Accepted 16 January 2024

exchangeable bonds [7].

Generally, the mechanism of the exchange reactions of CANs may proceed *via* two different pathways: associative or dissociative [8]. In the first case, the reaction occurs through a concerted mechanism, in which the viscosity gradually decreases with temperature like vitreous silica and were first reported by Leibler in 2011 [6]. In contrast, dissociative CANs experience a sudden drop of the viscosity with temperature because of a first cleavage and a later formation of the new bond [9].

In the past decade, the development of CANs has grown exponentially through the incorporation of many different dynamic bonds from well-known organic reversible reactions such as transesterification [10–12], imine metathesis [13–15], disulfide metathesis [16,17], Diels-Alder reaction [18] or reversible aza-Michael addition [19–21] among many others, which reveals the current increasing interest for this type of materials.

The reprocessability of CANs is one of the most important properties of these materials, which stems from the presence of internal dynamic bonds that allow the rearrangement of the network leading to stress relaxation when subjected to thermal excitation [22]. For this reason, incorporating multiple dynamic bonds into the polymer structure not only provides fascinating effects on recyclability but would also provide beneficial effects in terms of self-healing, self-welding, or 3D printing applications [23]. Xu *et al.* reported the introduction of dynamic imine and disulfide bonds in an epoxy-based polymer [24]. They described the synergistic effect of the disulfide dissociation upon the imine bonds, which provided fast exchange rates and good reprocessability. Zhang and co-workers described the introduction of β-hydroxy esters and disulfide bonds into the polymer matrix by preparing first, a carboxylic acid-extended epoxy resins and, secondly, curing through an epoxy-amine condensation [25]. Moreover, they could tailor the dynamic properties of the CANs by changing the ratio of the acid and the aromatic disulfide amine, obtaining rapid self-healing properties (80 % after heating for 10 min at 180 °C), demonstrating the significant advantages of dual dynamic networks. Dichtel *et al.* also introduced disulfide bonds into polyhydroxy urethane (PHU) networks using cystamine as a comonomer shorten the relaxation times (30 s at 150 °C) compared to the analogous rigid PHU [26]. More recently, Konuray *et al.* prepared a family of thiol-ene polymers containing both disulfide and hydroxyl esters dynamic groups [27]. Given the different kinetics of both exchange reactions, they were able to reprocess the material at moderate temperatures thanks to the disulfide metathesis, and even when the disulfide content was low, transesterification at higher temperatures allowed the recyclability.

For this reason, incorporating multiple dynamic covalent bonds into a polymer matrix can provide advantageous effects not only in recyclability but also in the design of tailorable multi-response materials with self-healing, self-welding, and many different applications [28].

Among all the possibilities to obtain thermosetting materials, dual curing is one of the most efficient and versatile methodologies for preparing thermoset devices in a controlled manner. This procedure consists of two different polymerization processes, sequential or simultaneous, that are triggered by external stimuli such as heat or UV light [29]. In particular, sequential dual curing allows obtaining, after a first curing stage, a stable viscous or gelled intermediate material with specific properties able to be applied or processed to get, after a second curing reaction, a fully cured material with higher mechanical properties. Another important added value of dual curing is the possibility to use “click-type” reactions which are especially suitable due to their orthogonality, selectivity, mild conditions, and high yields, which is of high importance in reducing processing energy costs [30]. Our group has deeply studied many dual-curing procedures for advanced applications in thermosetting materials by using “click” chemistry showing the high versatility of this methodology [31–35].

In the present work, we have prepared a family of thermosetting materials with multiple dynamic exchangeable bonds through a dual-curing methodology. We have synthesized through a sustainable procedure a new acrylate-epoxy derivative from biobased eugenol that has been cured firstly through an aza-Michael reaction at low temperatures and secondly via an epoxy-amine condensation of epoxy groups at high temperatures using Jeffamine D230 or cystamine as crosslinkers. Moreover, the tri acrylate derivative of glycerol has been successfully synthesized and added to the formulation to get gelled intermediate materials and tune the properties of the intermediate and final materials. DSC has been used to study the sequentiality of dual curing and to characterize intermediate and final materials. FTIR and TGA analyses have been performed to check the completion of both reactions during the curing times and the thermal stability of the final materials. The thermomechanical properties and the dynamicity of the obtained crosslinked polymers have been evaluated through DMA and rheology tests.

The recyclability of materials has been proved, and DMA has made it possible to evaluate the mechanical properties of the final materials to understand their behavior at service temperatures.

2. Experimental part

2.1. Materials

Eugenol (EU, 99 %), *m*-chloroperbenzoic acid (MCPBA, 70–75 %), glycerol (Gly, 98 %), sodium bicarbonate ($NaHCO_3$, 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 %), cystamine dihydrochloride (Cys, 97 %), benzylamine (BA), 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. Poly(oxypropylene) diamine (Jeff D230) was kindly donated by Huntsman. All chemicals were used without any purification except CALB that was put in a desiccator under vacuum overnight with anhydrous $MgSO_4$. Dichloromethane (DCM, Scharlau) was purified and dried by standard procedures.

2.2. Synthesis of monomers

The synthesis of the monomers has been conducted following a previous paper of our group [36] and the synthetic procedures are described in the Supporting Information.

2.3. Characterization

Characterization by NMR, Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical thermal analysis (DMA), strain–-stress at break in bending, and rheological analysis is described in detail in the Supporting Information.

2.4. Preparation of dual-cured materials

In a 20 mL vial, a certain amount of AEEU was added and melted at 70 °C for 10 min. Then, the corresponding amount of GTA was added and manually mixed with the melted AEEU. Finally, the stoichiometric amount (NH: acrylate + epoxy = 1:1) of the corresponding amine (cystamine or JeffamineD230) was rapidly added and vigorously stirred at room temperature. Then, the mixture was degassed for 10 min, poured into Teflon molds of 30 x 5 x 1.5 mm^3 dimensions, and cured in an oven at 50 °C for 1 h (first curing stage), 100 °C for 1 h, and 150 °C for 2 h (second curing stage). The materials were coded as polyX_Y, where X indicates the amine used and Y is ascribed to the intermediate material’s gelled or not gelled (viscous) characteristics. For example, polyCys_gel is the material in which cystamine was used as a crosslinker, and the intermediate material was gelled since the gelation point occurred in the first curing stage. Table 1 shows the composition of the different formulations studied.

3. Results and discussion

3.1. Synthesis of the starting monomers

The synthesis of the products was conducted according to a previous reported paper of our own group [36]. The difunctional epoxy acrylate derivative of eugenol (AEEU) was synthesized following the synthetic way depicted in Scheme 1.

The first step was the acylation of the phenol group with acryloyl chloride in the presence of TEA, obtaining a solid product with an 80 % of yield. We also tried the enzymatic esterification of eugenol with acrylic acid and CALB, but this reaction failed, and no product was obtained.

The subsequent synthetic step was the epoxidation of the allylic group by two synthetic methods, as represented in Scheme 1. The procedure of a higher yield was the traditional epoxidation with MCPBA, with a yield of 96 % in only 1 day where, in addition, no oxidation of the double bond of the acrylate group took place (see Figure S6) indicating a complete conversion and the obtention of the acrylate-epoxy eugenol (AEEU). The use of Oxone was also attempted using a biphasic system with TEBAC as a phase transfer catalyst, obtaining good yields after 3 days (80 %).

The acryloation of glycerol was also performed by two different synthetic procedures. The first one is the traditional based on the nucleophilic attack of the alcohol as a nucleophile to the activated acryloyl chloride in the presence of a base (TEA). The yield of the triacrylate by this methodology was 94 %. We also performed the enzymatic reaction of glycerol with methyl acrylate (MA) catalyzed by CALB. After 2 days of reaction, we obtained relatively low yields (30 %) but proved that a green methodology could be used to obtain GTA.

All products synthesized were characterized by spectroscopic techniques: ^{1}H, ^{13}C NMR, and FTIR. The spectra are collected in the supporting information (Figures S1-S8), where it can be observed that the products obtained have high purity.

3.2. Study of the dual-curing procedure

The preparation of materials by the dual-curing procedure involves a first aza-Michael addition of either Cys or Jeff230 at low temperatures and further epoxy-amine reaction at higher temperatures between the unreacted epoxy groups and the remaining free amines. The reaction pathways of both processes are represented in Scheme 2.

It has to be considered that primary amines react with acrylates much easier than secondary. According to that, it is foreseeable that the secondary amines produced by the aza-Michael addition will react mostly with epoxides. The lower reactivity of secondary amines will help delay the epoxy-amine reaction in the second step.

To check this, we studied the kinetics of the first reaction using AEEU and BA as model compounds. To do that, we mixed both reagents in bulk and heated them at 50 °C for 1 h, which are the same conditions used in the curing of the materials (see experimental details in SI). As it can be seen in Fig. 1, the aza-Michael reaction takes place very fast since by only mixing the compounds at this temperature, almost no acrylate signals appear in the spectrum at 0 min while two triplets corresponding to the methylene groups of the β-aminoester appear between 3.1 and 2.75 ppm. At 10 min, the signals of acrylate have fully vanished. Meanwhile the reaction is occurring, not only the aza-Michael reaction takes place but also small signals corresponding to the attack of the amine to the epoxide can be seen in the spectra (signal at 4.4 ppm attributable to OH group produced by the ring opening of the epoxy ring).

However, as the extent of this reaction is very low, we can consider it as negligible, especially when acrylate-rich formulations, as in the present study, are used which increase the viscosity and therefore diffusion phenomena play an important role. It is worth to say that the use of model compounds helps to comprehend the reactive processes, but it cannot be fully extrapolated to the curing process. For this reason, the curing procedure applied in the preparation of the materials may practically behave as a sequential dual curing.

If only AEEU and the corresponding amines are used in the dual curing procedure, no gelation will occur in the first step due to the single acrylate group in AEEU. Therefore, only viscous intermediate oligomers would be obtained. Thus, to obtain a gelled intermediate material, the trifunctional acrylate GTA must be added to obtain crosslinking points when amines have reacted.

To determine the amount of GTA necessary to get gelation, the theoretical conversion of the acrylate groups at the gel point α_{gel} during the aza-Michael reaction has to be calculated assuming the ideal random step-wise reaction, using the well-known Flory-Stockmayer equation (Eq. (1) [37,38]:

$$\alpha_{gel}^{theor} = \sqrt{\frac{r}{(f_1 - 1)\cdot(f_2 - 1)}} \tag{1}$$

where r is the hydrogen amine/acrylate equivalent ratio, f_1 the acrylate monomer functionality and f_2 the amine functionality.

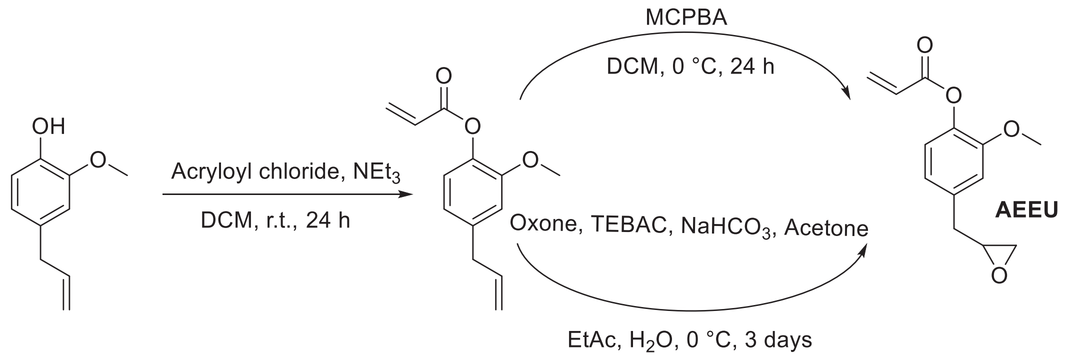
With this equation, a molar ratio nGTA/nAEEU = 0.11 was calculated as the lowest to achieve gelation at 100 % of conversion of acrylate groups. Thus, two different possibilities were studied herein: a) a molar ratio nGTA/nAEEU = 0.46, in which gelation will occur before full conversion to obtain a solid-like 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.

DSC analyses were performed to study the sequentiality of the system. However, only the intermediate and final materials could be characterized due to the fast rate of the aza-Michael addition at room temperature. Fig. 2 shows both the DSC tests of all intermediate materials (viscous or gelled) as well as the T_g of the final materials, and the data are collected in Table 2.

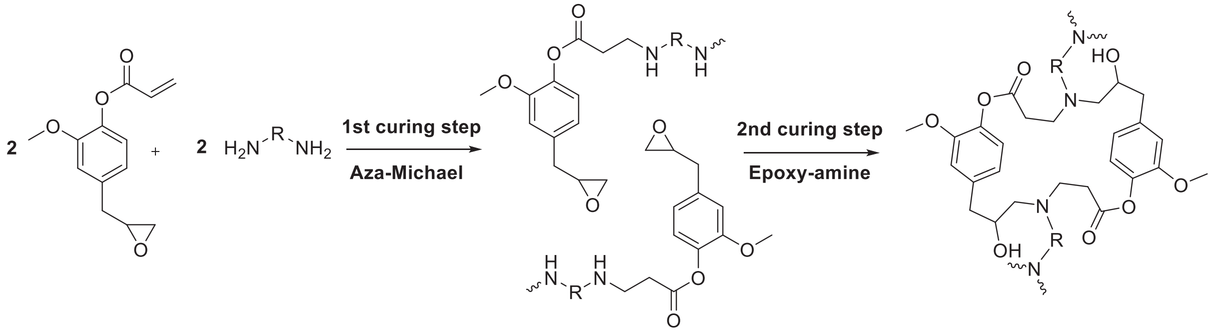
As can be seen in Fig. 2a, all intermediate materials show a T_g between −30 and −10 °C and an exothermal peak corresponding to the second epoxy-amine condensation reaction. As expected, materials with a gelled intermediate material display higher T_g values than their counterparts due to the higher crosslinking density achieved after the first step. Moreover, materials containing Cys as the hardener show higher T_gs than Jeff ones, thanks to the shorter amine chain that provides more compact networks. In addition, all materials release between 90 and 100 kJ/ee during the epoxy-amine reaction at high temperatures, which is in accordance with the values reported in the literature [39]. In

Table 1
Composition of the formulations prepared.

Formulation	AEEU		GTA		Cys		JeffD230	
	g	mmol	g	mmol	g	mmol	g	mmol
polyCys_gel	0.5	2.13	0.25	1	0.27	1.80	–	–
polyCys_nogel	0.5	2.13	0.05	0.2	0.18	1.21	–	–
polyJeff_gel	0.5	2.13	0.25	1	–	–	0.42	1.80
polyJeff_nogel	0.5	2.13	0.05	0.2	–	–	0.28	1.21



Scheme 1. Synthetic procedures used in the preparation of AEEU monomer.



Scheme 2. Reaction pathways of the first curing step (aza-Michael reaction) and the second curing step (epoxy-amine condensation).

the case of polyJeff_nogel material, the enthalpy is slightly lower due to the inaccuracy of the measure since the curing is not complete at the final scanning temperature.

Conversely, the final materials gelled after the first curing step display lower T_g values than the non-gelled ones. This fact can be ascribed to the increased amount of GTA and, consequently, to the higher amount of amine in the sample that, even producing more crosslinking points, also provides more aliphatic moieties which enable certain flexibility and mobility to the final polymer network, thus decreasing the glass transition temperature. This behavior is in accordance with the expected results of a dual-curing procedure [29,33].

FTIR spectroscopy confirmed the practical sequentiality and completion of both curing reactions. Spectra of AEEU, intermediate and final materials were recorded due to the impossibility of obtaining the spectrum of the unreacted mixture due to the rapid aza-Michael addition, which prevents the observation of the C = C bonds of the acrylate groups. As can be seen in Figure S10, the band at 1636 cm^{-1}, corresponding to the C = C of the acrylate group, wholly disappeared in the intermediate material, while the epoxy band at 825 cm^{-1} disappeared after the second curing reaction, confirming the completion of the curing process.

As mentioned, adding GTA into the system is crucial to achieving gelation at the first curing stage. To check if a gelled or a viscous intermediate material is obtained, rheological analyses of the first curing stage were carried out for all formulations for comparison purposes. All the results can be seen in Fig. 3.

Gelation is ascribed to the phenomena in which the material changes from a liquid to a solid behavior, thus meaning that the storage modulus (*G*', solid contribution) overpasses the loss modulus (*G*'', liquid contribution). As it can be seen, materials with an nGTA/nAEEU = 0.46 (theoretically gelled in the first stage) gel during the aza-Michael reaction (Fig. 3a, and c) since at the end of the test, the *G*' is higher than *G*''. It is important to highlight that when Cys is used, the gelation occurs immediately after starting the test at 50 °C whereas, in the case of Jeff, the reactive mixtures achieve gelation later, indicating a higher reactivity of Cys formulations. On the other hand, materials with nGTA/nAEEU = 0.09 (below the minimum ratio) do not gel during the first stage, as expected (Fig. 3b, and d). It is also worth saying that the values of *G*' and *G*'' for Cys materials are higher than their counterparts, due to the lower viscosity of Jeff formulations. The fact that we can control the gelation by the composition of the initial formulation applying the Flory-Stockmayer equation, confirmed us that the extent of the epoxy-amine reaction during the first step is negligible as stated before.

3.3. *Study of the thermal and thermomechanical properties of the materials*

To evaluate the thermal stability of the final materials as well as to confirm that further thermal tests are conducted in non-degradability conditions, thermogravimetric tests were performed. Fig. 4 shows the TGA curves and their derivatives, and the most significant thermogravimetric data extracted are presented in Table 3.

As can be seen, all materials show degradation curves with similar shapes and good thermal stability up to 220 °C indicating that a safe heat treatment or recycling can be done below this temperature. In the case of materials with Jeff, the main peak of degradation could be ascribed to the breakage of the propylene glycol repetitive units. In addition, disulfide groups are known to degrade before poly(hydroxy amine) moieties or polypropylene glycol units [17,32]. The values of char yield are in accordance with what is expected because polyCys_gel and polyJeff_gel have a higher content of amine and, therefore, a higher proportion of nitrogen which leads to higher values of char yield.

By DMA, we determined the thermomechanical properties of the final materials. Fig. 5 shows the evolution of the storage moduli (*E*') and the dependence of tan δ with temperature for all the materials, and the data extracted are presented in Table 3.

All materials display $T_{\tan\,\delta}$ values higher than room temperature, from 47.2 °C for polyJeff_gel to 70.1 °C for polyCys_nogel. Materials

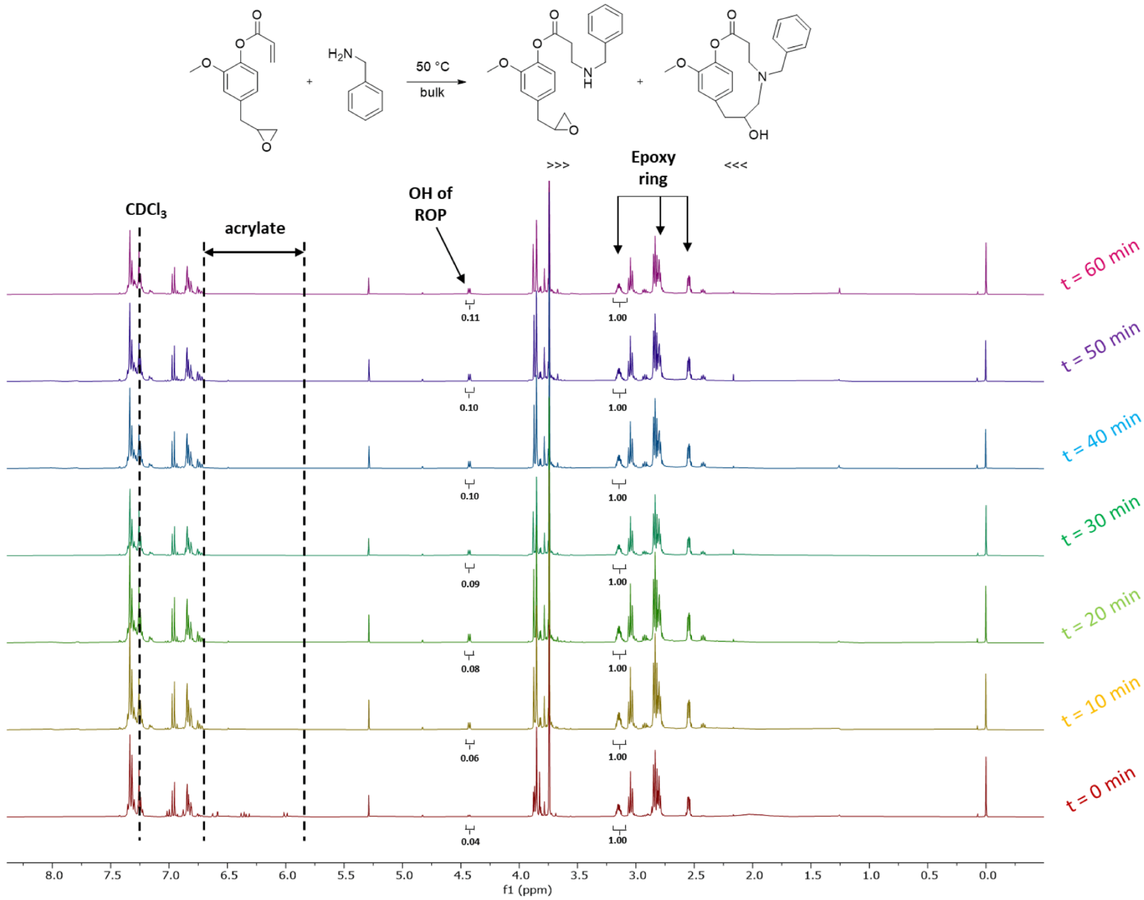


Fig. 1. Scheme of model reaction and ^{1}H NMR spectra of the kinetic study with model compounds AEEU and BA.

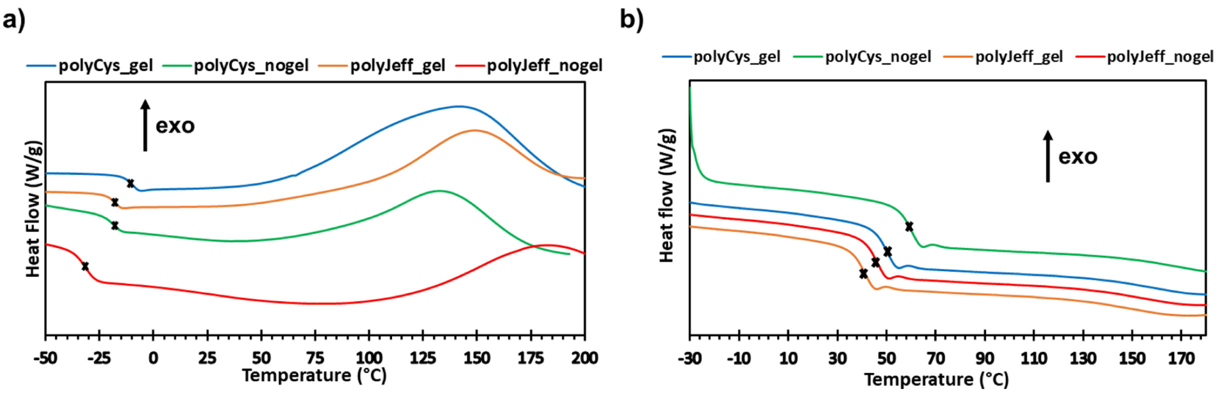


Fig. 2. DSC thermograms corresponding to the a) intermediate materials and second dynamic curing at 10 °C/min and b) final materials at 20 °C/min.

Table 2
Calorimetric data extracted from the DSC tests of intermediate and final materials.

Sample	$T_{g\ \text{intermediate}}$ (°C)	$T_{g\ \text{final}}$ (°C)	$\Delta H_{\text{epoxy-amine}}$[a] (kJ/ee)
polyCys_gel	−10.2	50.1	98.6
polyCys_nogel	−19.0	62.6	96.1
polyJeff_gel	−18.7	41.0	90.3
polyJeff_nogel	−30.1	45.2	80.2

[a] Enthalpy released in the epoxy-amine reaction by epoxy equivalent.

with a gelled intermediate network present lower values of $T_{\tan\,\delta}$ than their non-gelled counterparts, as expected for dual curing procedures. More content of the corresponding aliphatic amine (Jeff or Cys) and GTA leads to a more flexible network structure. Nevertheless, for the same reason, these materials have higher values of *E*’ in the rubbery state due to the higher crosslinking density of the final network. Foreseeably, materials containing Cys as hardener show higher values of storage modulus in the rubbery and in the glassy state, and higher values of $T_{\tan\,\delta}$ in comparison to Jeff due to its shorter chain that leads to less mobility of the network and, therefore, providing higher rigidity. In any case, it has been demonstrated that by controlling the stoichiometry of the formulation and using dual-curing methodologies, it is possible to tailor the thermomechanical properties of the final materials obtaining a wide

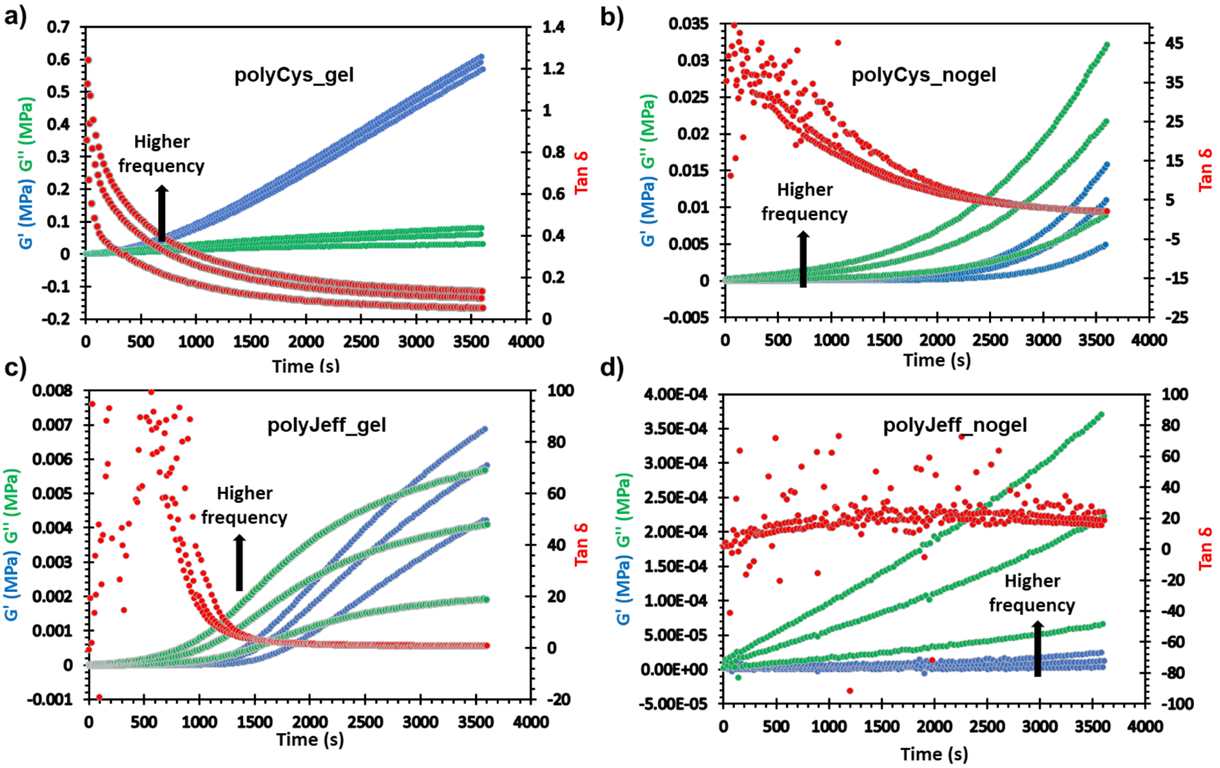


Fig. 3. Evolution of storage modulus (*G*'), loss modulus (*G*'') and tan δ vs. time at three different frequencies (0.5 Hz, 1.75 Hz and 3 Hz) for a) polyCys_gel, b) polyCys_nogel, c) polyJeff_gel and d) polyJeff_nogel at 50 °C.

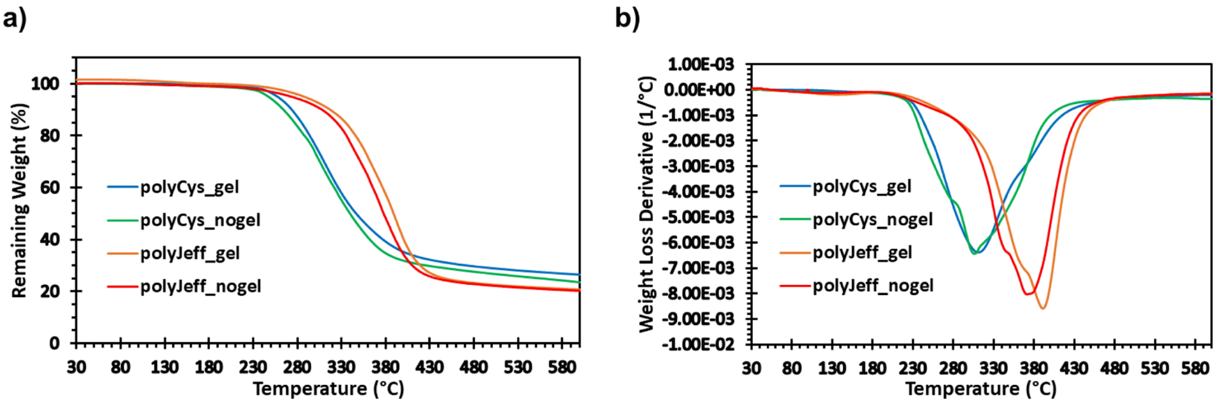


Fig. 4. a) thermogravimetric and b) dtg curves of the materials prepared.

Table 3
Thermogravimetric and thermomechanical data of all the materials prepared. Coefficients of variation less than 2% for $T_{\tan\,\delta}$ and less than 5% for storage moduli (*E*').

Sample	$T_{1\%}$[a] (°C)	T_{max}[b] (°C)	Char Yield[c] (%)	$T_{\tan\,\delta}$[d] (°C)	E'_{glassy}[e] (MPa)	$E'_{rubbery}$[f] (MPa)
polyCys_gel	220.6	311.0	26.5	61.4	3482	13.0
polyCys_nogel	221.4	306.3	23.5	70.1	3331	7.1
polyJeff_gel	225.3	391.0	20.9	47.2	2810	8.2
polyJeff_nogel	223.5	371.3	20.5	55.5	3103	3.7

[a] Temperature of 1% weight loss.
[b] Temperature at the maximum rate of degradation.
[c] Char residue at 600 °C.
[d] Temperature at the maximum of tan δ peak at 1 Hz.
[e] Glassy storage modulus at T_g – 50 °C determined by DMA.
[f] Rubbery storage modulus at T_g + 50 °C determined by DMA.

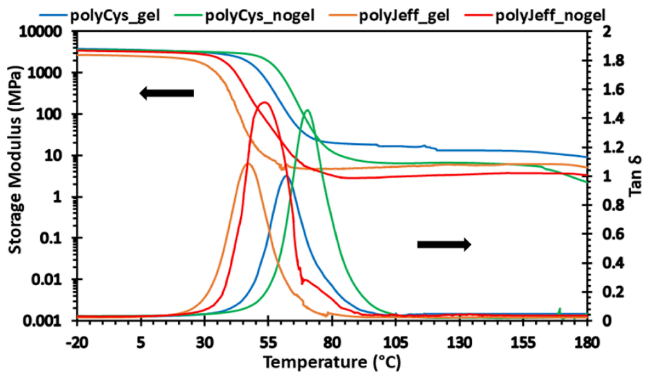


Fig. 5. Evolution of storage modulus and tan δ with temperature for all materials.

range of different polymers that may be interesting for several applications. In addition, in this way, advanced fabrication processes can be implemented.

Interestingly, a drop of the storage modulus above 160 °C can be seen in all the curves of the materials, especially in Cys materials, indicating a loss in the crosslinking density which may be attributed to the dissociative behavior of the dynamic aza-Michael reaction and the disulfide metathesis [19]. Later we will discuss the possible exchange reactions of the networks as well as their dynamic behavior.

3.4. *Study of the mechanical characterization of the materials*

The mechanical properties of these materials were investigated in 3-point bending at 20 °C to obtain the stress–strain relationship up to the break. The results from these tests can be seen in Fig. 6 and the corresponding data are collected in Table S1.

As expected, polyJeff materials exhibit higher values of strain at break in comparison to their Cys counterparts. This characteristic can be easily explained by the presence of Jeffamine in the materials, which has longer aliphatic chains that provide more flexibility to the network than Cys. For the Jeff materials, despite presenting similar ductility, the lower amount of aliphatic GTA in the no gelled sample and, consequently, the lower amount of the corresponding amine, resulted in higher stress at break value than the gelled one. However, this effect is not evident in materials containing Cys because the higher rigidity provided by the shorter chain of Cys hinders this contribution making this material more fragile presenting a premature breakage. Finally, it is important to highlight the outstanding bending strength of polyCys_gel and polyCys_no gel (91 MPa and 79 MPa, respectively), which are far bigger than similar vitrimeric materials [21,40]. This demonstrates that the use of dual-curing methodologies allows the mechanical properties of these materials to be easily tuned and tailored.

3.5. *Study of the dynamic behavior of the materials*

The materials prepared are expected to undergo different types of exchange reactions. CANs containing Jeff may relax the stress thanks to the dynamic aza-Michael reaction (dissociative-type) and to the transesterification (associative-type) originated from the esters of the former acrylates and the alcohols of the epoxy-amine condensation. In case of Cys materials, disulfide metathesis can also occur due to the S-S bond in its structure. The representations of the different network rearrangements produced by the three possible reversible processes in Cys materials are represented in Fig. 7.

Vitrimeric materials are widely recognized to exhibit an Arrhenius-type temperature dependence when the viscosity is controlled by an exchange reaction process similar to inorganic silica materials [41]. Thus, to further investigate the dynamic nature of these networks, time and temperature-dependent relaxation behavior was studied. Stress relaxation tests were performed by DMA, and the results are shown in Fig. 8a-d and Table 4.

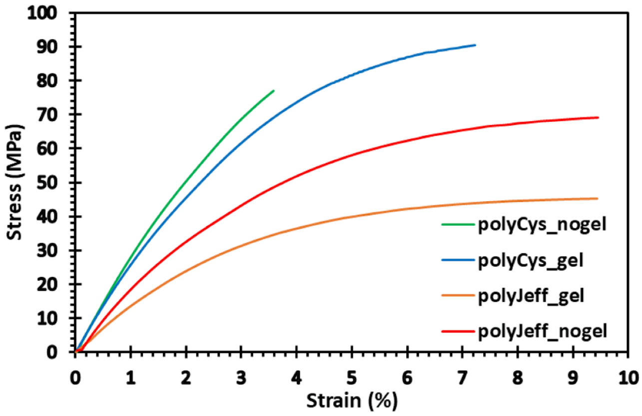


Fig. 6. Stress–strain at break curves in bending at 20 °C for all the materials prepared.

The stress relaxation curves provide compelling evidence of the capability of these materials to efficiently relax the stress, reaching a reference relaxation value of 63 % ($\sigma/\sigma_0 = 0.37$) in 32.5 s for polyCys_nogel, 47.5 s for polyCys_gel, 89.0 s for polyJeff_gel and 126.5 s for polyJeff_nogel at 160 °C.

It can be seen that materials containing Cys relax the stress faster than their Jeffamine counterparts which can be ascribed to the disulfide metathesis as a third exchange reaction in the network. Despite that polyCys_gel contains more exchangeable groups, either disulfide bonds, ester and hydroxyl, and β-aminoesters, polyCys_nogel could relax the stress faster (12.7 min and 10.1 min at 120 °C, respectively) probably due to the lower crosslinking density of the latest which allow more mobility of the network, thus increasing the probability of the exchangeable groups to be closer and therefore to make the exchange reaction more likely to occur. In fact, the storage modulus in the rubbery state is lower for polyCys_nogel, which favors the network relaxation process.

Interestingly, when Jeffamine is used, the opposite trend can be seen in the table (15.0 min for polyJeff_gel and 21.1 min for polyJeff_nogel at 120 °C). In the case of polyJeff_gel, as the Jeffamine has long chains, the higher amount of amine, the more flexible is the network, which enhances the relaxation rates. From these results, it can be confirmed that the flexibility and mobility of the network structure affect in a high considerable way the relaxation ability. In any case, all materials can completely relax the stress at 120 °C in less than 5000 s. It is also important to highlight that even obtaining high-T_g materials (up to 70 °C), they can relax 63 % of the initial stress at relatively low temperatures such as 100 °C, proving the great potential of these bio-based CANs.

To further characterize these CANs, the time required to relax the initial stress to e^{-1} ($\sigma/\sigma_0 = 0.37$) at all temperatures for these materials was obtained from the corresponding relaxation curves. By fitting the data to the Arrhenius-type equation, it is possible to calculate the activation energy (E_a) associated with the topological rearrangement (see Fig. 8e and Table 4). As observed, materials containing Cys display higher activation energy values demonstrating greater dependence of the relaxation time on the temperature, probably due to the higher content of dynamic bonds that can undergo exchange reactions.

Another critical parameter in dynamic networks is the topology freezing temperature (T_v). Chemically, it indicates the temperature below which the network rearrangements are almost negligible, and physically is the temperature at which the material reaches a viscosity of 10^{12} Pa·s. T_vs could be deduced from the Arrhenius relationships and using Maxwell equation and are presented in Table 4. As shown, Jeff materials display lower values of T_v, although they relax slower than their Cys counterparts. This can be associated with their lower crosslinking density, which is directly related to the $E'_{rubbery}$, which is used in the Maxwell relationship. All materials present values of T_v lower than their corresponding T_gs. Since materials are in the glassy state below their T_g, rearrangement will not occur until that temperature is exceeded. Thus, the glass transition temperature is the most important parameter to determine the start of the exchange kinetics.

As previously mentioned, these materials contain several dynamic bonds in their structure with either associative-type or dissociative-type exchange mechanisms. In DMA curves in Fig. 5, we observed a slight drop of the storage modulus at high temperatures, more drastic in Cys materials. To investigate that, rheological tests at different temperatures with frequency sweeps in oscillatory shear under a linear viscoelastic regime were performed for all the materials (Fig. 9).

The temperatures studied were the same as in the stress relaxation tests, and the frequency sweep was from 100 to 0.1 rad/s. As it can be observed, in both polyJeff materials (Fig. 9c and d), the storage modulus

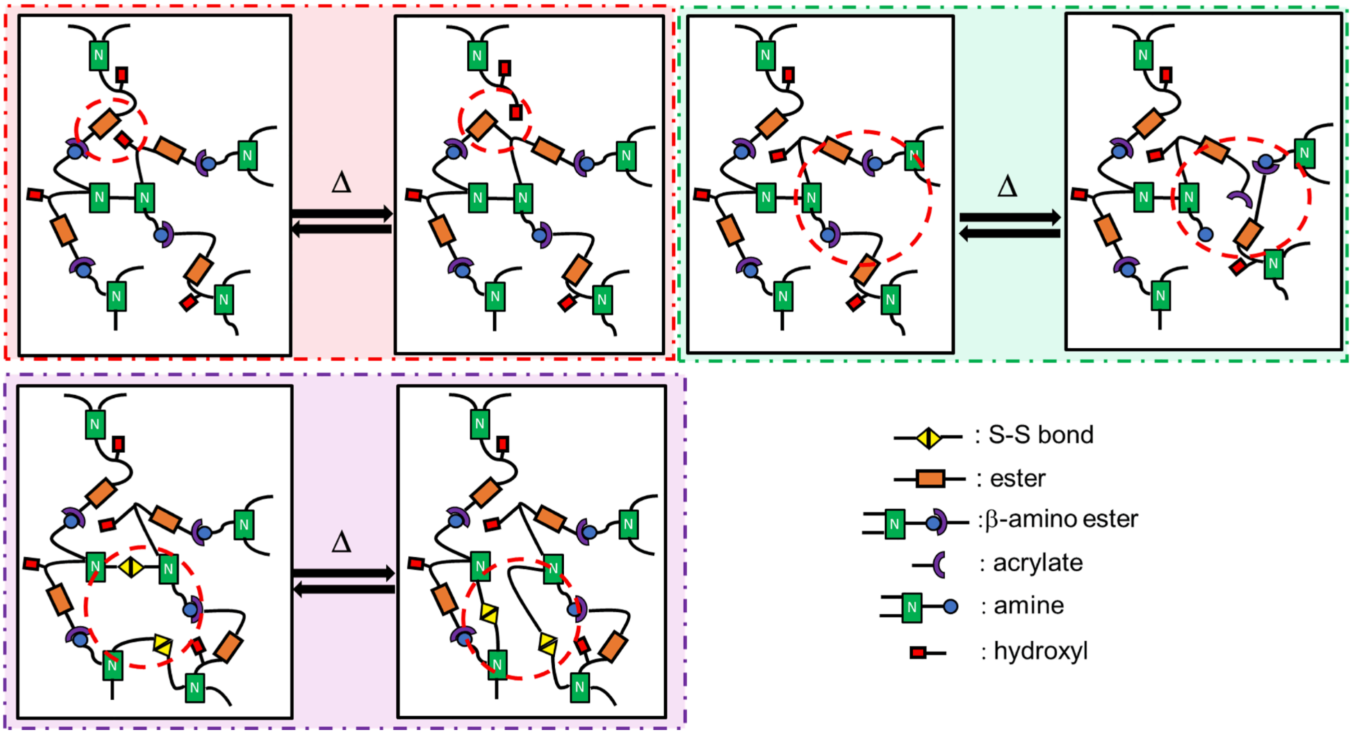


Fig. 7. Schematics of network exchanges via transesterification (top left), reversible aza-Michael reaction (top right) and disulfide metathesis in case of Cys materials (bottom left).

(G') is constant independently of the frequency and the temperature, indicating the associative behavior of these materials even at high temperatures and long relaxation times. Indeed, one of the main characteristics of vitrimers is keeping constant the crosslinking density with temperature and time which is directly related to the storage modulus at high temperatures. This can also mean that despite the chemically dissociative mechanism of the reversible aza-Michael reaction, the exchange kinetics may be governed by the transesterification reaction since it is reported to be faster than the previous one [21]. Moreover, the huge amount of tertiary amines present in the network can accelerate the transesterification reaction at low temperatures as previously reported [42].

Interestingly, in the case of polyCys_nogel, a clear drop of G' at 180 °C at low frequencies can be seen, indicating the loss of the integrity of the network and, therefore, the crosslinking density, which is a behavior of typical dissociative networks. The same happens with polyCys_gel, but in this material, the drop of storage modulus starts at 160 °C, which can be explained by the higher proportion of S-S bonds coming from higher amounts of Cys in the material. Here, the exchange may be controlled by the disulfide exchange and transesterification simultaneously. However, at high temperatures and long relaxation times, the first exchange reaction is to such an extent that it may produce this drastic drop of G'. It has been reported that tertiary amines can act as an internal catalyst for disulfide exchange in CANs [43]. The mechanisms of disulfide exchange have been reported to be [2 + 2] metathesis reaction and a [2 + 1] radical-mediated mechanism. However, when tertiary amines are present, they generate active thiolates by the rupture of the disulfide bond, as represented in Scheme 3. Another disulfide bond was then attacked by the nucleophilic thiolate formed, promoting the bond exchange, explaining in this way the dissociative character of the polyCys CANs. This mechanism can occur, in different extents, in addition to the disulfide metathesis. The authors of that paper conclude that the radical-mediated mechanism is not changed in the presence of tertiary amines, resulting in a significant enhancement of the overall bond exchange efficiency.

3.6. *Reprocessability of the CANs*

Once it has been shown that the prepared materials have good characteristics as CANs, it is necessary to study their recyclability, which will be key to achieve the sustainability of these materials. All the samples were ground into powder and hot-pressed in a manual press under 2 MPa in an aluminum mold to test the recyclability. The recycling tests were performed at 160 °C, a temperature that ensures not only that the exchange processes are taking place but also safe recycling since all materials start to degrade at 220 °C. Fig. 10 shows the pictures taken from the original, ground, and reprocessed samples, where it can be observed that the homogeneity and transparency are well-maintained in the recycled sample.

To confirm the good recycling ability, FTIR spectra of the virgin and the reprocessed samples of all the materials prepared herein were recorded. Figure S11 shows both spectra, demonstrating that no significant differences can be observed and confirming that the chemical structure of the polymer is well preserved. Moreover, DSC analyses were performed to compare the T_g of the recycled materials with the virgin ones (Figure S12). Table 5 collects the results obtained from that tests. As can be seen, the T_g values of all materials were very similar in comparison to the virgin samples indicating a successful recycling procedure for all cases.

Given the obtained results, it is evident that these materials have the potential for application as adhesives, owing to the precise control of the viscosity of the intermediate material during dual curing. Furthermore, their vitrimeric properties render them promising options for reversible bonding. Looking ahead, we intend to investigate this potential application alongside exploring their utility in malleable composite materials.

4. Conclusions

Materials with several dynamic exchangeable bonds could be prepared by reacting epoxy eugenol acrylate (AEEU) and glycerol triacrylate (GTA) with different amines (Cystamine, Cys, and Jeffamine

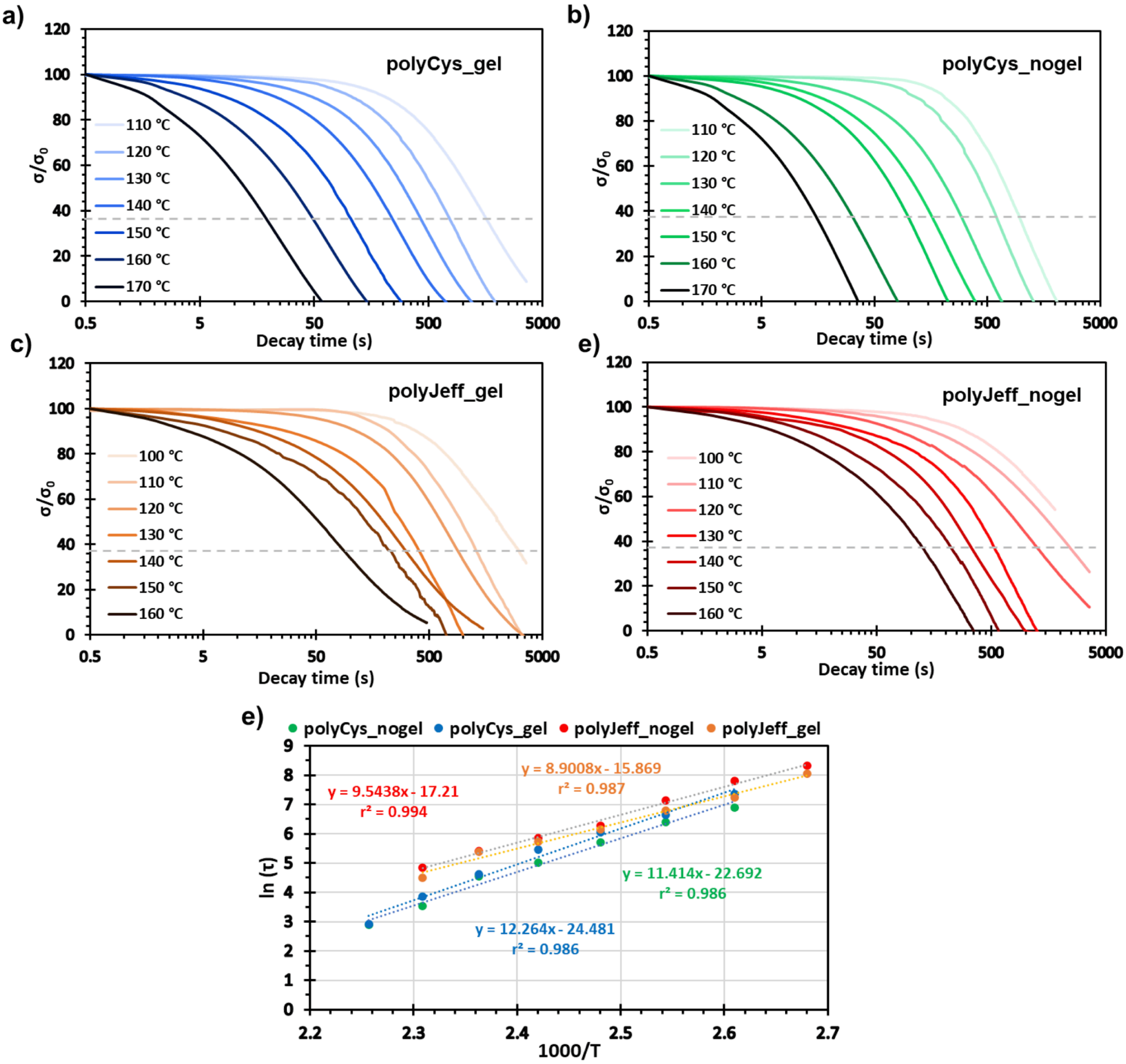


Fig. 8. Normalized stress relaxation plots as a function of time at various temperatures during 3600 s for polyCys_gel (a), polyCys_nogel (b), polyJeff_gel (c), and polyJeff_nogel (d) materials and e) Arrhenius plot of relaxation times against temperature for the different CANs.

Table 4
Relaxation time, activation energy, topology freezing temperature, and adjusting parameters for the Arrhenius equation of the CANs prepared.

Material	$\tau_{0.37}$ [a] (min)	$\tau_{100\%}$ [b] (min)	E_a (kJ/mol)	ln A (s)	T_v (°C)	r^2
polyCys_gel	12.7	31.8	89	24.48	64	0.986
polyCys_nogel	10.1	21.3	97	22.69	59	0.986
polyJeff_gel	15.0	55.1	73	15.87	45	0.987
polyJeff_nogel	21.1	83.3	79	17.21	51	0.994

[a] Time to reach a value of $\sigma/\sigma_0 = 0.37$ at 120 °C.
[b] Time to reach total relaxation at 120 °C.

D230, Jeff) using a dual-curing procedure. A first aza-Michael reaction between NH groups and acrylates at low temperatures and a second epoxy-amine condensation reaction between free amines and the remaining epoxy groups at higher temperatures allowed to obtain crosslinked materials. Adding GTA allowed us to achieve gelation in the first or second steps to get gelled or viscous intermediate materials depending on the ratio AEEU/GTA.

^{1}H NMR spectra, recorded at different reaction times, using model compounds demonstrated the practical sequentiality of the dual curing.

DSC studies evidence the sequentiality of this system by obtaining intermediate materials with different T_g values and a residual heat corresponding to an epoxy-amine reaction. Moreover, all final materials revealed glass transition temperatures above room temperature, higher when cystamine was used as a crosslinking agent. FTIR also confirmed the sequentiality of the dual curing and the completion of the second step.

All materials displayed thermal stability (up to 220 °C) and showed high values of $T_{\tan\delta}$ (from 47 to 70 °C) and high storage modulus values in the glassy state, demonstrating very good thermomechanical properties.

In all cases, incorporating multiple dynamic bonds in their polymer structure allowed them to relax 63 % of the initial stress in less than 20 min at 120 °C. Frequency sweep tests demonstrated that Jeff materials maintained the storage modulus (G') constant, even at high temperatures and longer times. In contrast, the storage modulus of Cys materials dropped at 180 °C (for polyCys_nogel) and 160 °C (for polyCys_gel), indicating a typical behavior of dissociative-type CANs.

The bending tests also showed that materials with Cys displayed high bending strength (91 MPa and 79 MPa) higher than many similar CANs

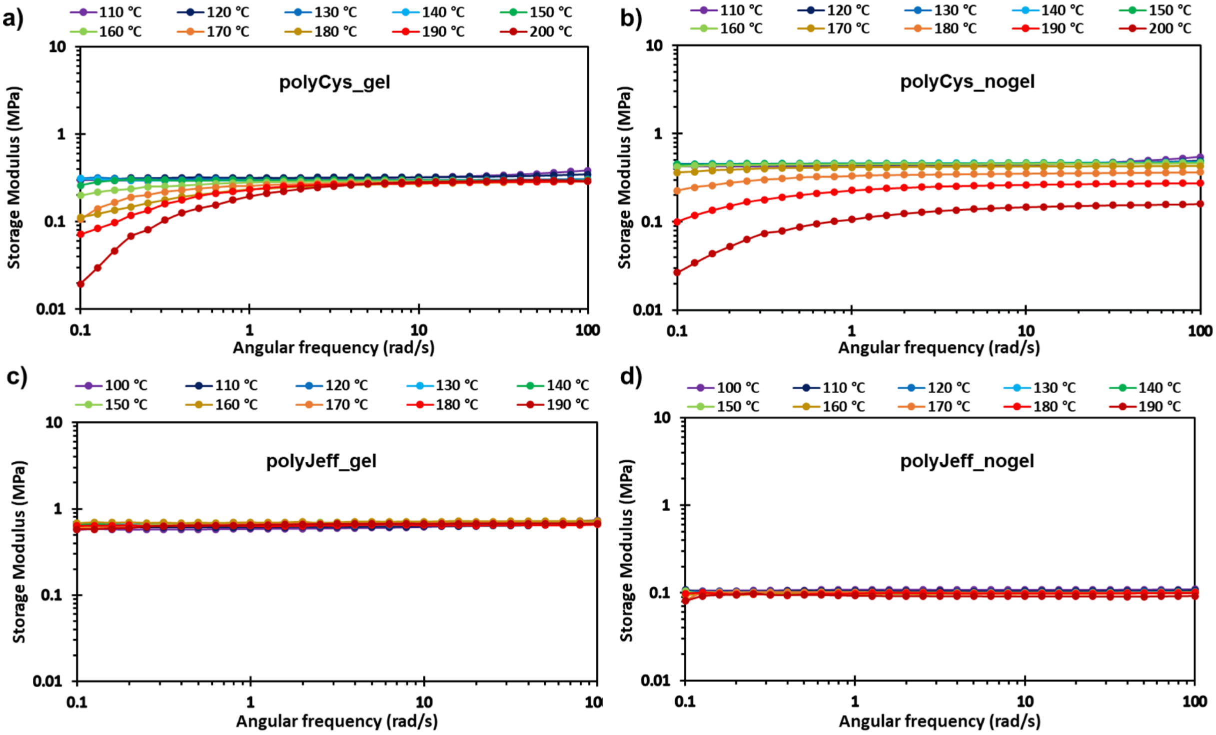
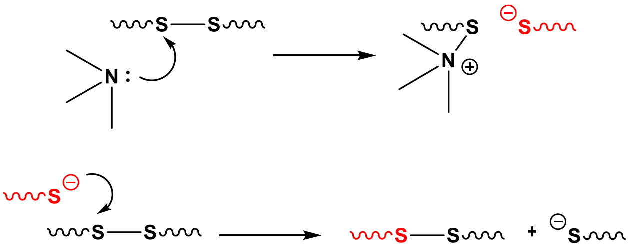


Fig. 9. Frequency sweep at different temperatures for polyCys_gel (a), polyCys_nogel (b), polyJeff_gel (c), and polyJeff_nogel (d).



Scheme 3. Proposed exchange mechanism of disulfide bonds catalyzed by amines.

and vitrimers.

The materials seem to present good reprocessability, allowing safe recycling without significant changes in their chemical structure as seen in the FTIR and DSC plots.

In conclusion, this study successfully demonstrates the feasibility of the dual-curing procedure to tailor the properties of vitrimers, enabling the design of a wide range of polymers synthesized from bio-based resources and, in a highly greener way, suitable for many different applications and environmentally attractive alternatives.

CRediT authorship contribution statement

Adrià Roig: Writing – original draft, Methodology, Investigation. **Xavier Ramis:** Writing – review & editing, Validation, Conceptualization. **Silvia De la Flor:** Writing – review & editing, Supervision, Data curation, Conceptualization. **Àngels Serra:** Writing – review & editing, Project administration, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Angels Serra reports financial support was provided by Spain Ministry of Science and Innovation.

Table 5
Glass transition temperatures of the virgin and recycled materials.

Sample	T_g virgin (°C)	T_g recycled (°C)
polyCys_gel	50.1	49.5
polyCys_nogel	62.6	62.1
polyJeff_gel	41.0	40.1
polyJeff_nogel	45.2	44.7

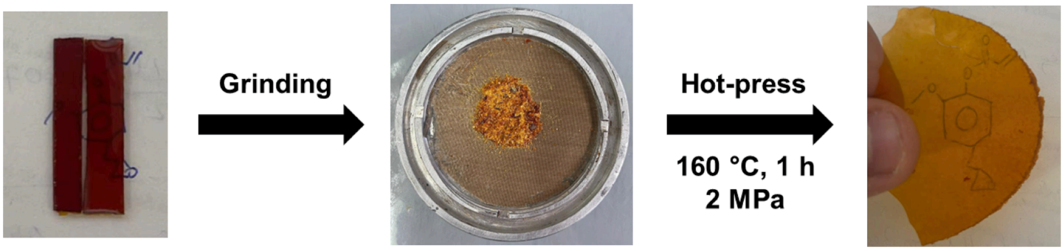


Fig. 10. Pictures of virgin, ground and recycled samples of the polyCys_nogel.

Data availability

Data will be made available on request.

Acknowledgments

This work is part of the R&D projects PID2020-115102RB-C21 and PID2020-115102RB-C22 funded by MCNI/AEI/10.13039/501100011033 and European Union "NextGenerationEU"/PRTR. We acknowledge these grants and we also thank to the Generalitat de Catalunya (2021-SGR-00154).

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2024.112782.

References

[1] T. Vidil, A. Llevot, Fully biobased vitrimers: future direction toward sustainable cross-linked polymers, Macromol. Chem. Phys. 223 (2022) 2100494, https://doi.org/10.1002/macp.202100494.

[2] D.K. Schneiderman, M.A. Hillmyer, 50th Anniversary perspective: there is a great future in sustainable polymers, Macromolecules 50 (2017) 3733–3749, https://doi.org/10.1021/acs.macromol.7b00293.

[3] M. Fache, B. Boutevin, S. Caillol, Vanillin, a key-intermediate of biobased polymers, Eur. Polym. J. 68 (2015) 488–502, https://doi.org/10.1016/j.eurpolymj.2015.03.050.

[4] R. Morales-Cerrada, S. Molina-Gutierrez, P. Lacroix-Desmazes, S. Caillol, Eugenol, a promising building block for biobased polymers with cutting-edge properties, Biomacromolecules 22 (2021) 3625–3648, https://doi.org/10.1021/acs.biomac.1c00837.

[5] I. Faye, M. Decostanzi, Y. Ecochard, S. Caillol, Eugenol bio-based epoxy thermosets: from cloves to applied materials, Green Chem. 19 (2017) 5236–5242, https://doi.org/10.1039/C7GC02322G.

[6] D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, Silica-like malleable materials from permanent organic networks, Science 334 (2011) 965–968.

[7] M. Podgórski, B.D. Fairbanks, B.E. Kirkpatrick, M. McBride, A. Martinez, A. Dobson, N.J. Bongiardina, C.N. Bowman, Toward stimuli-responsive dynamic thermosets through continuous development and improvement in covalent adaptable networks (CANs), Adv. Mater. 32 (2020) 1906876, https://doi.org/10.1002/adma.201906876.

[8] G.M. Scheutz, J.J. Lessard, M.B. Sims, B.S. Sumerlin, Adaptable crosslinks in polymeric materials: resolving the intersection of thermoplastics and thermosets, J. Am. Chem. Soc. 141 (2019) 16181–16196, https://doi.org/10.1021/jacs.9b07922.

[9] X.-L. Zhao, P.-X. Tian, Y.-D. Li, J.-B. Zeng, Biobased covalent adaptable networks: towards better sustainability of thermosets, Green Chem. 24 (2022) 4363–4387, https://doi.org/10.1039/d2gc01325h.

[10] M. Capelot, D. Montarnal, F. Tournilhac, L. Leibler, Metal-catalyzed transesterification for healing and assembling of thermosets, J. Am. Chem. Soc. 134 (2012) 7664–7667, https://doi.org/10.1021/ja302894k.

[11] F.I. Altuna, C.E. Hoppe, R.J.J. Williams, Shape memory epoxy vitrimers based on DGEBA crosslinked with dicarboxylic acids and their blends with citric acid, RSC Adv. 6 (2016) 88647–88655, https://doi.org/10.1039/C6RA18010H.

[12] T. Liu, C. Hao, L. Wang, Y. Li, W. Liu, J. Xin, J. Zhang, Eugenol-derived biobased epoxy: shape memory, repairing and recyclability, Macromolecules 50 (2017) 8588–8597, https://doi.org/10.1021/acs.macromol.7b01889.

[13] P. Taynton, K. Yu, R.K. Shoemaker, Y. Jin, H.J. Qi, W. Zhang, Heat- or water-driven malleability in a highly recyclable covalent network polymer, Adv. Mater. 26 (2014) 3938–3942, https://doi.org/10.1002/adma.201400317.

[14] A. Roig, P. Hidalgo, X. Ramis, S. De la Flor, À. Serra, Vitrimeric epoxy-amine polyimine networks based on a renewable vanillin derivative, ACS Appl. Polym. Mater. 4 (2022) 9341–9350, https://doi.org/10.1021/acsapm.2c01604.

[15] H. Geng, Y. Wang, Q. Yu, S. Gu, Y. Zhou, W. Xu, X. Zhang, D. Ye, Vanillin-based polyschiff vitrimers: reprocessability and chemical recyclability, ACS Sustain. Chem. Eng. 6 (2018) 15463–15470, https://doi.org/10.1021/acssuschemeng.8b03925.

[16] A. Ruiz de Luzuriaga, R. Martin, N. Markaide, A. Rekondo, G. Cabañero, J. Rodríguez, I. Odriozola, Epoxy resin with exchangeable disulfide crosslinks to obtain reprocessable, repairable and recyclable fiber-reinforced thermoset composites, Mater. Horiz. 3 (2016) 241–247, https://doi.org/10.1039/C6MH00029K.

[17] A. Roig, M. Agizza, À. Serra, S. De la Flor, Disulfide vitrimeric materials based on cystamine and diepoxy eugenol as bio-based monomers, Eur. Polym. J. 194 (2023) 112185, https://doi.org/10.1016/j.eurpolymj.2023.112185.

[18] C. Chapelle, B. Quienne, C. Bonneaud, G. David, S. Cailllol, Diels-Alder-chitosan based on dissociative covalent adaptable networks, Carbohydr. Polym. 253 (2021) 117222, https://doi.org/10.1016/j.carbpol.2020.117222.

[19] C. Taplan, M. Guerre, F.E. Du Prez, Covalent adaptable networks using β-amino esters as thermally reversible building blocks, J. Am. Chem. Soc. 143 (2021) 9140–9150, https://doi.org/10.1021/jacs.1c03316.

[20] H.Y. Song, G. Lee, S.-K. Ahn, K. Hyun, Linear viscoelasticity of covalent adaptable network (CAN) polymers comprising β-amino esters, Korea-Aust. Rheol. J. 35 (2023) 69–79, https://doi.org/10.1007/s13367-023-00054-1.

[21] G. Lee, H.Y. Song, S. Choi, C.B. Kim, K. Hyun, S.-K. Ahn, Harnessing β-hydroxyl groups in poly(β-amino esters) toward robust and fast reprocessing covalent adaptable networks, Macromolecules 55 (2022) 10366–10376, https://doi.org/10.1021/acs.macromol.2c01872.

[22] S. Yu, G. Zhang, S. Wu, Z. Tang, B. Guo, L. Zhang, Effects of dynamic covalent bond multiplicity on the performance of vitrimeric elastomers, J. Mater. Chem A 8 (2020) 20503–20512, https://doi.org/10.1039/D0TA06264B.

[23] Z. Jiang, A. Bhaskaran, H.M. Aitken, I.C.G. Shackleford, L.A. Connal, Using synergistic multiple dynamic bonds to construct polymers with engineered properties, Macromol. Rapid Commun. 40 (2019) 1900038, https://doi.org/10.1002/marc.201900038.

[24] X. Xu, S. Ma, H. Feng, J. Qiu, S. Wang, Z. Yu, J. Zhu, Dissociate transfer exchange of tandem dynamic bonds endows covalent adaptable networks with fast reprocessability and high performance, Polym. Chem. 12 (2021) 5217–5228, https://doi.org/10.1039/D1PY01045J.

[25] M. Wang, H. Gao, Z. Wang, Y. Mao, J. Yang, B. Wu, L. Jon, C. Zhang, Y. Xia, K. Zhang, Rapid self-healed vitrimers via tailored hydroxyl esters and disulfide bonds, Polymer 248 (2022) 124801, https://doi.org/10.1016/j.polymer.2022.124801.

[26] D.J. Fortman, R.L. Snyder, D.T. Sheppard, W.R. Dichtel, Rapidly reprocessable cross-linked polyhydroxyurethanes based on disulfide exchange, ACS Macro Lett. 7 (2018) 1226–1231, https://doi.org/10.1021/acsmacrolett.8b00667.

[27] O. Konuray, S. Moradi, A. Roig, X. Fernández-Francos, X. Ramis, Thiol-ene networks with tunable dynamicity for covalent adaptation, ACS Appl. Polym. Mater. 5 (2023) 1651–1656, https://doi.org/10.1021/acsapm.2c02136.

[28] L. Hammer, N.J. Van Zee, R. Nicolaÿ, Dually crosslinked polymer networks incorporating dynamic covalent bonds, Polymers 13 (2021) 396, https://doi.org/10.3390/polym13030396.

[29] X. Ramis, X. Fernández-Francos, S. De la Flor, F. Ferrando, À. Serra, Click-based dual-curing thermosets and their application, in: Q. Guo (Ed.), Thermosets Structure, Properties and Applications, Chapt. 16, 2nd ed., Elsevier, Amsterdam, Netherlands, (2018).

[30] H.C. Kolb, M.G. Finn, K.B. Sharpless, "Click" chemistry: diverse chemical function from a few good reactions, Angew. Chem. Int. Ed. 40 (2001) 2005–2021, https://doi.org/10.1002/1521-3773(20010601)40:11<2004::AID-ANIE2004>3.0.CO;2-5.

[31] X. Fernández-Francos, A.O. Konuray, A. Belmonte, S. De la Flor, À. Serra, X. Ramis, Sequential curing of off-stoichiometric thiol-epoxy thermosets with a custom-tailored structure, Polym. Chem. 7 (2016) 2280–2290, https://doi.org/10.1039/c6py00099a.

[32] A. Roig, X. Ramis, S. De la Flor, À. Serra, Dual-cured thermosets from glycidyl methacrylate obtained by epoxy-amine reaction and methacrylate homopolymerization, React. Funct. Polym. 159 (2021) 104822, https://doi.org/10.1016/j.reactfunctpolym.2021.104822.

[33] C. Russo, À. Serra, X. Fernández-Francos, S. De la Flor, Characterization of sequential dual-curing of thiol-acrylate-epoxy systems with controlled thermal properties, Eur. Polym. J. 112 (2019) 376–388, https://doi.org/10.1016/j.eurpolymj.2018.12.048.

[34] F. Gamardella, V. Sabatini, X. Ramis, À. Serra, Tailor-made thermosets obtained by sequential dual-curing combining isocyanate-thiol and epoxy-thiol *click* reactions, Polymer 174 (2019) 200–209, https://doi.org/10.1016/j.polymer.2019.04.041.

[35] A. Roig, X. Ramis, S. De la Flor, À. Serra, Sequential photo-thermal curing of (meth)acrylate-epoxy thiol formulations, Polymer 230 (2021) 124073.

[36] A. Roig, X. Ramis, S. De la Flor, À. Serra, Dual-cured thermosets based on eugenol derivatives and thiol chemistry, Eur. Polym. J. 200 (2023) 112499, https://doi.org/10.1016/j.eurpolymj.2023.112499.

[37] J.P. Pascault, H. Sautereau, J. Verdu, R.J.J. Williams, Thermosetting polymers, Marcel Dekker, New York, USA, 2002.

[38] J.P. Pascault, R.J.J. Williams, Overview of Thermosets: Present and Future, in: Q. Guo (Ed.), Structure, Properties and Application, Thermosets 2nd ed. Ch. 11, pp 3-34, Elsevier, Amsterdam, Netherlands, (2018).

[39] J. Brandrup, E.H. Immergut, W. McDowell, Polymer handbook, Wiley, New York, USA, 1975.

[40] Q. Yu, X. Peng, Y. Wang, H. Geng, A. Xu, X. Zhang, W. Xu, D. Ye, Vanillin-based degradable epoxy vitrimers: reprocessability and mechanical properties study, Eur. Polym. J. 117 (2019) 55–63, https://doi.org/10.1016/j.eurpolymj.2019.04.053.

[41] W. Denissen, J.M. Winne, F.E. Du Prez, Vitrimers: permanent organic networks with glass-like fluidity, Chem. Sci. 7 (2016) 30–38, https://doi.org/10.1039/C5SC02223A.

[42] F.I. Altuna, C.E. Hoppe, R.J.J. Williams, Epoxy vitrimers with a covalently bonded tertiary amine as catalyst of the transesterification reaction, Eur. Polym. J. 113 (2019) 297–304, https://doi.org/10.1016/j.eurpolymj.2019.01.045.

[43] K. Yamawake, M. Hayashi, The role of tertiary amines as internal catalysts for disulfide exchange in covalent adaptable networks, Polym. Chem. 14 (2023) 680–686, https://doi.org/10.1039/d2py01406h.