Enhanced Viscosity Control in Thermosets Derived from Epoxy and Acrylate Monomers based on Thermoreversible Aza-Michael Chemistry

Stéphanie Engelen,^a Filip Van Lijsebetten,^a Resat Aksakal, ^a Johan M. Winne^{* a} and Filip E. Du Prez^{*a}

^a Polymer Chemistry Research group, Centre of Macromolecular Chemistry (CMaC) and Laboratory of Organic Synthesis, Department of Organic and Macromolecular Chemistry, Faculty of Sciences, Ghent University, Krijgslaan 281-S4, Ghent, 9000, Belgium.

E-mail: Johan.Winne@UGent.be; *Filip.DuPrez@UGent.be*

KEYWORDS. Covalent adaptable networks, epoxy, acrylate, tuneable viscosity, recyclable thermoset

"For Table of Contents use only"



ABSTRACT

Epoxies, epoxy acrylates, and acrylic resins account for a large portion of the thermoset market, yet their inherently highly cross-linked nature prevents them from being reprocessed or recycled. Herein, we present a simple reversible epoxy-based curing strategy that can address these issues. First, an epoxy monomer is ring-opened with ammonia to result in β -hydroxy-amines through a straightforward and scalable synthesis that we have demonstrated on multiple examples. The epoxy-derived amines are then cured with bisacrylates, creating dynamic covalent β-amino ester cross-linkages through a thermoreversible aza-Michael reaction. The resulting networks show a very pronounced drop in viscosity in the temperature region of 150 to 180°C, which we were able to attribute mainly to significant de-cross-linking of the amine and acrylate moieties, rather than to activation of dynamic ester bond exchanges. Nevertheless, the materials do not fully liquify and retain their structural integrity as a result of the very fast amine-acrylate rebonding kinetics. As a result, cross-linked epoxy-based materials could be obtained with simultaneously enhanced (re)processability at high temperatures and strongly inhibited deformation at lower temperatures $(<120^{\circ}C)$. The protocol is demonstrated for both petrochemically-based building blocks (such as bisphenol A), as well as for fully bio-based compounds (vanillin-epoxy and a Velvetol®-based bisacrylate), showing its versatility. As a result of the widespread use of epoxy resins, the ease of implementation and its interesting temperature window for debonding/rebonding, industrial applications can be foreseen for this thermoreversible curing strategy.

INTRODUCTION

Many commercial thermosets that are used in coatings, adhesives and in structural components or composites make use of epoxies, epoxy acrylates or acrylic resins, due to their ease of production,

low cost and high chemical resistance and dimensional stability.^{1–3} Conventionally, epoxy compounds are irreversibly cured with acid or amine hardeners, and epoxy acrylates are cured using UV-radiation. However, due to the permanent covalently cross-linked structure of these materials, these resins cannot flow and thus cannot be recycled or reshaped after they have been synthesized, and any structural damage cannot be fully healed.⁴

Covalent adaptable networks (CANs), also referred to as dynamic polymer networks (DPNs), contain cross-linked yet reconfigurable bonds that allow the network to rearrange within an applicable temperature window. Because highly cross-linked thermoset materials and corresponding composite materials are often disposed of after use, the field of CANs has grown considerably in the last two decades by introducing a wide range of dynamic covalent bonds.^{5–10} A significant challenge in CAN manufacturing is to achieve low viscosities and fast network rearrangement at a high yet reasonable temperature (below polymer degradation onset temperature). Rapid thermoplastic-like flow within a short time frame, enabling continuous manufacturing methods, has proven so far to be hard to reconcile while having acceptable structural integrity (e.g. minimal creep and solvent resistance) at normal service temperatures.¹¹

In dissociative CANs, such as the by now well-known furan-maleimide based polymer networks, debonding is easily triggered, even at a low temperature, and also solvent swelling can readily induce bond reversal (and thus polymer dissolution).^{14–16} On the other hand, in so-called 'associative' CANs, or vitrimers, such premature undesired structural damage can be prevented using a chemical strategy in which debonding is impossible or at least made much more unlikely, as bond exchange reactions can be promoted without depolymerizing the network.^{17–20} Since Leibler's first report on polyester vitrimers derived from acid cured epoxies (Scheme 1A),²¹

several alternatives have been proposed to increase the rate of the material flow, as typically only a gradual decrease in viscosity can be achieved.^{17,22–27} One attractive approach in this context is the use of neighbouring group participation (NGP) to stimulate internal catalysis.^{28–32}

Control of the rheological properties of vitrimer-like networks can be achieved, but mostly within narrow application windows, and by using 'exotic' building blocks or catalysts that so far have not found use in industrial polymer applications. Of particular interest is the dynamic curing system that our group developed for epoxy-acrylates with amine hardeners, giving dynamic β -amino ester (BAE) aza-Michael linkages (Scheme 1B).³³ Densely crosslinked materials could be obtained with glass transition temperatures (Tg) ranging from -60 to 90 °C. Moreover, by the introduction of OHcontaining building blocks, faster reprocessing was observed. In all examples, the BAE linkages included a tertiary amine, which is an internal catalyst for transesterification. Moreover, the BAE linkages were shown to be thermoreversible, giving a more pronounced thermal response and a high apparent activation energy (~150 kJ/mol). In comparison to the dissociative furan-maleimide Diels-Alder chemistry, where the adducts lose their crosslinking and thus network connectivity already at lower temperatures (< 120 °C),^{34–36} this recently developed and easily implementable BAE chemistry especially allows to have this crosslinking drop at higher temperatures (> 160 °C), making this dissociative chemistry more accessible and attractive for manufacturing approaches.³³ In follow-up studies, we reported biobased BAE-networks based on pripol and priamine³⁷ and also BAE-networks that have been combined with the vinylogous urethane associative chemistry.³⁸ Subsequently, the BAE dynamic chemistry was implemented by Caillol, Ladmiral and co-workers, where they aimed to speed up the reactivity rates of the corresponding materials by either the incorporation of additional hydroxy-groups or fluorine neighbouring groups.^{39,40} Further, Lee et al. incorporated this dynamic chemistry in their materials by utilizing BPA-based acrylates and a triamine crosslinker to obtain materials with shape memory and healing properties.⁴¹ While it is clear that the BAE-chemistry has been picked up rapidly, its mechanistic understanding and the control over the reactivity of the bonds should be improved. Several exchange pathways are conceivable and further mechanistic investigations are required for their rational applications in material design.



Scheme 1. A. Leibler's transesterification based epoxy vitrimers²¹; B. Epoxy-based CANs using amine hardeners as internal catalysts for transesterification, enhanced by a reversible β -amino ester (BAE) linkage (Taplan et al.).³³ C. The presented protocol shows a more pronounced debonding behaviour of the BAE linkages, related to the influence of the β -hydroxyl moiety. The applied amine and acrylate building blocks and a picture of the grinded and compression moulded material are shown below.

In BAE chemistry, the reconfigurable bonds can relax external stresses via two pathways, namely an associative trans-esterification and a dissociative (retro)-aza-Michael pathway. The associative transesterification and dissociative (retro)-aza-Michael reactions can be differentially effected by the network architecture as they rely on different reactive groups. In dynamic polymer networks, neighbouring groups can have a profound influence on reactivity.^{28,42-44} In this context, we can expect that the proximity of a relatively nucleophilic and acidic hydroxyl moiety can influence the reactivity of BAE linkages. Thus, we here report our studies of 'next generation' BAE epoxybased networks (Scheme 1C), in which the epoxy-derived hydroxyl group is located at the β position of the nitrogen. This approach is still very easily implemented on commercially available and widely used monomer types, yet we can expect some pronounced effects from the relative rearrangement of the reactive and neighbouring groups.

Our initial material design starts from a β -hydroxy-amine monomer that can be easily derived from bisphenol A diglycidyl ether (DGEBA), which can be cross-linked using a bisacrylate compound. This approach using only commercially available monomers actually allows additional optionality in network design compared to the previous approach (Scheme 1B vs. 1C), as it does not require a polyamine. Our study of the material properties and rheological behaviour show a more pronounced and dominant contribution of the retro-Michael reactivity, which results in a remarkable increase in thermal responsivity of the dynamic network behaviour. Moreover, a fully bio-based dynamic material, derived from a vanillin-epoxy and a Velvetol® bisacrylate, could also be prepared using the same approach.

RESULTS AND DISCUSSION

Synthesis of the CAN-series

To study the effect of the neighbouring β -hydroxyl group on the bond exchange reactivity of the BAE moieties within an epoxy network (in transesterification and aza-Michael reversibility), a series of materials have been prepared (Scheme 2). First, a reference material without any free hydroxyl groups was prepared by reacting a mixture of m-xylylene diamine (1 equiv.) with a bisacrylate of polypropyleneglycol (PPG-bisacrylate) (2 equiv.) with an average molecular weight of 800, resulting in reference BAE networks (A) (orange box, Scheme 2).

Second, for the investigation of the effect of a neighbouring hydroxyl on BAE linkages, we prepared an alternative bisamine, conveniently derived from the diglycidyl ether of bisphenol A (DGEBA) through ring-opening with aqueous ammonia in a pressure tube. The resulting di(3-amino-2-hydroxypropyl)ether of bisphenol A (DAHP-BA) (Synthetic protocol in SI), when combined with the PPG-bisacrylate cross-linker in solution, resulted in materials that are further referred to as epoxy-derived amine (EA) acrylate-cured networks EA-1, EA-2 and EA-3 (equimolar, excess and limiting amine-based formulations) (respectively 1, 1.2, 0.8 equiv. amine to 2 equiv. acrylate) (blue box, Scheme 2).

Finally, an amine acrylate-cured based network was made that is entirely derived from bio-based monomers (EA-Bio) (1 equiv. amine to 2 equiv. acrylate). For this, the diglycidyl ether of methoxy hydroquinone, derived from vanillin, and its corresponding bisamine (DAHP-MHQ)⁴⁵ was cured with a new bio-based bisacrylate, synthesized from Velvetol®, with an average molecular weight of 1000 (green box, Scheme 2).⁴⁶ Velvetol® is obtained from 100% bio-based 1,3-propanediol, originating from corn sugar ^{47,48}, while the vanillin derived epoxy compound can be obtained from

lignocellulosic biomass.⁴⁵ The synthesis of the bisacrylate version from Velvetol® was confirmed with size exclusion chromatography (SEC), MALDI-TOF and ¹H-NMR spectroscopy (Figure S2, S4 and S5).



Scheme 2. Schematic representation of this work: three different types of materials are obtained by combining amines with PPG (800 g/mol) or Velvetol® (1000 g/mol) bisacrylates. The compounds for the reference material (A-R) (1 equiv. amine to 2 equiv. acrylate) are described in the orange box (upper right) and the ones of the key materials series (EA-1,2,3) (respectively 1, 1.2, 0.8 equiv. amine to 2 equiv. acrylate) in the blue box (middle). The green box represents the used compounds for a fully bio-based version of the aforementioned materials (EA-Bio) (1 equiv. amine to 2 equiv. acrylate).

The formulations of the three DAHP-BA-derived EA networks (EA-1, -2 and -3) were varied by changing the ratios of the amines with respect to the acrylates (respectively using 1, 1.2 and 0.8 equiv. of amine to 2 equiv. acrylate). The amount of amine in a network formulation is indicated with respect to the amount of acrylate used, and the monomer ratio is expressed in Table 1 also as an 'index' to show how much acrylate is used relative to the amine. It should be noted that a primary amine group can react with two acrylate functionalities, while a secondary amine can only react with one acrylate moiety, with primary amines reacting faster than secondary amines for this reaction as demonstrated earlier.^{49,50} An index of 100 refers to a 1:1 ratio where every primary and secondary amine can in principle react with an acrylate functionality (2 mole of acrylates per 1 mole of amines), which constitutes a perfect network structure. Deviation of this index to either side will lead to a decrease in cross-link density. An index of 83 thus refers to 0.83 mole of acrylates per 0.5 mole of amines (or 1.0 mole of reactive N-Hs), and it will contain a lot of unreacted secondary amine moieties, but very few free primary amines, and theoretically no free acrylates. Conversely, an index of 125 refers to 1.25 mole of acrylate functions versus 0.5 mol of amine functions (1.0 mole of reactive N-H's) and is expected to contain an excess of free acrylates, and almost no unreacted secondary amines. It should be noted that a network with an index of 50 would theoretically correspond to a fully linear polymer while a network with an index of 100 is the most densely cross-linked one. This stoichiometry will affect the network topology and the associated material flow.

Excess amines (> 1 equiv. or index 83) (material EA-2 and EA-4) can be expected to give some additional cross-linking ('higher index') as a result of permanent amide bond formation to the ester moieties, releasing some additional hydroxyl groups at the same time. Conversely, a relative excess of acrylates and thus limiting amount of amines (amines < 1 equiv. or index 125) may give

a lower cross-link density, but could also result in additional secondary cross-links by thermal oligomerisation of the acrylic bonds. In both cases, however, the main bulk of the cross-links are expected to be made up from dynamic BAE aza-Michael linkages. The formation of irreversible amide bond formation was confirmed through FTIR on a sample that had gone through prolonged thermal treatment up to 180°C during rheological analysis (Figure S7).

Based on previous observations for vitrimers that are based on transesterification chemistry,²⁸ we expected ester exchange in the EA networks to be relatively slowed down by the absence of a neighbouring hydroxyl group compared to previously reported networks (Scheme 1B), while we envisaged that the BAE aza-Michael linkages could become more reactive due to the proximity of the hydroxyl group to this reactive bond. In the A-R reference material, all bond exchanges should be limited to aza-Michael reactivity, as no free hydroxyls are present to engage in transesterification reactions. As an additional reference material to investigate the exact role of hydroxyl moieties, we also prepared the same A-R reference material in which dodecan-1-ol is added as a reactive diluent (A-R_{OH}). Protic environments (or solvents) have indeed been found to accelerate bond exchange reactions.

All the experimental data gathered for the four EA networks and the two reference 'pure BAE' networks A-R and A-R_{OH} are gathered in Table 1. The formulations were typically cured at 90 °C for 12 hours and post-cured for 2 hours at 120 °C, while the reduction of the acrylate double bond was qualitatively monitored with online-FTIR (signal at 1638 cm⁻¹) (Figure 1A, Figure S6). For all networks displayed in Table 1, reprocessing was performed *via* compression moulding at 180 °C, under 4 metric tonnes for 1 hour.



Figure 1. A. Structural characterization of the materials with FT-IR. B. DSC-analysis of the recyclable thermosets based on acrylate (A) and epoxy-derived amine acrylate (EA) building blocks.

CAN	Acrylate	Eq. -NH2 (index) ^a	Tg ^b (°C)	Td5% ^c (°C)	Swelling ratio ^d (wt.%)	Soluble fraction ^d (wt.%)	Ea ^e (kJ mol ⁻ ¹)	η _{180°C} (Pa s) ^f	η _{150°C} (Pa s) ^f	≠ in order of magnitude ^g	v' (mol m ⁻³) ^h	ε _{40°C} (s ⁻¹) ⁱ
A - R	PPG	1.0 (100)	-50	320	327	6	112.0 ± 1.0	4.9 10 ⁸	4.0 10 ⁹	0.91	147.2	2.0 10 ⁻⁶
A – R _{OH}	PPG	1.0 (100)	-52	320	454	7	140.6 ± 1.9	2.8 10 ⁸	6.6 10 ⁹	1.37	139.5	9.2 10 ⁻⁸
EA – 1	PPG	1.0 (100)	-45	320	459	21	158.1 ± 6.7	1.7 10 ⁸	6.1 10 ⁹	1.56	169.2	1.9 10 ⁻⁷
EA – 2	PPG	1.2 (83)	-50	321	431	20	146.0 ± 5.7	$7.9 \\ 10^{7}$	2.9 10 ⁹	1.56	175.9	1.5 10 ⁻⁶
EA – 3	PPG	0.8 (125)	-60	319	560	35	$\begin{array}{c} 188.0 \pm \\ 7.0 \end{array}$	6.6 10 ⁷	$1.2 \\ 10^{10}$	2.27	191.5	3.8 10 ⁻⁷
EA-4	PPG	2.0 (50)	-38	313	290	4	$\begin{array}{c} 126.6 \pm \\ 6.3 \end{array}$	3.1 10 ⁸	3.1 10 ⁹	1.01	169.2	2.9 10 ⁻⁶
EA – Bio	Velvetol ®	1.0 (100)	-72*	325	-	25 ^d	157.4 ± 5.5	4.9 10 ⁶	9.1 10 ⁷	1.27	11.3	3.8 10 ⁻⁷
Ref	BPA	1.0 (100)	-40	340	425	14	$\frac{180}{24} \pm$	-	-	-	-	-

Table 1. Overview of the recyclable thermosets of acrylate (A) and epoxy-derived amine acrylate (EA) building blocks and their corresponding thermal, soluble and rheological properties.

^a Stoichiometric details: equivalents of primary amine to 2 equivalents of acrylate and index details in brackets showing how much acrylate is used relative to amine. ^b Glass transition temperature (T_g) obtained from second heating (rate 10°C/min). ^c TGA onset-degradation temperatures for 5% weight-loss. ^d Swelling ratio and soluble fraction in THF for 24h at r.t. averaged from four sample measurements. ^e E_a, activation energy; determined in the high temperature region (180 -150 °C) where a linear viscosity profile is present. ^f Viscosity η determined via equation 1. ^g The difference in order of magnitude was calculated from the difference in logarithm of $\eta(180 °C)$ and $\eta(150 °C)$. ^h The crosslinking density determined from G' modulus of frequency sweeps at 120 °C and 1 rad/s *via* v'= G' / R T ⁱ The creep rate at 40°C determined in the final 10% region of the creep measurement for a stress of 1000 Pa. Note that the creep viscosity can be calculated from this value by dividing the shear stress with the creep rate. ^{*}The material with Velvetol® displays a melting temperature (T_m) at 6 °C, next to a T_g .

The two reference materials (A-R and A-R_{OH}) were obtained from equimolar amounts of amine and acrylate (A-R; 1 equiv. amine to 2 equiv. acrylate), with further addition of 0.2 equiv. of dodecan-1-ol as a reactive 'protic' diluent in A–R_{OH}. The network EA-1 was obtained with equimolar amounts of both functionalities, similar to A-R. To investigate whether changes in equivalents would alter the material properties, two additional EA materials were synthesised, respectively EA-2 with an excess and EA-3 with a limiting amount of amines (resp. 1.2 and 0.8 equiv. amine to 2 equiv. of acrylate). A supplementary off-stoichiometric material EA-4 was synthesised with 2 equiv. of amines to 2 equiv. of acrylate, thus a material in which the primary amines will react predominantly with the acrylate groups. The bio-based amine acrylate cured network was obtained using equimolar ratios only (EA-Bio), and was also characterized by a slightly higher molar mass acrylate (1000 vs 800 g/mol). Besides the aforementioned materials, a reference material (Ref) corresponding to Scheme 1B, i.e. a BAE network with BPA-based bisacrylate and bisamine (Jeffamine), was adopted from the study of Taplan et al³³ and was added to Table 1.

Exchange pathways and material properties

The thermal analysis results are summarised in Table 1 and displayed in Figure 1B and Figures S8 - S10. Both reference materials (A-R and A-R_{OH}) showed similar thermal properties for the glass transition temperatures (T_g around -50°C) and the thermal degradation temperatures (T_{d5%}). As expected, the thermal properties of the EA-materials lie in a similar range as these reference materials, as they are mainly built up from the same acrylate PPG backbone structure. Apart from EA-4, the equimolar network EA-1 exhibits the highest T_g (-45 °C). The lowest T_g (- 60 °C) was observed for the material made with an excess of acrylates, as can be expected because of the higher incorporated amount of PPG-backbone relative to the amines. The Velvetol® based network (EA-Bio) showed an even lower T_g, which is readily ascribed to the higher flexibility of the backbone. Isothermal TGA showed that there was no significant mass loss for the materials at 180

 $^{\circ}$ C (temperature in compression moulding of the EA networks) under N₂ flow for 120 minutes (Figure S10).

Comparison of the synthesized networks in terms of swelling and gel fraction showed some interesting trends. First of all, the addition of 10 mol% of the reactive diluent dodecan-1-ol has a large effect on the swelling ratio in THF as the ratio increases significantly (A-R vs A-R_{OH}). This improved swelling is also seen in all EA networks, which contain a lot more hydroxyl moieties (theoretically 100 mol%).

The crosslinking density (v') of the materials (Table 1) was derived from the frequency sweeps (Figure S38 – S44) at 120°C. A slightly higher v' was obtained for EA-3 (191 mol m⁻³), whereas the alternative EA materials had similar crosslinking densities (~ 170 mol m⁻³).

The very high swelling degree results in relatively high soluble fractions for the β-hydroxy-amine cured networks, but not for the normal amine cured networks, which is in line with previous observations in BAE-networks.^{38,39,41} The 'neighbouring group effect' of the hydroxyl can indeed affect the kinetics and thermodynamics of the expected associative and dissociative network rearrangement reactions, but can also give rise to new pathways. One particular option here is a dissociative transesterification pathway, via the reversible formation of a seven-membered lactone (Scheme 3). In contrast to previous BAE-cured networks, a transesterification equilibrium exist in which chains are cleaved via 'back biting' of the hydroxyl onto the BAE moiety, resulting in depolymerisation. The resulting lactone ring remains a dynamic ester bond, but can also give a more pronounced de-cross-linking effect compared to previous formulations, explaining the higher soluble fractions. Two supporting schemes are shown in Figure S13 and S14 in which the differences in dissociation pathways are outlined for the two different amines.



Scheme 3. Three possible reaction pathways are outlined. 1) Aza-Michael reaction of the primary amine with the electrophilic acrylate, followed by a second Aza-Michael reaction, in which the secondary amine reacts with a new acrylate; 2) Aza-Michael reaction, followed by direct transesterification, in which the hydroxyl group, originating from the epoxy functionality, reacts with a second acrylate. 3) An alternative dissociative exchange pathway: Aza-Michael reaction, followed by transesterification *via* NGP-based cyclisation with the formation of an activated cyclic ester and an alcohol. Supporting DFT calculations and computational details are provided in Figures S65 and Figure S66.

In order to further investigate the difference in soluble fraction observed for normal amine-cured acrylates and β -hydroxy amine-cured acrylates, we investigated both the networks and the soluble fractions that could be extracted from them. Using FTIR, there were no indications that the acrylate groups were not fully consumed in the reference samples A-ref, but some minor residual absorbance could be seen in the EA-networks, especially in the limiting amine EA-3 network (Figure 1A and Figure S6). In conclusion, incomplete curing can be ruled out as a major factor contributing to the high soluble fractions. Moreover, by immersing the EA-3 network (2 – 4 mm diameter, ±12 mg) in 40 mL of (anhydrous) THF, followed by removal of the material, evaporation

of the soluble fraction and analysis with ¹H-NMR spectroscopy (Figure S11), only the acrylate monomer was observed, with no trace of the amine hardener. For all soluble fractions, only the acrylate monomer was observed (see SI). This observation indicated that the second addition (which is known to be kinetically slower) is likely also thermodynamically more reversible. To confirm this result, an equimolar amine acrylate cured material, with no excess of acrylates, was synthesised with an easier to analyse 'short chain' dodecane diacrylate (rather than with PPG diacrylate, SI EA-5). The soluble fraction was analysed via GC-MS (Figure S12). Again, the acrylate compound could be retrieved as the only solubilized compound, next to some monoacrylate. This mono-acrylate with one OH- and one acrylate-functionality can be obtained by either pathway 2 or 3, as can be observed in Scheme 3 (ROH). The result of the analysis of the soluble fraction is in agreement with the fact that statistically every amine compound in the reaction mixture is tetrafunctional, while the acrylate compound is bi-functional. An additional confirmation was obtained by synthesising an EA material from 2 equiv. of amines and 2 equiv. of acrylates (EA-4, Table 1). Indeed, this experiment showed that all acrylate moieties reacted and a much lower soluble fraction of 4% was obtained for a swelling ratio of 290% in THF under similar conditions. It is therefore concluded that one of the secondary amine-acrylate linkages are more dynamic and more readily reversible than the primary amine-acrylate links.

Investigation of the kinetic and thermodynamic behaviour of the networks

To investigate the viscoelastic flow for the different types of networks, stress-relaxation was measured at different temperatures. Whereas A- R_{OH} showed, similarly to EA-1, a fast relaxation behaviour at high temperatures, the behaviour of the relaxation modulus showed remarkable differences (Figure 2). More specifically, the relaxation moduli of A- R_{OH} and EA-1 at high and low temperatures for both materials are very different from each other.



Figure 2. Non-normalized stress-relaxation figures of network A-R_{OH} and amine acrylate cured networks EA-1, 2, 3, 4 from 180°C to 120°C. A much more pronounced dissociation can be observed for the EA networks in comparison to the A-R_{OH} network.

From the relaxation curves, it can be seen that the β -hydroxy-amine cured acrylate EA-1 is shifted significantly to the dissociated state at high temperatures, much more than in the reference material that has been cured with a normal amine (A-R_{OH}). This result is in agreement with the higher soluble fractions obtained for the EA materials (EA-1,-2,-3) compared to the reference materials. Again, two possible dissociative mechanisms are expected to contribute to the drop of the relaxation modulus: the retro-Aza Michael and the intramolecular transesterification pathway (lactone forming de-cross-linking). Even more pronounced stress-relaxation curves, showing a quite significant thermal de-cross-linking, can be seen for the off-stoichiometric networks EA-2 and EA-3. For material EA-4, the material with only primary amine-acrylate linkages, a less

pronounced dissociative relaxation profile is observed, which is in accordance with the soluble fractions (*vide supra*).

From the stress-relaxation (SR) measurements, where a stretched exponential Maxwell model was used to fit the data (See Table S2 for stretching exponents, Figures S15 – S28 for (non)-normalized SR-curves and for overlay at 180°C and 150 °C Figures S29 and S30), the apparent activation energies (E_a) were determined in the high temperature region (180 -150 °C) where a linear viscosity profile is present (SI Figures S31 - S37). The highest value of apparent activation energy is ascribed to material EA-3, with a thermal response that can be largely attributed to a drop in cross-linking density and hence in relaxation modulus. This result is similar to our first report on BAE-CANs, where the OH-containing BAE materials with a similar T_g (Ref in Table 1) also had a higher apparent activation energy.³³

Next, the rheological properties of the aforementioned materials were further investigated. From the stress-relaxation measurements, the viscosity and its multiplying factors could be retrieved according to Equation 1 (see Figure 3).

$$\eta = \tau * G_0 \qquad [Equation 1]$$

According to the Maxwell relation, the change in material flow or viscosity can be attributed to the relaxation dynamics τ [T] and the modulus G [T] of the underlying dynamic chemistry.⁵³ The viscosity plot can be obtained from the Maxwell relation by multiplying the stress relaxation time with the relaxation modulus, thus combining the kinetics (Arrhenius) and the thermodynamics (Van 't Hoff) respectively. Whereas the relaxation kinetics represent the time needed for the polymer chains to relax, the modulus is a measure for the crosslinking density of the material.



Figure 3. By multiplying the relaxation time τ (Arrhenius plot) and the relaxation modulus (Van 't Hoff plot), the viscosity (bottom figure) can be obtained. The Arrhenius plot (left figure) follows a linear behaviour for all materials, whereas the Van 't Hoff plot (right figure) shows a steep decrease in relaxation modulus, also noticeable in the viscosity plot.

The Arrhenius plot in Figure 3 shows that all materials follow a similar viscoelastic regime related to a linear behaviour. Moreover, it is seen that at 180 °C, the EA materials show the shortest relaxation times (EA-2 > EA-1 > EA-3 > EA-4), followed by the reference material with the protic moiety (A-R_{OH}) and finally the reference material A-R. At the lowest temperature, 150 °C, EA-2,

EA-4 and EA-1 showed the fastest relaxation times, followed by the reference materials while the relaxation time of EA-3 was the highest. This is noteworthy as EA-3 had a short stress relaxation time at the highest temperature, yet can slow down its reconfigurations at lower temperatures, which is a desirable characteristic for CANs in the context of creep resistance during use.¹² The very low creep rates at 40°C ($< 10^{-6} \text{ s}^{-1}$) and creep measurements of the materials can be retrieved in Table 1 and in Figures S45-S56. Much lower creep rates are obtained compared to previous dissociative networks, suggesting a slower permanent network deformation.⁵⁴

Remarkable trends are observed from the Van 't Hoff plot in Figure 3. While the equimolar materials (A-R, A-R_{OH} and EA-1) show a very similar decrease in crosslinking density upon temperature increase, a sudden viscosity drop is seen for the material EA-2 (2 equiv. acrylate to 1.2 equiv. amine), which is even more pronounced for the material EA-3 (2 equiv. acrylate to 0.8 equiv. amine). Note here that for material EA-4 (2 equiv. acrylate to 2 equiv. amine) in the Van't Hoff plot, the relaxation modulus remains merely unaltered over different temperature ranges, as a result of the constant crosslinking density. This vitrimer-like behaviour indicates that the retro-aza-Michael of the primary β -hydroxy-amines is less likely to happen compared to its secondary analogues. In addition, this result is in line with the aforementioned lower soluble fractions obtained for EA-4, where no decrosslinking occurs (even in swollen state) compared to the EA-1, 2, 3 series.

The remarkable drop in relaxation modulus in the Van't Hoff plot is also manifested in the viscosity plot because of multiplying factors τ and G₀. By altering the stoichiometry of the networks, the viscosity difference between high and low temperatures (180 and 150 °C) can be altered to reach over 2 orders of magnitude. Among the EA networks and the reference networks, the largest drop in viscosity was seen for EA-3, followed by EA-2 and EA-1, A-R_{OH}, EA-4 and

A-R (see Table 1). Indeed, the difference in orders of magnitude of the viscosity of EA-1 is the same as the one of EA-2 (1.56), indicating that an excess of amines (EA-2) is not having a major influence on the viscosity (EA-1), while a deficient amount has a clear impact (EA-3).

For the bio-based EA-Bio network, with a higher MW backbone, lowering the crosslinking density, it is observed that the thermal stability (after onset degradation) of the material with Velvetol® slightly increased as expected from the high oxidative stability of the polyol (Table 1, Figure S9).⁵⁵ In addition to the low T_g of -72 °C, the EA-Bio also demonstrated a melting temperature at 6 °C, related to the Velvetol® backbone (Figure 1B, Figure S3). Equally to the EA materials (EA-1, EA-2 and EA-3), this bio-based material showed high swelling ratios, comparable soluble fractions and a large drop in viscosity upon heating in the 120-180°C range.

While the mechanical properties of the materials prepared in this manuscript are not competitive with the conventional and usually high T_g epoxy-based thermosets (for tensile and adhesive properties see SI figure S57-63 and S64 respectively), we strongly believe that this curing strategy and its mechanistic insights on the rheological behaviour might be valuable for future applications.

CONCLUSION

Epoxy-derived amine acrylate cured networks could be obtained with remarkable increase in thermal responsivity at high temperatures and simultaneously strongly inhibited deformation at lower temperatures. Therefore, they are considered as a promising alternative to conventional non-recyclable thermosets. We have shown innovative formulations for such dynamic networks in which the viscosity is very responsive in a highly attractive temperature window for material applications and polymer reprocessing (150-180°C), with steep viscosity profiles over that range, an interesting feature for manufacturing approaches. While the solvent resistance of some of the

EA-materials can still be optimized, for example by using a mixture of epoxy and non-epoxyderived amine monomers, as a result of the fast dissociation of the secondary amines in a swollen state and the possibility for the formation of an activated ester, the overall properties of the reference material were in good coherence with previous reports on BAEs, and the properties could be enhanced by simply varying monomer stoichiometry. The materials showed excellent creepresistant properties. Furthermore, we showed that the material design could also be translated into a sustainable and bio-based thermoset, by combining a vanillin-epoxy derivative with a Velvetol® bisacrylate, showing that recyclable thermosets can be tuned into more circular materials by utilizing bio-based resources. We conclude here that the tuneable stoichiometry and thermoresponsive viscosity profiles offer a very practical opportunity for the manufacturing of dissociative networks, while their solvent resistance remains an inherent challenge. Finally, we believe that reversible aza-Michael chemistry could show a very promising profile and tuneability through protic additives and/or polymer matrix fine tuning.

AUTHOR INFORMATION

Corresponding Authors

- * Johan Winne: Johan.Winne@UGent.be
- * Filip E. Du Prez: <u>Filip.DuPrez@UGent.be</u>

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

SUPPORTING INFORMATION

The supporting information is available at ...

Monomer and material synthesis, network characterization (rheology, tensile tests, etc.) (PDF)

ACKNOWLEDGMENT

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme 101021081 (ERC-AdG-2020, CiMaC-project). S.E. and F.V.L. acknowledge the Research Foundation-Flanders (FWO) for their Ph.D. fellowships (Application 1SD4821N and 1S49122N respectively). The authors would like to thank Bernhard De Meyer and Jan Goeman for the technical support while Dr. Christian Taplan, Dr. Lucas Stricker and Dr. Nezha Badi are thanked for the fruitful discussions. Tim Maiheu is thanked for the help with the tensile tests. Dr. Susanne Fischer and Dr. Guillaume Acke are acknowledged for their help with the DFT calculations. The computational resources and services used in this work were provided by the VSC (Flemish Supercomputer Center), funded by the Research Foundation-Flanders (FWO) and the Flemish Government – department EWI.

REFERENCES

- Kinloch, A. J. Mechanics and Mechanisms of Fracture of Thermosetting Epoxy Polymers. In *Epoxy resins and composites I Advances in Polymer Science, vol 72*; Springer, Ed.; Berlin, Heidelberg., 1985; pp 45–67.
- Pham, H. Q.; Marks, M. J. Epoxy Resins. Ullmann's Encyclopedia of Industrial Chemistry;
 Wiley VCH, 2012; pp 156–238.
- (3) Engels, T. Thermoset Adhesives: Epoxy Resins, Acrylates and Polyurethanes. In

Thermosets: Structure, Properties and Applications; 2012; pp 228–253.

- Kloxin, C. J.; Bowman, C. N. Covalent Adaptable Networks: Smart, Reconfigurable and Responsive Network Systems. *Chem. Soc. Rev.* 2013, 42 (17), 7161–7173.
- (5) Rowan, S. J.; Cantrill, S. J.; Cousins, G. R. L.; Sanders, J. K. M.; Stoddart, J. F. Dynamic Covalent Chemistry. *Angew. Chemie Int. Ed.* 2002, *41* (6), 898–952.
- (6) Kloxin, C. J.; Scott, T. F.; Adzima, B. J.; Bowman, C. N. Covalent Adaptable Networks
 (CANs): A Unique Paradigm in Cross-Linked Polymers. *Macromolecules* 2010, 43 (6), 2643–2653.
- Bowman, C. N.; Kloxin, C. J. Covalent Adaptable Networks: Reversible Bond Structures Incorporated in Polymer Networks. *Angew. Chemie Int. Ed.* 2012, *51* (18), 4272–4274.
- (8) Denissen, W.; Winne, J. M.; Du Prez, F. E. Vitrimers: Permanent Organic Networks with Glass-like Fluidity. *Chem. Sci.* 2016, 7 (1), 30–38.
- (9) Zheng, N.; Xu, Y.; Zhao, Q.; Xie, T. Dynamic Covalent Polymer Networks: A Molecular Platform for Designing Functions beyond Chemical Recycling and Self-Healing. *Chem. Rev.* 2021, 121, 1716–1745.
- (10) Zhang, V.; Kang, B.; Accardo, J. V; Kalow, J. A. Structure-Reactivity-Property Relationships in Covalent Adaptable Networks Structure-Reactivity-Property Relationships in Covalent Adaptable Net-Works. *J. Am. Chem. Soc.* **2022**, *144*, 22358–22377.
- (11) Elling, B. R.; Dichtel, W. R. Reprocessable Cross-Linked Polymer Networks: Are Associative Exchange Mechanisms Desirable? ACS Cent. Sci. 2020, 6 (9), 1488–1496.
- (12) Van Lijsebetten, F.; Debsharma, T.; Winne, M. J.; Du Prez, F. E. Dynamic Covalent Polymer Network without Creep : Mission Impossible ? *Angew. Chemie Int. Ed.* 2022, *61*, e202210405.

- (13) Hubbard, A. M.; Ren, Y.; Picu, C. R.; Sarvestani, A.; Konkolewicz, D.; Roy, A. K. Creep Mechanics of Epoxy Vitrimer Materials. ACS Appl. Polym. Mater. 2022, 4 (6), 4254–4263.
- (14) Chen, X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H.; Nutt, S. R.; Sheran, K.; Wudl, F. A Thermally Re-Mendable Cross-Linked Polymeric Material. *Science (80-.).* 2002, 295 (5560), 1698–1702.
- (15) Herbert, K. M.; Getty, P. T.; Dolinski, N. D.; Hertzog, J. E.; Jong, D. De; Lettow, J. H.; Romulus, J.; Onorato, J. W.; Foster, E. M.; Rowan, S. J. Dynamic Reaction-Induced Phase Separation in Tunable, Adaptive Covalent Networks. *Chem. Sci.* **2020**, *11*, 5028–5036.
- (16) Ying, H.; Zhang, Y.; Cheng, J. Dynamic Urea Bond for the Design of Reversible and Self-Healing Polymers. *Nat. Commun.* 2014, *5*, 3218.
- (17) Brutman, J. P.; Delgado, P. A.; Hillmyer, M. A. Polylactide Vitrimers. *ACS Macro Lett.* **2014**, *3* (7), 607–610.
- (18) Denissen, W.; Rivero, G.; Nicolaÿ, R.; Leibler, L.; Winne, J. M.; Du Prez, F. E. Vinylogous Urethane Vitrimers. *Adv. Funct. Mater.* **2015**, *25* (16), 2451–2457.
- (19) Debsharma, T.; Amfilochiou, V.; Alicja, A.; Baere, I. De; Paepegem, W. Van; Du Prez, F.
 E. Fast Dynamic Siloxane Exchange Mechanism for Reshapable Vitrimer Composites. J.
 Am. Chem. Soc. 2022, 144 (27), 12280–12289.
- (20) Guerre, M.; Taplan, C.; Winne, J. M.; Du Prez, F. E. Vitrimers: Directing Chemical Reactivity to Control Material Properties. *Chem. Sci.* 2020, *11* (19), 4855–4870.
- Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. Silica-like Malleable Materials from Permanent Organic Networks. *Science (80-.).* 2011, *334* (6058), 965–968.
- (22) Self, J. L.; Dolinski, N. D.; Zayas, M. S.; Read De Alaniz, J.; Bates, C. M. Brønsted-Acid-Catalyzed Exchange in Polyester Dynamic Covalent Networks. ACS Macro Lett. 2018, 7

(7), 817–821.

- (23) He, C.; Shi, S.; Wang, D.; Helms, B. A.; Russell, T. P. Poly(Oxime-Ester) Vitrimers with Catalyst-Free Bond Exchange. J. Am. Chem. Soc. 2019, 141 (35), 13753–13757.
- (24) Han, J.; Liu, T.; Hao, C.; Zhang, S.; Guo, B.; Zhang, J. A Catalyst-Free Epoxy Vitrimer System Based on Multifunctional Hyperbranched Polymer. *Macromolecules* 2018, *51* (17), 6789–6799.
- (25) Lossada, F.; Jiao, D.; Yao, X.; Walther, A. Waterborne Methacrylate-Based Vitrimers. ACS Macro Lett. 2020, 9 (1), 70–76.
- (26) Debnath, S.; Kaushal, S.; Ojha, U. Catalyst-Free Partially Bio-Based Polyester Vitrimers. ACS Appl. Polym. Mater. 2020, 2 (2), 1006–1013.
- (27) Berne, D.; Cuminet, F.; Lemouzy, S.; Joly-duhamel, C.; Poli, R.; Caillol, S.; Leclerc, E.; Ladmiral, V. Catalyst-Free Epoxy Vitrimers Based on Transesterification Internally Activated by an A–CF3 Group. *Macromolecules* 2022, 55 (5), 1669–1679.
- (28) Van Lijsebetten, F.; Holloway, J. O.; Winne, J. M.; Du Prez, F. E. Internal Catalysis for Dynamic Covalent Chemistry Applications and Polymer Science. *Chem. Soc. Rev.* 2020, 49, 8425–8438.
- (29) Cuminet, F.; Caillol, S.; Dantras, É.; Leclerc, É.; Ladmiral, V. Neighboring Group Participation and Internal Catalysis Effects on Exchangeable Covalent Bonds: Application to the Thriving Field of Vitrimer Chemistry. *Macromolecules* 2021, *54* (9), 3927–3961.
- (30) Delahaye, M.; Tanini, F.; Holloway, J. O.; Winne, J. M.; Du Prez, F. E. Double Neighbouring Group Participation for Ultrafast Exchange in Phthalate Monoester Networks. *Polym. Chem.* 2020, *11* (32), 5207–5215.
- (31) Delahaye, M.; Winne, J. M.; Du Prez, F. E. Internal Catalysis in Covalent Adaptable

Networks: Phthalate Monoester Transesterification As a Versatile Dynamic Cross-Linking Chemistry. J. Am. Chem. Soc. 2019, 141 (38), 15277–15287.

- (32) Zhang, H.; Majumdar, S.; Van Benthem, R. A. T. M.; Sijbesma, R. P.; Heuts, J. P. A. Intramolecularly Catalyzed Dynamic Polyester Networks Using Neighboring Carboxylic and Sulfonic Acid Groups. ACS Macro Lett. 2020, 9 (2), 272–277.
- (33) Taplan, C.; Guerre, M.; Du Prez, F. E. Covalent Adaptable Networks Using β Amino Esters as Thermally Reversible Building Blocks. J. Am. Chem. Soc. 2021, 143 (24), 9140–9150.
- (34) Araya-Hermosilla, R.; Fortunato, G.; Pucci, A.; Raffa, P.; Polgar, L.; Broekhuis, A. A.;
 Pourhossein, P.; Lima, G. M. R.; Beljaars, M.; Picchioni, F. Thermally Reversible Rubber-Toughened Thermoset Networks via Diels-Alder Chemistry. *Eur. Polym. J.* 2016, 74, 229–240.
- (35) Yang, K.; Grant, J. C.; Lamey, P.; Joshi-Imre, A.; Lund, B. R.; Smaldone, R. A.; Voit, W. Diels–Alder Reversible Thermoset 3D Printing: Isotropic Thermoset Polymers via Fused Filament Fabrication. *Adv. Funct. Mater.* 2017, *27* (24).
- (36) Cornellà, A. C.; Tabrizian, S. K.; Ferrentino, P.; Roels, E.; Vanderborght, B.; Assche, G.
 Van; Brancart, J. Self-Healing, Recyclable, and Degradable Castor Oil-Based Elastomers for Sustainable Soft Robotics. *ACS Sustain. Chem. Eng.* 2023, *11*, 3437–3450.
- (37) Stricker, L.; Taplan, C.; Du Prez, F. E. Biobased, Creep-Resistant Covalent Adaptable Networks Based on β-Amino Ester Chemistry. ACS Sustain. Chem. Eng. 2022, 10 (42), 14045–14052.
- (38) Holloway, J. O.; Taplan, C.; Du Prez, F. E. Combining Vinylogous Urethane and β-Amino Ester Chemistry for Dynamic Material Design. *Polym. Chem.* 2022, *13*, 2008–2018.

- Berne, D.; Coste, G.; Morales-cerrada, R.; Boursier, M.; Pinaud, J. Taking Advantage of β-Hydroxy Amine Enhanced Reactivity and Functionality for the Synthesis of Dual Covalent Adaptable Networks. *Polym. Chem.* 2022, *13*, 3806–3814.
- (40) Berne, D.; Quienne, B.; Caillol, S.; Leclerc, E.; Ladmiral, V. Biobased Catalyst-Free Covalent Adaptable Networks Based on CF3-Activated Synergistic Aza-Michael Exchange and Transesterification. *J. Mater. Chem. A* 2022, *10* (47), 25085–25097.
- (41) Lee, G.; Song, H. Y.; Choi, S.; Kim, C. Bin; Hyun, K.; Ahn, S. Harnessing B-Hydroxyl Groups in Poly(β-Amino Esters) toward Robust and Fast Reprocessing Covalent Adaptable Networks. *Macromolecules* **2022**, *55* (23), 10366–10376.
- (42) Fortman, D. J.; Brutman, J. P.; Cramer, C. J.; Hillmyer, M. A.; Dichtel, W. R. Mechanically Activated, Catalyst-Free Polyhydroxyurethane Vitrimers. *J. Am. Chem. Soc.* 2015, *137* (44), 14019–14022.
- (43) Chen, X.; Li, L.; Jin, K.; Torkelson, J. M. Reprocessable Polyhydroxyurethane Networks Exhibiting Full Property Recovery and Concurrent Associative and Dissociative Dynamic Chemistry: Via Transcarbamoylation and Reversible Cyclic Carbonate Aminolysis. *Polym. Chem.* 2017, 8 (41), 6349–6355.
- (44) Majumdar, S.; Mezari, B.; Zhang, H.; Van Aart, J.; Van Benthem, R. A. T. M.; Heuts, J. P. A.; Sijbesma, R. P. Efficient Exchange in a Bioinspired Dynamic Covalent Polymer Network via a Cyclic Phosphate Triester Intermediate. *Macromolecules* 2021, 54 (17), 7955–7962.
- (45) Engelen, S.; Wroblewska, A. A.; De Bruycker, K.; Aksakal, R.; Ladmiral, V.; Caillol, S.;
 Du Prez, F. E. Sustainable Design of Vanillin-Based Vitrimers Using Vinylogous Urethane
 Chemistry. *Polym. Chem.* 2022, *13* (18), 2665–2673.

- (46) Droesbeke, M. A.; Prez, F. E. Du; Prez, F. E. Du. Sustainable Synthesis of Renewable Terpenoid-Based (Meth)Acrylates Using the CHEM21 Green Metrics Toolkit. ACS Sustain. Chem. Eng. 2019, 7, 11633–11639.
- (47) Sardon, H.; Mecerreyes, D.; Basterretxea, A.; Avérous, L.; Jehanno, C. From Lab to Market: Current Strategies for the Production of Biobased Polyols. *ACS Sustain. Chem. Eng.* 2021, 9 (32), 10664–10677.
- (48) Morales-cerrada, R.; Tavernier, R.; Caillol, S. Fully Bio-Based Thermosetting Polyurethanes from Bio-Based Polyols and Isocyanates. *Polymers (Basel)*. 2021, 13, 1255.
- (49) Desmet, G. B.; D'Hooge, D. R.; Omurtag, P. S.; Espeel, P.; Marin, G. B.; Du Prez, F. E.; Reyniers, M. F. Quantitative First-Principles Kinetic Modeling of the Aza-Michael Addition to Acrylates in Polar Aprotic Solvents. J. Org. Chem. 2016, 81 (24), 12291–12302.
- (50) Hebner, T. S.; Mccracken, J. M.; Bowman, C. N.; White, T. J. The Contribution of Oligomerization Reaction Chemistry to the Thermomechanical Properties of Surface-Aligned Liquid Crystalline Elastomers. *Macromolecules* 2022.
- (51) Takenaka, K.; Kaneko, K.; Takahashi, N.; Nishimura, S. Retro-Aza-Michael Reaction of an o -Aminophenol Adduct in Protic Solvents Inspired by Natural Products. *Bioorg. Med. Chem.* 2021, 35, 116059.
- (52) Lu, G.; Godfrey, S.; Herrlein, M.; Brook, M. A. Aza-Michael Silicone Cure Is Accelerated by β -Hydroxyalkyl Esters. J. Polym. Sci. 2021, 59, 1935–1941.
- Jourdain, A.; Asbai, R.; Anaya, O.; Chehimi, M. M.; Drockenmuller, E.; Montarnal, D.
 Rheological Properties of Covalent Adaptable Networks with 1,2,3- Triazolium Cross-Links: The Missing Link between Vitrimers and Dissociative Networks. *Macromolecules* 2020, *53*, 1884–1900.

- (54) Lijsebetten, F. Van; Bruycker, K. De; Spiesschaert, Y.; Winne, J.; Eduard, F.; Prez, D.
 Suppressing Creep and Promoting Fast Reprocessing of Vitrimers with Reversibly Trapped
 Amines. Angew. Chemie Int. Ed. 2022, 61.
- (55) WeylChem. Velvetol® | High Performance Polyether Polyols | WeylChem https://www.weylchem.com/products/velvetolr (accessed 2023 -03 -02).