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Research Article

Vanillin-Based Epoxy Vitrimers: Looking at the Cystamine Hardener from a Different Perspective

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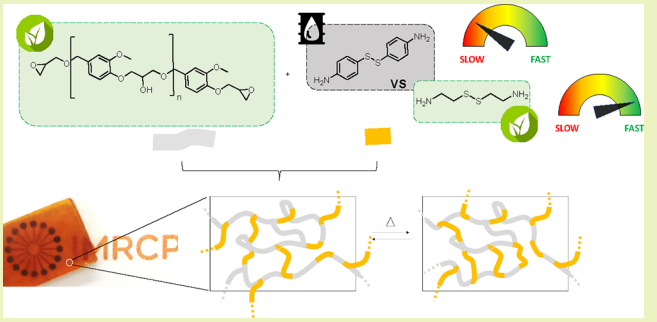
ABSTRACT: Epoxy vitrimers encompass many advantages compared to traditional epoxy materials such as recyclability, repairability, and reprocessability. These properties are induced by the incorporation of dynamic reversible covalent bonds. Recently, the incorporation of aromatic disulfide bridges that are dynamic has expanded the development of new eco-friendly epoxy materials. Herein, we studied a bio-based aliphatic disulfide based on cystamine as a hardener with a vanillin-derived bio-sourced epoxy to prepare fully bio-based epoxy vitrimers. This article provides a comparative study between cystamine and an aromatic disulfide benchmark hardener issued from petrol resources. This work demonstrated that the presence of this aliphatic hardener has a significant influence not only on the reactivity, but most importantly on the resulting dynamic properties. An interesting yet counterintuitive accelerating effect of the dynamic exchanges was clearly demonstrated with only 2 to 20% of molar fraction of cystamine added to the aromatic disulfide formulation. A similar glass transition was obtained compared to the purely aromatic analogue, but relaxation times were decreased by an order of magnitude.



KEYWORDS: *vanillin, epoxy, vitrimers, recyclability, disulfide*

INTRODUCTION

Thermosets are commonly used for numerous applications such as coatings, electronics, adhesives, and composites. Owing to their highly crosslinked polymeric structure, they are able to form networks with high dimensional stability, mechanical properties, and chemical resistance.[1,2] Among them, epoxy resins are the second most widely used thermoset materials after polyurethanes, representing more than 70% of the remaining global market.[2,3] However, due to their irreversible three-dimensional structures, epoxy thermosets cannot be reshaped and recycled after their initial formation and tend to have a limited re-use application. Recently, an attractive chemical strategy to introduce plasticity in crosslinked polymer networks, such as epoxy resins, is offered by the introduction of dynamic covalent bonds. These reversible covalent materials pioneered by Bowman and co-workers[4−6] and so-called covalent adaptable networks (CANs) share both the advantages of thermoplastics with ease of reprocessing and mechanical resistance of thermosets. These materials have the ability to reversibly rearrange their network structure through exchange reactions of dynamic covalent bonds under external stimuli such as heat, pH, or UV light.[6,7] Owing to this topological rearrangement, CANs can be easily recycled, repaired, and reprocessed. In 2011, Leibler and co-workers popularized the concept of vitrimers, associative CANs, based on a thermally triggered transesterification reaction resulting in materials that show similar viscosity dependence as vitreous silica.[8] Vitrimers are covalently crosslinked polymer materials that can be directly reprocessed at temperatures above the glass transition without depolymerization through an associative mechanism, resulting in a constant crosslink density during network rearrangement.[9−11] This concept was extended to various chemistries such as transamination, olefin metathesis, disulfide exchange, and transalkylation, to name a few.[12−16]

Disulfide exchanges that undergo both associative and dissociative mechanisms through radical-mediated reactions[17] have been especially studied. In the course of developing original dynamic chemistries applied to vitrimer materials, Ruiz de Luzuriaga et al. pioneered the use of 4-aminophenyl disulfide (4AFD) as a dynamic hardener for epoxy resin formulation.[18] Their seminal article described materials with fast reprocessing and paved the way to multiple reports based on this dynamic hardener.[15,19−24] The combination of bio-based monomers with vitrimer properties and more specifically disulfide exchanges were also investigated.[25,26] In this context,

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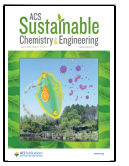

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the use of a vanillin building block has attracted considerable attention owing to its large availability and its (1,4) phenol/aldehyde functionalities that can be directly reacted with amine (aldehyde) or chemically modified to prepare various reactive building blocks.[27] For a more exhaustive literature on vanillin-based vitrimers, the reader is directed to a recent review[28] and some other related reports.[29−31] For instance, Genua and coworkers reported the formulation of vitrimer resins synthesized from vanillin and phloroglucinol precursors derived from naturally occurring feedstocks, but with petro-based 4AFD as a curing agent.[32] In view of replacing 4AFD by a more environmentally friendly analogue, the development of bio-based dynamic hardeners also attracted significant attention. Cystamine, a reactive aliphatic diamine disulfide derived from an amino acid, appears as a suitable hardener in the context of dynamic materials.[33,34] The curing kinetics and thermal stability of DGEBA-based materials with cystamine as a hardener were investigated by Khalafi et al.[33] However, the dynamic properties were not studied and no information was given regarding the reprocessability of materials. Li et al.[35] developed adaptative adhesives by crosslinking poly((phenylglycidyl ether)-*co*-formaldehyde) networks with cystamine. They found that this innovative adhesive can overcome internal stresses thanks to disulfide exchange, leading to enhanced adhesive performance, but here again, dynamic properties were not investigated. Recently, cystamine has been used by Fortman et al.[34] as a co-curing agent for the synthesis of polyhydroxyurethane vitrimers. This work evaluated the dynamic properties, but no specific characterization was conducted for pure disulfide exchanges as each network was based on a dual transcarbamoylation/disulfide exchange mechanism. In addition, no comparison was made with regard to the aromatic counterpart 4AFD. In summary, the dynamic properties of pure cystamine-based vitrimers was never investigated and can represent a viable substitute compared to 4AFD.

In this work, epoxy vitrimers based on vanillin with 4AFD and cystamine as disulfide hardeners were synthesized and compared in order to assess the suitability of cystamine as a potential bio-sourced alternative. The dynamic properties of each material and mixtures thereof were particularly investigated and revealed an unexpected dynamic behavior.

EXPERIMENTAL SECTION

Materials and Methods. 4AFD (98%) was purchased from Sigma-Aldrich. Diglycidyl ether of vanillyl alcohol (DGEVA, SP-9S-5-005, EEW (epoxy equivalent weight) = 139 g/eq) and cystamine (SP-2-4-001, AHEW (amine equivalent weight) = 38 g/eq) were synthetized and provided by SPECIFIC POLYMERS. The DGEVA building block was synthesized through a two-step procedure from vanillin and epichlorohydrin following an already reported protocol.[32] Cystamine was purchased as cystamine dihydrochloride and desalinated following the procedure by Khalafi et al.[33] Tetrahydrofuran (THF), chloroform ($CHCl_3$), dichloromethane (DCM), and 4-mercaptoethanol (>95%) were purchased from Sigma-Aldrich and used as received.

Preparation of Vitrimers. Following a previous work,[32] an excess of disulfide hardener is recommended to exhibit fast enough dynamic exchanges. Hence, 1.2 equivalent of curing agent was introduced in all formulations. This amount was easily calculated from the epoxide equivalent weight (EEW) and amine hydrogen equivalent weight (AHEW), according to eq 1:

$$\text{phr} = \frac{1.2 \times \text{AHEW}}{\text{EEW}} \times 100 \quad (1)$$

phr, corresponding to the quantity of hardener to add for 100 g of epoxy resin, was determined to be 53.6 and 33.4 g for 4AFD and cystamine, respectively.

Synthetic Procedure. In a typical procedure, the epoxy resin (DGEVA, 1 g) was first melted at 100 °C for 10 min to afford a viscous resin, easier to manipulate. Then, the diamine hardener (0.536 g of 4AFD or 0.334 g of cystamine) was added in molar ratio 1/1.2 and stirred mechanically for 5 min at room temperature to afford a homogeneous viscous liquid. The mixture was then cured at 90 °C for 2 h for DGEVA/cyst and at 150 °C for 2 h for DGEVA/4AFD.

Instrumentation. *Differential Scanning Calorimetry (DSC).* DSC was conducted on a Mettler Toledo Differential Scanning Calorimeter under a constant nitrogen flow rate (50 mL min^{-1}). The samples of about 6−10 mg were heated from 20 to 250−300 °C at the rate of 10 °C min^{-1} with nitrogen as a purged gas. Then, the glass transition temperature was measured in the second heating cycle from 20 to 250 °C at the rate of 10 °C min^{-1} under a nitrogen atmosphere and no residual curing heat was observed. An isothermal study was conducted at 120, 140, and 160 °C for epoxy/4AFD and at 50, 70, and 90 °C for epoxy/cystamine under a nitrogen atmosphere.

Thermogravimetric Measurements (TGA). TGA was performed on a DuPont Instruments 951 Thermal Analyzer (USA) using 8−10 mg of the cured sample. Samples were heated under a nitrogen atmosphere (N_2) at a constant ramp rate of 10 °C min^{-1} from room temperature to 800 °C.

Fourier Transform Infrared Spectroscopy (FTIR). FTIR was recorded on a Thermo Nicolet NEXUS spectrophotometer equipped with an ATR diamond. All samples were analyzed through 16 scans and within a range of 400−4000 cm^{-1} for both cured and uncured states.

Cross-Linking Kinetic Experiments. Cross-linking kinetic experiments were carried out on an Anton Paar MCR 302 stress-controlled rheometer using a 20 mm geometry at 2 mm thickness. Crosslinking studies were conducted at a 1 rad s^{-1} frequency with 1% deformation at 90, 100, and 110 °C for epoxy/4AFD and at 30, 40, and 50 °C for the cystamine-based epoxy system.

Stress Relaxation Experiments. Stress relaxation experiments were performed for each cured material to evaluate the rate of reorganization. These characterizations were carried out using a 8 mm plate−plate geometry on epoxy resin samples with thicknesses of 0.8−0.4 mm. Prior to the experiments, it was checked that 1% deformation was within the linear range using amplitude sweep experiments at 170 °C. A 1% strain was applied for all samples at temperatures ranging from 110 to 200 °C with a constant normal force of 5 N. The materials were reprocessed on a lab press instrument (Carver Model C laboratory press) at 150 °C under 1 metric ton for 35 to 60 min.

Crosslinking density was calculated by Flory's expression,[36] as shown in eq 2:

$$\nu = \frac{G'}{RT} \quad (2)$$

where G' is the storage modulus of the thermoset in the rubbery plateau region at Tg +50 °C, R is the universal gas constant, and T is the absolute temperature in kelvin.

Soluble Fraction and Swelling Ratio. Solubility tests were performed by Soxhlet extraction. A sample of approximately 50 mg of initial mass (mi) was extracted with $CHCl_3$ during 48 h at 90 °C. The swollen samples were weighed to obtain wet sample mass (ms). Then, dried mass md was determined after a drying procedure in a vacuum oven at 120 °C overnight. The soluble fraction (Sf) and swelling ratio (Sr) were calculated according to eqs 3 and 4:

$$\text{Sf} = \frac{mi - md}{mi} \times 100 \quad (3)$$

$$\text{Sr} = \frac{ms - mi}{mi} \times 100 \quad (4)$$

Chemical Recycling. A small fragment of the epoxy vitrimers DGEVA/AFD and DGEVA/cyst was immersed in a solution of 2-

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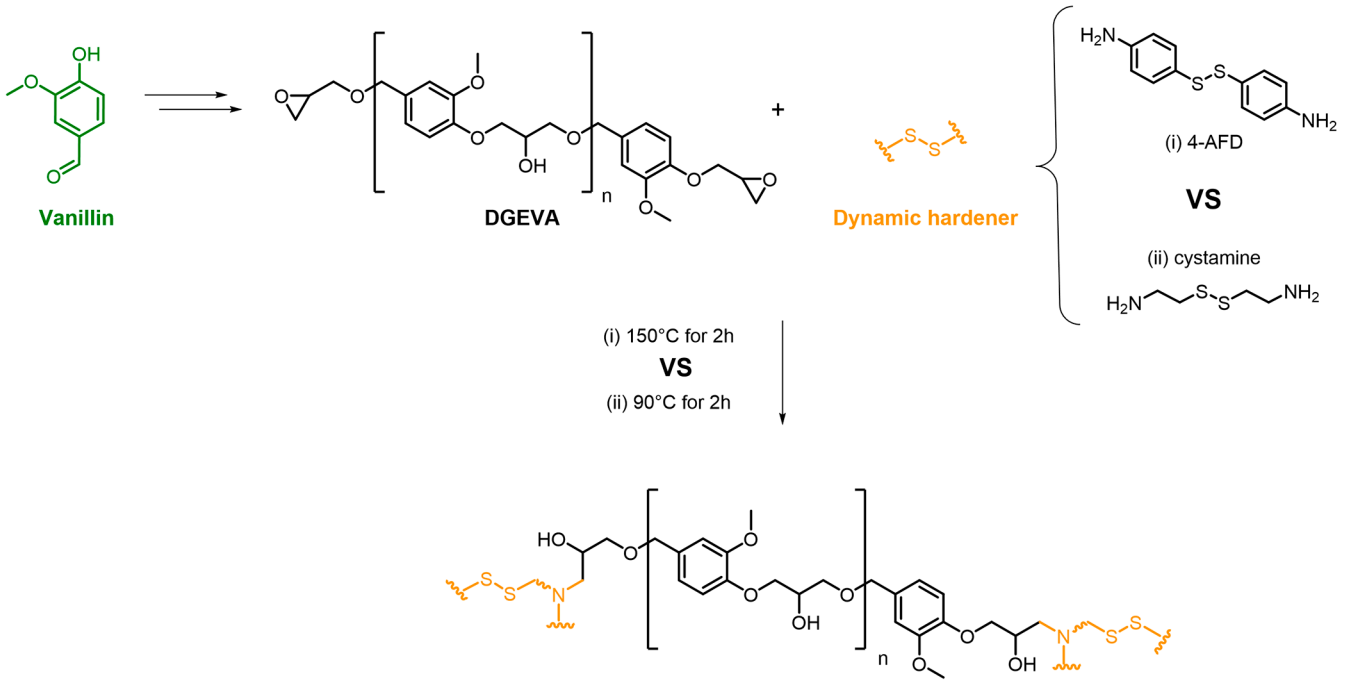

Figure 1. Synthesis of DGEVA-based vitrimers with (i) 4AFD and (ii) cystamine as a hardener.

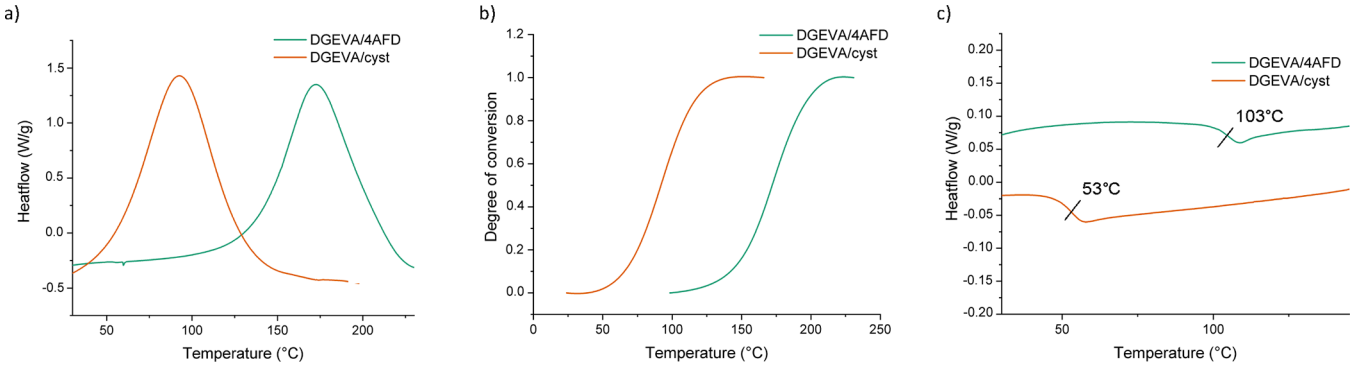

Figure 2. (a) DSC thermograms obtained at a heating rate of 10 °C min^{-1} for DGEVA/4AFD and DGEVA/cyst vitrimers; (b) corresponding degree of conversion with temperature; (c) Tg obtained during a second heating ramp at 10 °C min^{-1}.

mercaptoethanol 5 wt % in DMF. The system was magnetically stirred at room temperature for a few hours, after which the epoxy matrix was completely dissolved.

RESULTS AND DISCUSSION

Synthesis and Thermal Characterization of Epoxy Vitrimers. Epoxy vitrimers based on dynamic exchanges of aromatic disulfides have already been widely reported in previous works.[15,22,37−39] However, even though these dynamic systems showed good recyclability and attractive vitrimer properties, the aromatic hardener was still prepared from petro-based compounds. Our objective was thus to provide an alternative to aromatic disulfides by incorporating a cystamine hardener (Figure 1), which can be produced from amino acids, and evaluate its impact over materials. The selected epoxy resin (DGEVA) is also bio-sourced and based on vanillin, which is one of the most available pure monoaromatic phenols currently produced at an industrial scale from lignin.[40] Epoxy vitrimers are prepared following the conditions depicted in Figure 1 from a synthesized vanillin-based diepoxide (DGEVA) and a diamine hardener (cystamine or 4AFD). Amines react with epoxy functions to form tertiary amines and hydroxyl groups with embedded disulfide bonds that can promote dynamic exchanges through thiol-disulfide radical exchanges.[17] The crosslinking is conducted in a low-viscosity liquid state, without solvent, and does not release any volatile compounds, which are important prerequisites for composite manufacturing processes. The reactivity between aliphatic and aromatic amines being significantly different, the chemical reactivity has been carefully evaluated as it represents a crucial part of material design.

Recently, Ruiz de Luzuriaga et al.[24] demonstrated that the presence of secondary amines issued from an excess of hardener accelerates the exchange reaction of disulfides into epoxy vitrimers. By mixing the epoxy resin and diamine hardener with a molar ratio of 1:1.2, respectively, the excess of amine is expected to generate about 20% of partially reacted amine, resulting in a −NH-Ar-S-S− structure that has been predicted to be more dynamic than its fully reacted −N-Ar-S-S− analogue.[17] This strategy has been employed many times in literature to induce swifter disulfide exchanges.[18,24,32,41] However, the higher the secondary amine group concentration

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Table 1. Overview of Composition and Physicochemical Properties of the Synthetized DGEVA/4AFD and DGEVA/Cyst Vitrimers

name	cystamine (%)	4AFD (%)	Tg DSC (°C)	Td (5%) (°C)	G'^{a} (MPa)	ΔH (J g^{-1})	crosslink density[b] (mol m^{-3})
DGEVA/4AFD	0	100	103	280	1.30	470.9	361.2
DGEVA/cyst	100	0	53	253	0.766	568.4	240.6

[a]Storage modulus determined at 1 rad s^{-1} and Tg +50 °C. [b]Calculated according to eq 2.

Table 2. Thermomechanical Properties of Mixture Formulations Containing Various Ratios of 4AFD/Cyst Compared to Reference DGEVA Materials with 100% 4AFD or 100% Cystamine[a]

	cystamine	4AFD	Tg DSC	Td (5%)	Arrhenius plot, stress relaxation	
name	mol %	mol %	°C	°C	E_a (kJ mol^{-1})	R^2
DGEVA/4AFD	0	100	103	280	124	0.99
DGEVA/cyst	100	0	53	253	57	0.99
DGEVA/4AFD$_{0.60}$cyst$_{0.40}$	40	60	69	276	n.d	n.d
DGEVA/4AFD$_{0.80}$cyst$_{0.20}$	20	80	83	277	77	0.99
DGEVA/4AFD$_{0.90}$cyst$_{0.10}$	10	90	90	274	87	0.99
DGEVA/4AFD$_{0.95}$cyst$_{0.05}$	5	95	91	279	109	0.99
DGEVA/4AFD$_{0.98}$cyst$_{0.02}$	2	98	98	280	135	0.99

[a]n.d.: not determined.

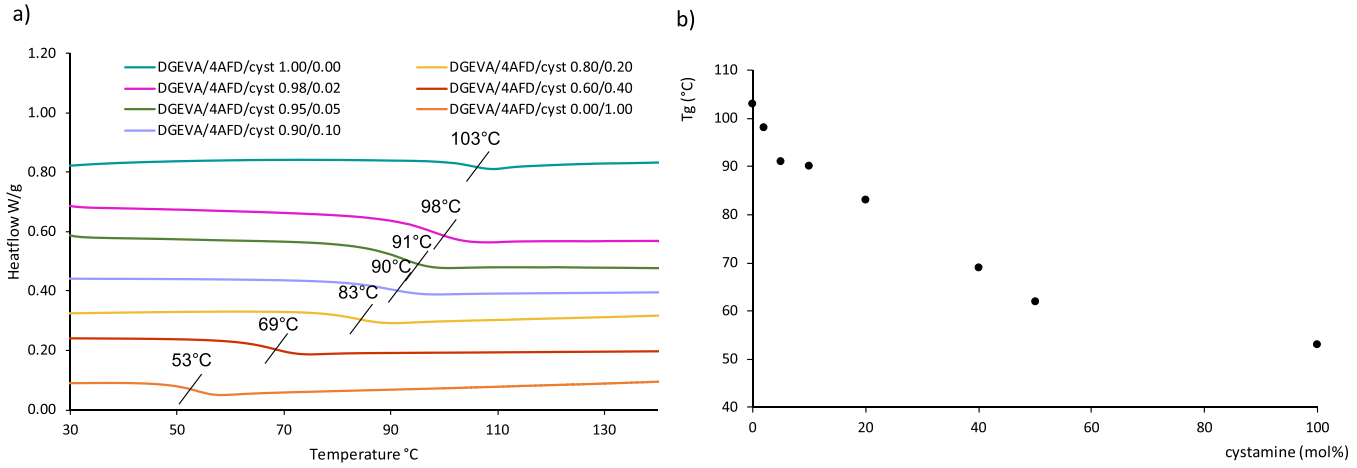

Figure 3. (a) DSC thermograms recorded for the different 4AFD/cyst formulations; (b) Tg measurements determined by DSC analysis for formulations containing from 2 to 100 mol % of cystamine.

will be, the lower the Tg.[24] Thus, these off-stoichiometric conditions must be carefully employed in order to not significantly impair material properties. The 1:1 and 1:1.2 formulations were evaluated for a DGEVA-4AFD vitrimer. The overall properties were maintained although a slight decrease of Tg (110 vs 103 °C) was noticed for 1:1 and 1:1.2 formulations, respectively. In contrast, the dynamic properties were significantly impacted with a decrease of relaxation time from 330 to 180 s at 190 °C (Figure S1). For this reason, all following materials have been prepared with a ratio of 1:1.2. Then, the reactivity of DGEVA/4AFD and DGEVA/cyst systems was evaluated by dynamic DSC studies. The two formulations were first followed from 20 to 200 °C for cystamine and from 20 to 300 °C for 4AFD at a heating rate of 10 °C min^{-1} (Figure 2a). The onset temperature for DGEVA/AFD was 136 vs 52 °C for DGEVA/cyst, meaning that the aliphatic hardener is much more reactive toward epoxy groups (Figure 2a, Table 1).

Full conversion was attained at 150 °C for DGEVA/cyst and at 225 °C for DGEVA/AFD at 10 °C min^{-1} (with an identical reaction time of approximately 13 min (Figure 2b)). The enthalpy values were not in the same order with a lower reaction enthalpy measured for the DGEVA/4AFD network (471 J g^{-1}) compared to the DGEVA/cyst network (568 J g^{-1}). Moreover, a significant drop of Tg was noticed (Figure 2c) for cystamine compared to 4AFD with values of 53 and 103 °C, respectively. This difference can be easily explained by the less rigid structure of cystamine compared to 4AFD. No residual heat flow was observed during the second temperature ramp, confirming the complete conversion and infinite characteristics of the obtained Tg.

The apparent activation energy (E_a) is an important kinetic parameter to understand the curing procedure. In order to determine the kinetic parameters of both epoxy networks, DSC analyses were performed at heating rates of 5, 7.5, and 10 °C min^{-1} from 20 to 250 °C. Figure S2 illustrates the obtained DSC thermograms as a function of the heating rate for DGEVA/4AFD (Figure S2a) and DGEVA/cyst (Figure S2c). The Kissinger equation is commonly used to calculate the apparent E_a of the curing reaction[42] and assumes that the maximum reaction rate occurs at the peak temperature of the exothermic peak of the curing reaction, and the reaction order

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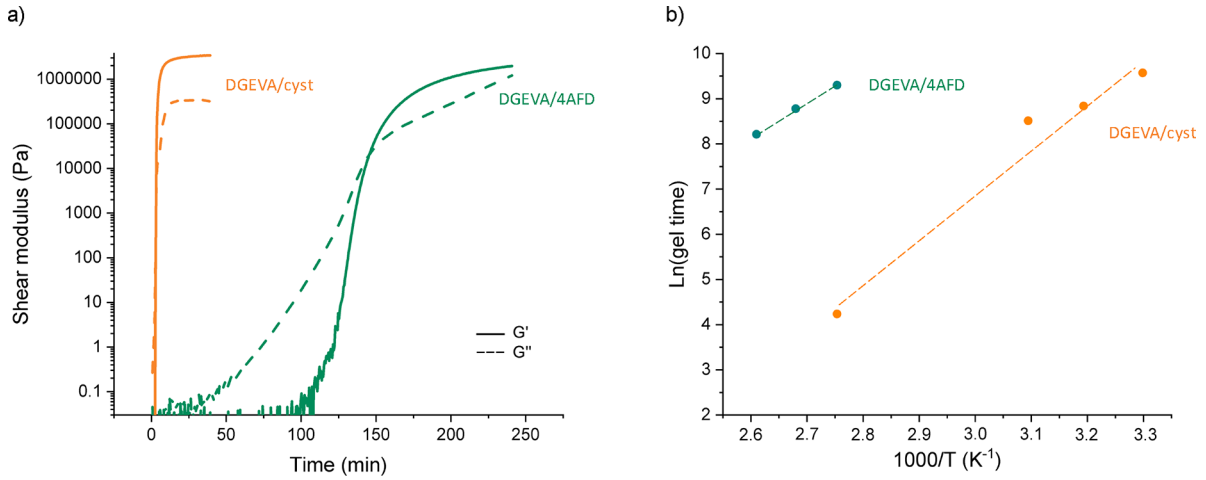

Figure 4. (a) Curing profile of DGEVA/4AFD and DGEBA/cyst at 90 °C with a strain of 1% and frequency of 1 rad s^{-1}. (b) Comparison of Arrhenius plot of DGEVA/4AFD and DGEVA/cyst gel time as a function of temperature.

remains constant during the curing reaction.[33] Based on Kissinger's method, the E_a can be obtained using eq 5:

$$\ln\left(\frac{\beta}{T^2_{peak}}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_{peak}} \quad (5)$$

where R is the universal gas constant, β is the heating rate, and T_{peak} is the temperature of the exothermic peak. A linear fitting was observed in both cases, suggesting that the experimental data are in good agreement with the Kissinger model. According to the linear regression displayed in Figure S4, activation energies were calculated from the slope of the equation $\ln(\beta/T^2_{peak}) = f(1/T_{peak})$ and 46 and 53 kJ mol^{-1} were obtained for DGEVA/4AFD and DGEVA/cyst, respectively. The lower E_a of the DGEVA/4AFD system indicated that the curing reaction of DGEVA with the aromatic diamine is less temperature dependent although the difference remains low.

A low glass transition around 50 °C obtained with DGEVA/cyst may provide easy repairing and recycling but can considerably restrain the industrial potential of these materials.[43] For this reason, we also investigated the use of a mixture of aromatic and aliphatic hardeners in order to reach sufficiently high Tg and short relaxation times. A series of vitrimers presented in Table 2 were prepared with different ratios of aromatic/aliphatic diamine DGEVA/4AFD$_x$cyst$_y$ (with x and y standing for the molar fraction of 4AFD and cystamine, respectively).

Thermal properties of new formulations were obtained by DSC with a cycle from 20 to 250 °C at a 10 °C min^{-1} heating rate (Figure 3). It is important to note that DSC thermograms were bimodal due to the difference of reactivity of cystamine and 4AFD with epoxies (Figure S5). Nonetheless, since the dynamic exchanges occur concomitantly with the curing, network reshuffling should prevent the formation of a heterogeneous network. This is clearly visible in Figure 3a with the appearance of a single Tg, which was observed with different 4AFD/cystamine ratios.

Moreover, a gradual decrease of Tg with increasing amount of cystamine is also observed as exhibited in Figure 3b. The addition of 2 mol % of cystamine into DGEVA/4AFD barely influenced the Tg of the original matrix with values decreasing from 103 to 98 °C. When the concentration of cystamine is increased until 10 mol %, a high Tg of 90 °C is still obtained. Nonetheless, increasing the aliphatic proportion up to 20% has a considerable influence over the glass transition temperature that decreases by more than 20 °C, reaching 69 °C for 40 mol %. The effect of cystamine over dynamic exchanges will be more deeply investigated and discussed in the section dealing with rheological analyses.

Based on the abovementioned analyses, the vitrimer materials were then cured following two strategies depending on the proportion of cystamine. A heating cycle at 90 °C was performed for 2 h to prepare DGEVA/cystamine vitrimers. For DGEVA/4AFD, the material was cured at 150 °C for 2 h. For all mixtures, from 2 to 40 mol % of cystamine, curing processes were based on the DGEVA/4AFD curing method. All the blends with a mixture of diamine crosslinkers were characterized in the following studies.

Thermogravimetric analysis at 5 wt % loss showed that both materials do not degrade up to 250 °C, as depicted in Figure S6. Nonetheless, the dynamic DGEVA/cyst networks showed a slightly lower degradation temperature of 253 versus 280 °C. This effect is less pronounced for 4AFD/cystamine mixtures, which exhibited a degradation temperature in the range of 270−280 °C for AFD/cyst compositions ranging from 60/40 to 98/2 (Figure S7). These results show that replacing a fraction of the aromatic hardener with an aliphatic moiety has only a slight influence on the degradation temperature of the resulting materials. Following the above descriptions, crosslinking kinetics and dynamics of exchange were further studied via rheological analyses with regard to the structure/properties relationship of disulfide bonds and mixtures thereof.

Thermomechanical Study. To evaluate the reaction kinetics, both crosslinking reactions were studied by rheological analysis. Shear moduli (G' storage modulus, G'' loss modulus) were measured over time in frequency mode (1 rad s^{-1}) at different temperatures such as 30, 40, and 50 °C for DGEVA/cyst and 90, 100, and 110 °C for DGEVA/4AFD (Figure S8). In agreement with DSC analyses, the reaction with cystamine is considerably faster than with 4AFD. Full crosslinking is achieved within 26 min at 90 °C for the DGEVA/cyst system while more than hours are required at the same temperature to reach a plateau for the DGEVA/4AFD mixture (Figure 4a). As expected, the gel time corresponding to the crossover of G' and G'' tends to be reduced with

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ACS Sustainable Chem. Eng. 2023, 11, 6021−6031

increasing temperature for both systems, as depicted in Figure S8. According to the gelation theory and assuming that the kinetic rate constant follows an Arrhenius-type dependence, the E_a of the crosslinking reactions can be extracted by plotting the gel time versus the inverse of the temperature. Through linear regression fitting (Figure 4b), apparent E_a values of 69 and 63 kJ mol^{-1} have been determined for DGEVA/cyst and DGEBA/4AFD, respectively. These values follow the same trend as ones calculated via the Kissinger model and are reported in Table 3.

Table 3. Comparative Study of Arrhenius Calculations of DGEVA/4AFD and DGEVA/Cyst

	crosslinking kinetics Arrhenius plot		Kissinger method Arrhenius plot	
name	E_a (kJ mol^{-1})	R^2	E_a (kJ mol^{-1})	R^2
DGEVA/4AFD	63	0.99	46	0.97
DGEVA/cyst	69	0.98	53	0.99

Rheological studies such as stress relaxation provide a specific fingerprint to evaluate deformation and flow properties of the material. In order to characterize the malleability of our disulfide networks at elevated temperatures, both DGEVA/cyst and DGEVA/4AFD vitrimers were subjected to stress relaxation analyses at high temperatures from 110 to 170 °C and from 170 to 200 °C, respectively. A constant strain of 1% was applied, which is comprised in the linear viscoelastic region at the measured temperatures, and the normalized relaxation modulus G/G_0 was monitored as a function of time at different temperatures. The experiments were repeated two times for each temperature to ensure reproducibility. Full stress relaxation was obtained for DGEVA/cyst (Figure 5a), suggesting the formation of a fully dynamic network. In contrast, the DGEVA/4AFD vitrimer still exhibits residual stress at temperatures below 200 °C even after long period of time.

To better evaluate this effect, these relaxation curves were fitted to a Kohlrausch–Williams–Watts (KWW) stretched exponential decay[44−46] (eq 6, Figure 5a,b) and the corresponding relaxation times (τ^*), β stretching exponent, and fraction of the residual relaxation modulus G_{res}/G_0 were extracted for each temperature (Table S1). The characteristic average relaxation time $<\tau>$ of a stretched exponential decay was calculated using eq 7.

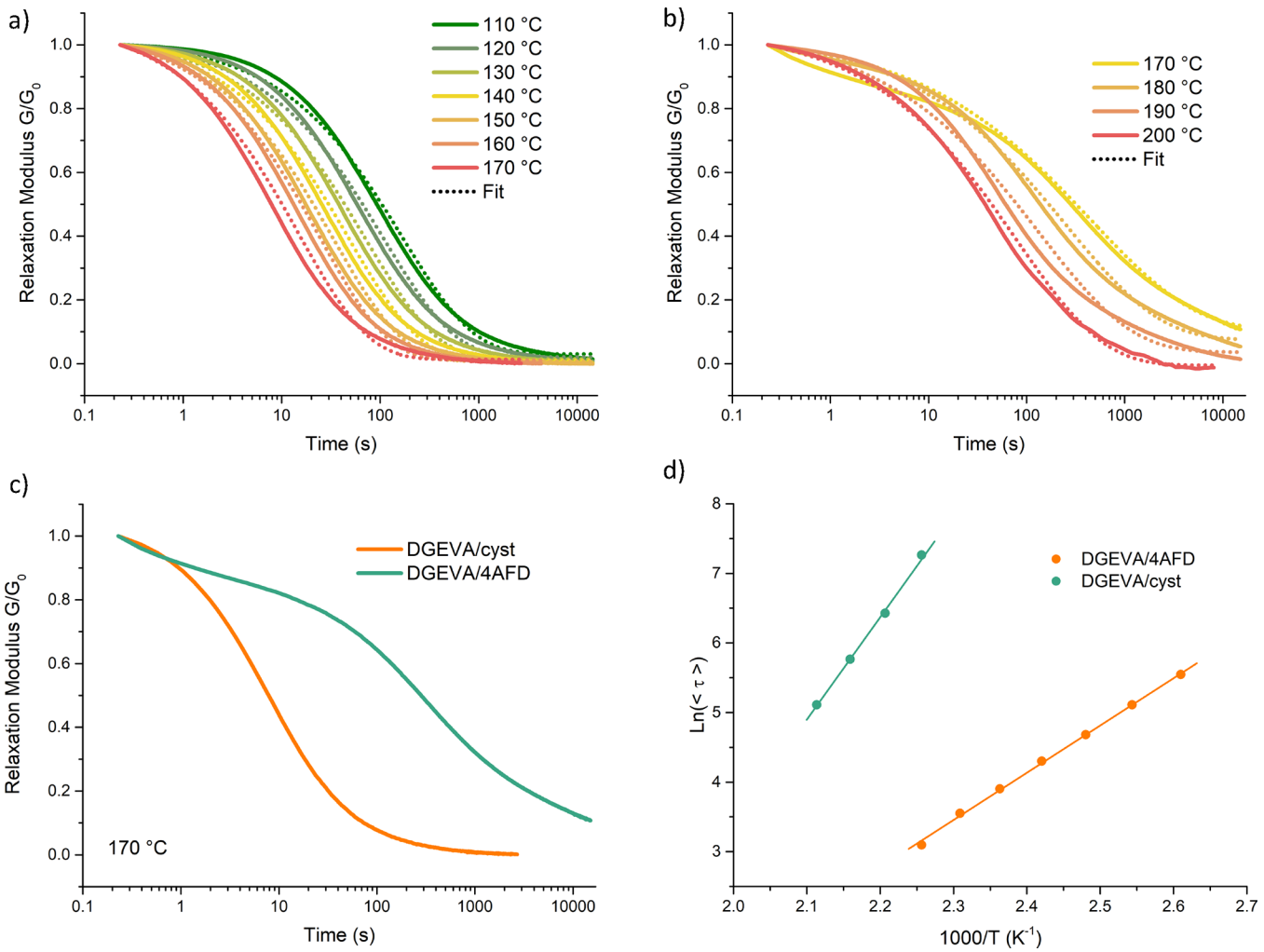

Figure 5. Normalized stress relaxation curves of dynamic epoxy networks. (a) DGEVA/cyst and (b) DGEVA/4AFD at different temperatures. (c) Stress relaxation comparison of DGEVA/4AFD and DGEVA/cyst at 170 °C. (d) Arrhenius temperature dependence.

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$$\frac{G(t)}{G_0} = \frac{G_{res}}{G_0} + \left(1 - \frac{G_{res}}{G_0}\right)\exp^{\left(-\frac{t}{\tau^*}\right)^{\beta}} \quad (6)$$

$$<\tau> = \frac{\tau^*\Gamma(1/\beta)}{\beta} \quad (7)$$

with Γ as the gamma function.[47,48]

A good fitting was obtained for both materials with R^2 of 0.99 for all relaxation curves. Average β values in the range of 0.60 for DGEVA/cyst and 0.45 for DGEVA/4AFD were obtained indicating a broader distribution of relaxation times for the DGEVA/AFD formulations compared to DGEVA/cyst materials. These beta values are usual for vitrimer materials.[47,48] A residual relaxation modulus was obtained for the DGEVA/4AFD material at temperatures below 190 °C, while DGEVA/cyst is able to completely relax stresses over the whole range of temperature (G_{res}/G_0 < 1%, 110−170 °C). This leveling off of the relaxation modulus over time can be caused by the formation of permanent domains due to irreversible side reactions or restricted network mobility. In addition, a significant difference of average relaxation time $<\tau>$ can be noticed (Figure 5c) with more than 23 min obtained at 170 °C for the DGEVA/4AFD vitrimers while 22 s was determined for DGEVA/cystamine. Also, when the temperature is increased from 110 to 170 °C for DGEVA/cystamine, $<\tau>$ decreased of an order of magnitude. From those relaxation times, the relationship between $\ln(<\tau>)$ and $1000/T$ was fitted to the Arrhenius equation (Figure 5d) and the corresponding viscous flow E_a was calculated from the slope. Viscous flow E_a values of 124 and 57 kJ mol^{-1} were determined for DGEVA/4AFD and DGEVA/cyst, respectively. As a basis for comparison, Luzuriaga et al.[18] calculated an E_a of 167 kJ mol^{-1} for a similar DGEBA/4AFD system but no available data for cystamine is available. In addition to this significant difference of temperature dependency, faster exchange dynamics for DGEVA/cyst is clearly noticeable.

This latter result is rather counterintuitive as S-S α-alkyl disulfides are theoretically stronger bonds than aromatic counterparts with a bond dissociation energy of about 68 kcal mol^{-1} (butyl-S-S-butyl) versus 46 kcal mol^{-1} for 4AFD.[49] A faster stress relaxation could have been predicted for DGEBA/4AFD as a result of a higher radical concentration available for thiol-disulfide radical exchanges. Indeed, while both materials exhibit a 50 °C difference in Tg, all stress relaxation experiments were conducted at Tg + 60 °C; therefore, the influence of Tg should be limited. This unexpected phenomenon can be ascribed to the difference of reactivity and stability of the generated radicals (aliphatic vs aromatic) toward disulfides and/or concomitant mechanism with base-catalyzed thiolate anion-mediated exchanges.[50,51] This feature is more deeply investigated in the section dealing with 4AFD and cystamine mixtures and will be the focus of a dedicated study with model reactions and DFT calculations.

DGEVA/4AFD appears strongly temperature dependent, meaning that topology rearrangement can be achieved within a narrow temperature range. Moreover, the E_a of DGEVA/cyst implies a more gradual decrease of viscosity with moderate dependence with temperature. It is important to note that for both materials, the presence of molecular dissociation was clearly visible on non-normalized stress relaxation curves (Figure S9). Figure 6 displays the relaxation modulus G_0 for both materials as a function of temperature. G_0 slightly decreased with temperature in the case of DGEVA/cyst, reducing from 5.9 to 5.1 MPa from 110 to 170 °C, which is consistent with low molecular dissociation. In contrast, a small temperature change led to a more abrupt decrease of relaxation modulus for the DGEVA/4AFD system, which decreased from 6.4 to 3.6 MPa from 170 to 200 °C.

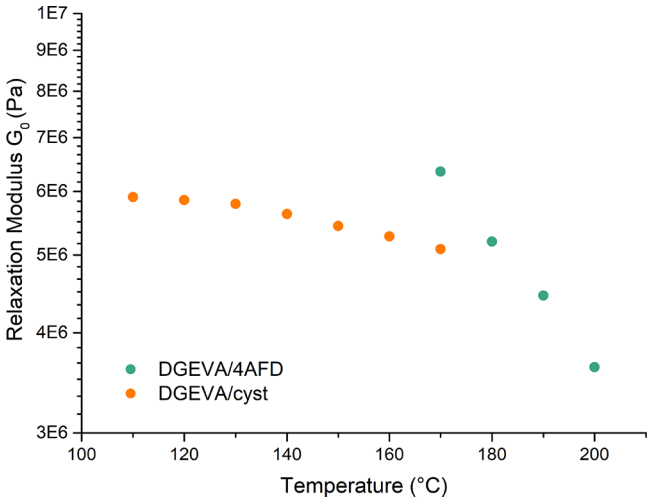

Figure 6. Relaxation modulus G_0 as a function of temperature for DGEVA/4AFD and DGEVA/cyst vitrimers.

These results seem to confirm theoretical expectations: dissociation occurs preferentially with 4AFD aromatic disulfide. As a result, DGEVA/4AFD is presumably based on dual exchange mechanisms involving radical dissociation and associative exchanges, while the DGEVA/cyst vitrimer is rather kinetically controlled by the associative exchange. To better understand this effect, the synthesized materials reported above in Table 2 with different proportions of cystamine and 4AFD were also investigated by stress relaxation (Figure S10 and fitting parameters in Table S2). Regarding molecular dissociation, the 4AFD/cystamine mixtures showed an intermediate behavior between both references (Figure S11). The proportion of dissociation is gradually decreased with increasing amount of cystamine, with this trend leveling off for DGEVA/4AFD$_{0.80}$cyst$_{0.20}$. All Arrhenius curves ranging from DGEVA/4AFD$_{0.98}$cyst$_{0.02}$ to DGEVA/4AFD$_{0.80}$cyst$_{0.20}$ formulations are summarized in Figure 7a. Increasing the cystamine proportion results in a gradual yet non-linear acceleration of the stress relaxation process.

For instance, the relaxation time at 170 °C of the DGEVA/4AFD reference decreased from 24 min down to 45 s with only 20 mol % of cystamine. Surprisingly, only 20 mol % of cystamine is necessary to achieve comparable relaxation time than the DGEVA/cyst reference (Figures 7b and Figure 8). Similar relaxation times τ^* (15 vs 18 s for cystamine reference and DGEVA/4AFD$_{0.80}$cyst$_{0.20}$, respectively) were obtained, but the combination of 4AFD and cystamine decreased the β stretching coefficient from 0.61 (DGEVA/cyst reference) to 0.46 for DGEVA/4AFD$_{0.80}$cyst$_{0.20}$ (Table S2). The decrease of β means that the degree of distribution of relaxation time is more significant for the 4AFD/cystamine mixture than for the DGEVA/cyst reference, resulting in an overall increase of the average relaxation time $<\tau>$ compared to initial τ^*. This accelerating effect and modification of β stretching exponent suggests that the introduction of cystamine into the DGEVA/

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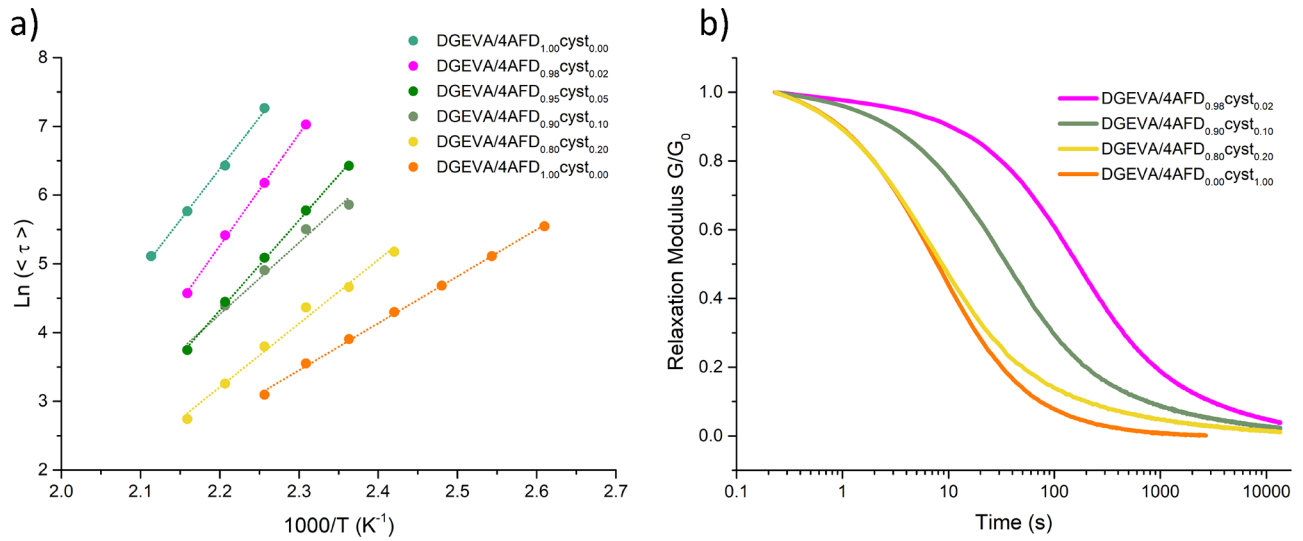

Figure 7. (a) Arrhenius temperature dependence of DGEVA/4AFD$_x$cyst$_y$ formulations. (b) Comparison of stress relaxation behavior with various proportions of cystamine relative to 4AFD (from 2 to 100 mol %) at 170 °C.

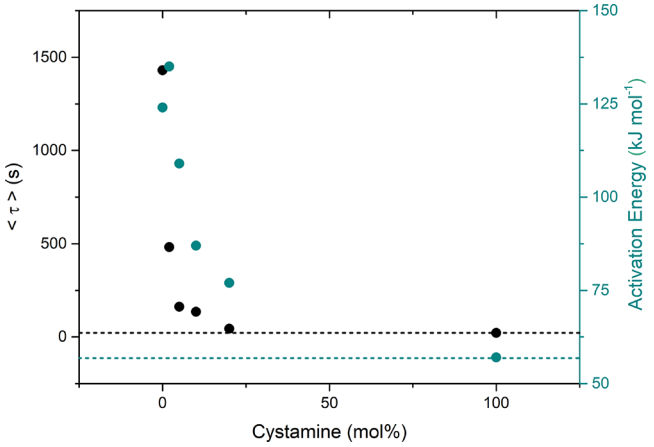

Figure 8. Plots of relaxation times at 170 °C (black) and activation energies (blue) as a function of the proportion of cystamine relative to 4AFD.

4AFD network considerably modifies the underlying exchange kinetics.

The possible better dissociation of the newly formed adduct (/−Ar-S-S-CH$_2$−/) issued from the exchanges between cystamine and 4AFD can be partly responsible for the observed acceleration. In addition, the faster exchanges evidenced above for aliphatic disulfides in combination with recently reported base-catalyzed thiolate anion-mediated exchanges should not be neglected.[50,51] The in situ formation of tertiary aliphatic or aniline amine within the network (i.e., arising from the reaction between amine or aniline with epoxy) with different basicity can also act as an internal catalyst. In summary, the underlying mechanism of disulfide exchanges is certainly more complex than anticipated with strong dependency on intrinsic parameters. Thus, instead of giving too much credit to BDE values, which were initially used to anticipate the dynamic properties, we recommend to perform full material characterization through stress relaxation and creep experiments. Yet, this simple modification of dynamic structure can

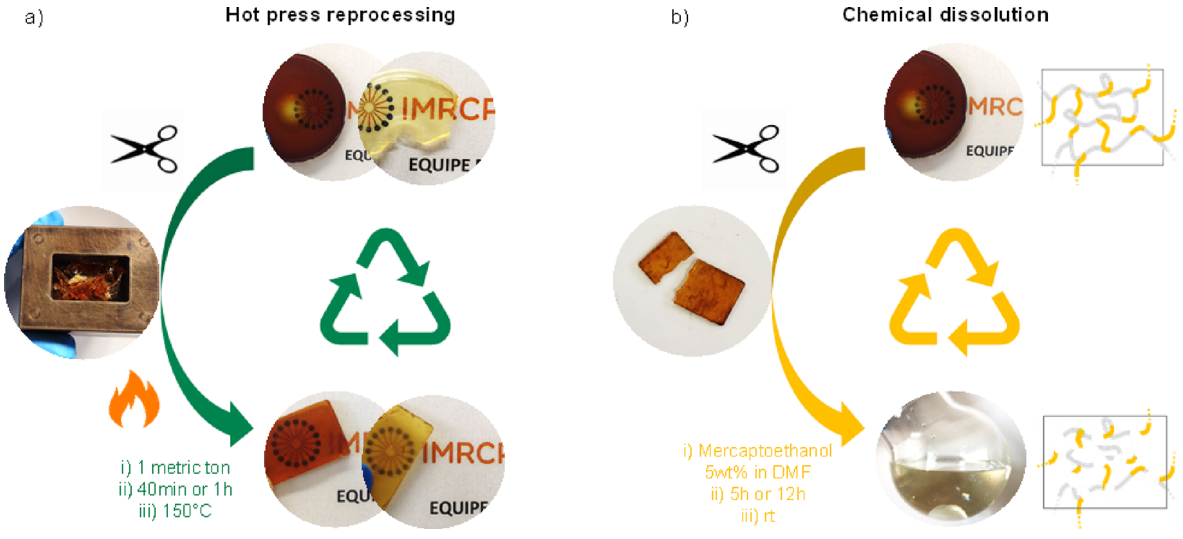

Figure 9. (a) Reprocessing experiments of vitrimer materials via compression molding of DGEVA/AFD and DGEVA/cyst in a hot press at 150 °C. (b) Chemical dissolution in swollen conditions using mercaptoethanol as reactive species.

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Table 4. Recycling Properties of DGEVA/4AFD, DGEVA/Cyst, and DGEVA/4AFD$_{0.80}$cyst$_{0.20}$[a]

	Tg DSC (°C)	G_0 (Pa)	E_a (kJ mol^{-1})	R^2	swelling ratio (%)	soluble fraction (%)
DGEVA/4AFD	103	5.2E6	124	0.99	6	0.5
DGEVA/4AFD (R)	90	6.7E6	155	0.97	7	0.4
DGEVA/cyst	53	5.8E6	57	0.99	102	3.5
DGEVA/cyst (R)	50	4.6E6	56	0.99	103	4
DGEVA/4AFD$_{0.80}$cyst$_{0.20}$	83	7.1E6	77	0.99	9	0.2
DGEVA/4AFD$_{0.80}$cyst$_{0.20}$ (R)	86	6.5E6	90	0.99	17	0.3

[a]With G_0 standing for the relaxation modulus at t = 0 measured at 180, 120, and 140 °C for DGEVA/4AFD, DGEVA/cyst, and DGEVA/4AFD$_{0.80}$cyst$_{0.20}$, respectively.

enable a fine control of the exchange pathways. E_a values also follow a similar trend yet less drastically with values gradually decreasing from 124 kJ mol^{-1} for the 100% 4AFD reference down to 77 kJ mol^{-1} for DGEVA/4AFD$_{0.80}$cyst$_{0.20}$. This discovery is very interesting as it can promote an additional level of control of the exchange dynamics without significantly impairing the material properties. Indeed, the replacement of 4AFD with cystamine decreased the Tg from 103 to 53 °C, which can restrain the potential of this material. Therein, by only adjusting the composition of the material, similar relaxation times can be obtained compared to the cystamine reference yet with glass transition in the range of 80 °C for the DGEVA/4AFD$_{0.80}$cyst$_{0.20}$ composition, for instance.

The reprocessability of materials was evaluated through compression molding experiments. DGEVA/4AFD, DGEVA/cyst, and DGEVA/4AFD$_{0.80}$cyst$_{0.20}$ samples were broken into small pieces and were reprocessed by compression molding in a hot press at 150 °C for 1 h, 40 min, and 45 min respectively (reprocessed samples now exhibit the acronym (R)). As shown in Figure 9, hot pressing gave access to reshaped objects, which have essentially the same mechanical properties. First, recycled materials were analyzed by DSC measurements. As depicted in Table 4, similar Tg was reported for aliphatic or mixed networks (53 vs 50 °C and 83 vs 86 for DGEVA/cyst and DGEVA/4AFD$_{0.80}$cyst$_{0.20}$, respectively) while a small decrease was noticed for the aromatic network (from 103 to 90 °C) (Figures S12−S14). FTIR analysis showed no significant modification over reprocessing steps (Figures S15−S16).

Stress relaxation experiments were also conducted on reprocessed samples (R) (Figure S17). Similar relaxation times were obtained for all vitrimers, and an acceleration was even noticed for the DGEVA/cyst (R) sample (Table S3). The E_a (Figure S18) was identical for DGEVA/cyst (R), but an increase was observed for DEGVA/4AFD (R) (124 to 155 kJ mol^{-1}) and DGEVA/4AFD$_{0.80}$cyst$_{0.20}$ (R) (77 to 90 kJ mol^{-1}). While for DGEVA/4AFD (R), the increase is likely related to fitting quality (R^2 = 0.97), DGEVA/4AFD$_{0.80}$cyst$_{0.20}$ (R) showed a good fitting (R^2 = 0.99). For the mixed DGEVA/4AFD$_{0.80}$cyst$_{0.20}$ vitrimer, reprocessing seems to modify the underlying exchange mechanism with the appearance of important dissociation at high temperature, as exhibited on non-normalized curves (Figure S17). We attributed this change to disulfide reshuffling during reprocessing between aliphatic and aromatic disulfides forming a new (/−Ar-S-S-CH_2−/) adduct with possible facilitated dissociation. This dissociation at high temperature was not present on the original materials (Figure S11), suggesting that the structure of 4AFD and cystamine remained unaltered during the curing procedure with no or negligible 4AFD/cystamine adduct formation. Finally, a slight decrease of modulus G_0 is observed after reprocessing for DGEVA/cyst (R) and DGEVA/4AFD$_{0.80}$cyst$_{0.20}$ (R) within the range of G_0 dissociation, which means that the dissociation mechanism might not be fully reversible. This important feature suggests that a gradual decrease of modulus can be expected for disulfide vitrimers over multiple recycling steps, and this decrease can be directly correlated with the percentage of disulfide dissociation. In contrast, DGEVA/4AFD (R) showed an increased modulus as a result of possible side reactions due to a high radical concentration (Table 4).

Swelling experiments were also performed in order to assess the network integrity of the vitrimer materials and optimize the degradation conditions with free thiols. The materials were immersed in $CHCl_3$, and the swelling ratio and soluble fraction were calculated using eqs 3 and 4. Soxhlet extraction was conducted with $CHCl_3$ at 90 °C for 48 h. As exposed in Table 4, soluble fractions were similar with only low % for both networks, suggesting a good network integrity. In contrast, the swelling ratio appears much higher for DGEVA/cyst than for DGEVA/4AFD as a result of the aliphatic nature of cystamine and the higher crosslink density of DGEVA/4AFD vitrimers. DGEVA/4AFD$_{0.80}$cyst$_{0.20}$ (R) exhibited swelling properties similar to the DGEVA/4AFD reference with a slight increase of swelling ratio arising from the aliphatic content. Overall, the recycled samples showed very similar swelling and gel content properties, confirming the successful reprocessing.

Depending on the nature of the dynamic chemical bonds, chemical recycling can be achieved.[52] This strategy is very appealing especially for the composites industry in view of recovering the fibers using soft depolymerization conditions. In this case, due to the reversible nature of the disulfide crosslinks, our resins can be easily dissolved in the presence of free thiols owing to the thiol−disulfide exchange reactions.[53] Therefore, mercaptoethanol was selected to depolymerize the thermosets. Sample pieces of the DGEVA/cystamine and DGEVA/4AFD resins were stirred with 10 equiv of 5 wt % mercaptoethanol in DMF at room temperature for 4 and 12 h, respectively. Full degradation of the material was noticed in both conditions. It should be noted that the degradation DGEVA/cyst was much faster than for the aromatic counterpart in agreement with previous observations, suggesting a higher reactivity of aliphatic disulfides. Figure 9 and Figure S19 present the full degradation and chemical recycling ability of both vitrimer materials.

CONCLUSIONS

In conclusion, we report the synthesis of vanillin-based vitrimers with cystamine, a bio-sourced hardener issued from amino acids, as a possible alternative to the widely used petro-sourced 4AFD. The newly synthesized and fully bio-sourced vitrimers were strictly compared to petro-sourced counterparts based on 4AFD. Cystamine exhibited much higher reactivity

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toward epoxy groups, but similar activation energies were determined. A significant acceleration of the exchange dynamics was revealed with decreased relaxation times from 23 min to 22 s at 170 °C for 4AFD and cystamine formulations, respectively. This observation was rather counterintuitive, as aromatic disulfides were especially designed to exhibit low BDE and thus accelerate exchanges as a result of a high radical concentration. In contrast, cystamine-based vitrimers are more dynamic than their aromatic counterparts. This phenomenon was also investigated through 4AFD and cystamine mixtures for which an unexpected accelerating effect was evidenced. Only 20 mol % of cystamine is necessary in 4AFD/cystamine formulations to achieve comparable relaxation times as for the fully cystamine-based analogue. Beyond the bio-based character of cystamine, this discovery opens new perspectives as it can enable a fine tuning of the exchange dynamics by simply adjusting the ratio of cystamine in any epoxy formulation. This is especially true since the more flexible segments arising from the aliphatic structure of cystamine considerably impact the Tg with a sharp drop of values from 103 to 53 °C (4AFD vs cystamine, respectively). Therein, with only 20 mol % of cystamine in 4AFD-based formulations, similar relaxation times to cystamine-based analogues can be obtained with a competitive Tg of 80 °C. Thus, the exchange dynamics offered by our aliphatic bio-based hardener can become considerably attractive as a viable alternative to the petrochemical-based counterparts with possible suitability for a wide range of applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.3c00379.

Stress relaxation experiments, DSC and TGA thermograms, FTIR, and images of reprocessed materials (PDF)

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Notes

The authors declare no competing financial interest.

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