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Sustainable Design of Vanillin-Based Vitrimers Using Vinylogous Urethane Chemistry

Stéphanie Engelen,^a Aleksandra Alicja Wróblewska,^a Kevin De Bruycker,^a Resat Aksakal,^a Vincent Ladmiral,^b Sylvain Caillol^b and Filip E. Du Prez^{*a}

Research on bio-based covalent adaptable networks is popular nowadays in the search for an optimal implementation of thermoset materials and composites in a circular context. Herein, a vanillin derivative is integrated into vitrimers with promising material properties in which the vinylogous urethane associative chemistry has been used as dynamic covalent chemistry platform. The vanillin derivative, 2-methoxyhydroquinone, is epoxidised and aminated by aqueous ammonia, with the formation of a bi-functional aromatic β -hydroxy-amine. The straightforward synthesis protocol is high yielding and up-scalable, without the need of any chromatographic purification step. The presented rigid, catalyst-free vitrimers have a high renewable carbon content (up to 86 %), glass transition temperatures up to 80 °C, show very fast reprocessing and consequently a swift recyclability with relaxation times in the range of seconds by virtue of the applied β -hydroxy-amine functionality. This research thus provides a sustainable approach to vanillin-based vitrimers and fits in the growing interest for the design of recyclable crosslinked polymer materials.

Introduction

The pursuit for more sustainable alternatives for commodity materials and petrochemistry-based molecules is nowadays one of the key research themes because of the ever-increasing environmental concerns, social awareness, as well as the persistently rising prices of fossil feedstocks related to their decreasing availability.^{1,2} Likewise, overall greenness implies the prevention of waste and thus indirectly the recyclability of materials, a well-known issue with the class of thermoset materials.^{3,4} These crosslinked materials are mechanically robust and chemically stable, yet lack the recyclability, reprocessability and malleability of thermoplastics.⁵ The introduction of exchangeable covalent bonds that lead to network topological rearrangements upon a trigger such as temperature or light, enables the recycling of thermoset-like materials, resulting in a sustainable alternative to commodity materials.

Covalent adaptable networks (CANs) have attracted extensive interest in the past years.^{6,7} Emerging from the network chemistry, the crosslink exchange mechanism can follow either an associative or a dissociative path, resulting in different material properties.⁸ Whereas associative CANs exhibit a fixed crosslinking density, dissociative CANs lose network integrity upon a trigger. Vitrimers, introduced by the pioneering work of Leibler et al.⁹, are thermally triggered associative CANs that experience an Arrhenius-like viscosity decrease, rather than a sudden viscosity decrease, as seen for dissociative CANs upon a thermal trigger.¹⁰ Among bio-based CANs, many types of renewable building blocks, ranging from terpenes to oils,^{11,12} fatty acids,¹³ fructose,¹⁴ lipoic acid¹⁵, ferulic acid,¹⁶ or vanillin^{17–20} have been incorporated into

dynamic materials. Very recently, the field of bio-based CAN-materials has been reviewed.²¹

With lignin being the second most abundant biopolymer, after cellulose, and vanillin the only bio-based aromatic building block so far produced on an industrial scale from lignin, vanillin has attracted an immense interest.^{22–24} The aromatic structure of vanillin is one of its attractive features, in contrast to vegetable oils that often do not result in materials with sufficiently high glass transition temperatures (T_g).²⁵ Besides its use in thermoset resins or thermoplastics,²⁶ vanillin has also paved its way to CANs. Liu et al., for instance, transformed vanillin into a trifunctional epoxy that could dynamically react with an anhydride, *via* transesterification in the presence of a catalyst.²⁷ Yet, so far, mainly the dynamic imine-based covalent bonds have been explored for vanillin-containing materials. The imine moiety is typically formed by a condensation reaction between vanillin, its aldehyde functionality and an amine. For example, Memon et al. combined diglycidyl ether of ethylene glycol and diglycidyl ether of bisphenol A resins with vanillin-derived imine hardeners, resulting in dynamic epoxy materials with a closed loop recycling.²⁰ In parallel, Zhao et al. combined epoxidised soybean oil with a dynamic vanillin-derived Schiff base.²⁸ In both cases, vanillin was combined with a di-amine, resulting in a phenolic dynamic hardener, which is able to cure the epoxy compounds.

Next to polyimine-based vitrimers, vinylogous urethane (VU)-based vitrimers are at least equally interesting. VU moieties are easily obtained by combining primary amines with any alcohol-derived acetoacetate. Moreover, by varying different parameters, ultra-fast processing can be targeted, thus making thermal recycling more convenient. Denissen et al. chemically controlled the viscoelastic properties of VU by studying the influence of different catalysts.²⁹

Later on, Spiesschaert et al. showed that the introduction of vinylogous urethanes into an epoxy matrix resulted in an accelerating effect of the transamination, as a result of the presence of hydroxyl groups after reaction of an epoxy with a nucleophilic amine.³⁰ In addition, the presence of these epoxy units resulted in better network properties, as a result of a partial permanent crosslinking.³⁰ More recently, Taplan et al. were able to continuously process low-viscosity VU-based vitrimers, by altering the stoichiometry of amines and by the addition of an organic acid catalyst p-toluenesulphonic acid.³¹

Conventionally, the synthesis of suitable bio-based building blocks often requires tedious chromatographic purification steps. The resulting process mass intensity (PMI)³², a parameter used to assess the sustainability of reactions conjointly introduced in the CHEM21 toolkit,^{33,34} is often high as large amounts of solvents and silica are consumed.

Keeping the green chemistry principles in mind³ and aiming for very fast processable, bio-based and high T_g vitrimers, the work reported here will focus on the sustainable design of vanillin-based building blocks, containing a β -hydroxy-amine functionality and their incorporation in dynamic vinylogous urethane-based networks with high bio-based content. In this context, emphasis was put on 2-methoxyhydroquinone (MHQ), a vanillin derivative that can easily be epoxidised with epichlorohydrin and ring-opened with aqueous ammonia.^{35,36}

The first part of the study focused on a significant optimisation of the synthetic protocols for the MHQ-derivatives, starting from previously reported procedures,^{24,36–38} with the aim to obtain relatively pure monomers without the need of tedious purification techniques such as column chromatography. In a second part, the corresponding bis-amines will be reacted, without further purification, with a terpene-based bis-acetoacetate,³⁹ resulting in a fast processable vinylogous urethane curing agent, for which the reactivity is ascribed to the increased nucleophilicity of the amine by the adjacent hydroxyl group. Figure 1 illustrates the bio-mass origin of the bis-amine, referred to as dihydroxyamino propane of methoxyhydroquinone (DHAP-MHQ), and the 1,4-bis(hydroxymethyl)cyclohexane bis-acetoacetate (CDM-AA) building blocks as well as their incorporation into a VU-based polymer network. It will be described that the latter step will be realised either by means of a tri-functional amine crosslinker tris (2-aminoethyl)amine (TREN), added in different ratios, or by using the diglycidyl ether of methoxyhydroquinone (DGE-MHQ) as crosslinker. The chemical nature of the used compounds was chosen with the aim to design vitrimer materials with elevated T_g 's, helping to restrain molecular motions of polymeric fragments at typical usage temperature.

Results and discussion

Optimised synthesis of DGE-MHQ and DHAP-MHQ

Because of the known beneficial influence of a protic environment on the transamination exchange rate in vinylogous urethanes, as investigated in previous studies^{30,31},

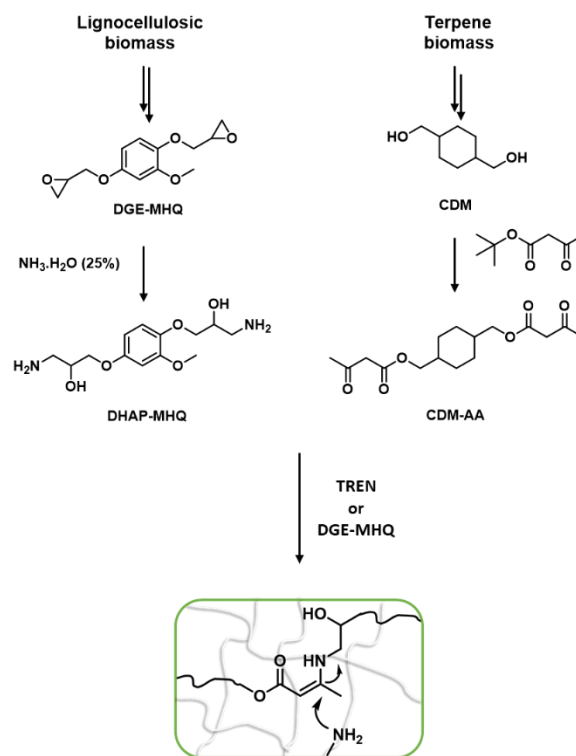


Figure 1. Schematic overview of the vinylogous urethane dynamic network synthesis. Diglycidyl ether of methoxyhydroquinone (DGE-MHQ) can be obtained from lignocellulosic bio-mass and can be transformed into a bis-functional β -hydroxy amine, dihydroxyamino propane of methoxyhydroquinone (DHAP-MHQ), by reaction with aqueous ammonia. 1,4-Bis(hydroxymethyl)cyclohexane (CDM) can be obtained from terpene bio-mass and can be easily transformed into 1,4-bis(hydroxymethyl)cyclohexane bis-acetoacetate (CDM-AA) by reaction with tert-butyl acetoacetate. By combining DHAP-MHQ and CDM-AA with either TREN or DGE-MHQ, fast dynamic materials have been obtained.

the starting point of this research was the straightforward design and use of a bio-based β -hydroxy-amine. By ring-opening an epoxy group with aqueous ammonia, this protic functional handle can be incorporated within the amine building block, rather than in the matrix.^{40,41} However, amination of epoxides with aqueous ammonia often results in oligomeric products, as the resulting primary amine is a more reactive nucleophile than ammonia itself.⁴² Moreover, epoxidation can result in oligomer formation by polyaddition of a diphenol.²⁵ At the start of this research, we aimed for the significant suppression of these side reactions in order to establish well-defined crosslinked materials based on bio-based β -hydroxy-amines.

Methoxyhydroquinone can be synthesised by a straightforward and environmentally-friendly Dakin oxidation starting from renewable vanillin and sodium percarbonate.⁴³ In contrast to other renewable vanillin-based diols, such as vanillyl alcohol, MHQ possesses two hydroxyl groups with similar reactivity. Furthermore, these hydroxyl groups are placed in para position with respect to each other, which prevents the formation of benzodioxane derivatives by *o*-glycidylation, a side reaction observed e.g. with gallic acid.³⁸

In a first step, epichlorohydrin is used as a reactive solvent to epoxidise MHQ (Figure 2b, step 1). Epichlorohydrin owes its

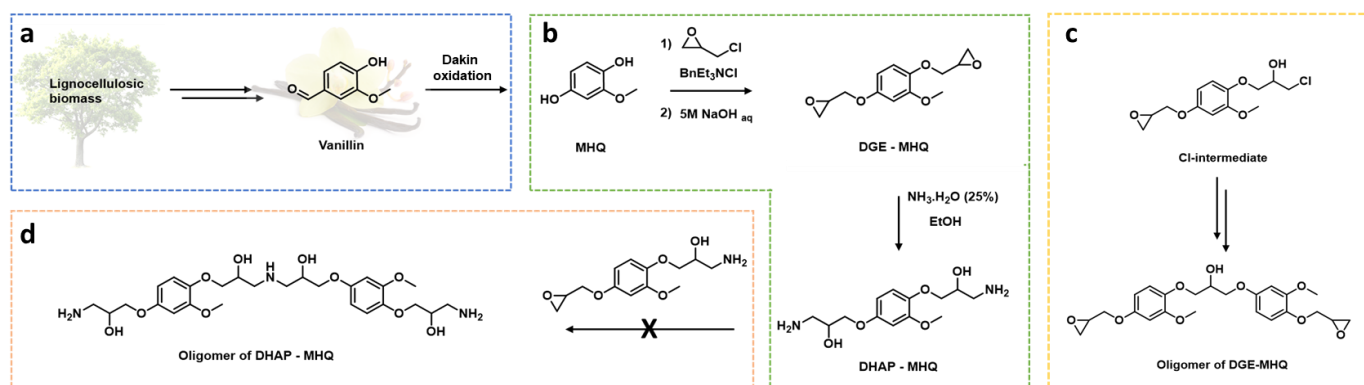


Figure 2. Synthesis of DHAP-MHQ from MHQ. a. Vanillin can be obtained from lignocellulosic biomass. b. Synthesis of DHAP-MHQ from MHQ. c. Competitive dimerisation upon reaction with epichlorohydrin. d. Possible undesired dimerisation during the amination process.

bio-based nature to glycerol, which is used in the Epicerol® process from Solvay. Compared to previously published synthetic procedures^{24,37,38}, more equivalents of epichlorohydrin (15 M eq./ OH-functionality) are used in this work. This large excess of epichlorohydrin, which can be recycled for further synthesis (Fig. S1, ESI[†]), allows to reduce the amount of dimer and oligomer formation or impurities, by favouring the glycidylation over condensation of a phenol with an epoxide or a chlorinated-intermediate (Cl-intermediate). The Cl-intermediate, represented in Figure 2c, is formed by ring-opening of epichlorohydrin with a phenolic group in the presence of a phase transfer catalyst, here benzyltriethylammonium chloride. The Cl-intermediate itself can be easily transferred back to the epoxy group by further reacting with 5M NaOH (Figure 2b, step 1). Consequently, when less or almost no oligomers are formed, a chromatographic work-up can be avoided, which is beneficial for the upscaling of the monomer synthesis. The corresponding PMI, which represents the total mass of materials used to produce a specified product, including reactants, reagents, solvents and other materials used in the reaction or the work-up, was calculated to be 34 g/g (Equation 1, ESI[†]), whereas a PMI involving the use of silica column chromatography would have resulted in a 2.5 times higher value. The prevention of tedious work-ups is thus in line with the green chemistry principles.

In a next step (Figure 2b, step 2), the amination of DGE-MHQ is carried out for the synthesis of the desired bis-functional β -hydroxy-amine, DHAP-MHQ. Aqueous ammonia is the reactive solvent of choice, because of its low cost, availability and its bio-based nature. Other amination reactions, using e.g. a Gabriel synthesis, a Curtius reaction, a Hofmann rearrangement or direct catalytic conversion of alcohols with ammonia,^{44,45} have been proven to be low-yielding, while requiring harsh conditions and generating a lot of by-products. In previous studies, amination either took place in a microwave, in an autoclave or in a reactor.^{36,41,46} We opted for the use of a reactor because of its upscaling potential.

The amination of the bis-epoxide can result in oligomeric products by nucleophilic attack of the formed primary amine onto unreacted epoxide moieties (Figure 2d). In order to suppress the formation of those oligomers, it is important to work in a diluted environment. Indeed, it was observed that the volume ratio of ammonia to solvent has a significant impact on the oligomer formation and thus purity of the obtained compound (Table 1). The purest product is found by using a large excess of ammonia (Entry 3 and 4, Table 1 and Fig. S2, ESI[†]). Also a higher volume fraction of ammonia in water to ethanol is desired from the viewpoint of working in a diluted environment.

Table 1. Different molar equivalents and solvent combinations tested in a pressure tube/reactor for 1h30 at 85 °C, resulting in different DHAP-MHQ purities. For all entries, 1 eq. of DGE-MHQ is used.

Entry	Eq. NH ₃ .H ₂ O (25 %)	NH ₃ .H ₂ O (25 %)/EtOH (v/v)	Purity (%) ^a
1	50	6/5	70
2	50	3/4	25
3	50	5/1	97
4	60	5/1	97

^a The product purity was evidenced using LC-MS ($\lambda = 214$ nm).

Model compound study

With the intention to verify whether a β -hydroxy-amine functionality truly has an accelerating effect, compared to a non-hydroxy amine in the transamination, a low molecular weight (MW) model compound study was conducted. The latter allowed to assess the kinetics of the conjugate transamination in the vinylogous urethane chemistry. To this purpose, N-octyl vinylogous urethane (**1**) and amino-3-phenoxypropan-2-ol (**2**) were prepared by condensation of ethyl acetoacetate with octylamine and, amination of the glycidyl ether of phenol, respectively.²⁹

After mixing compound (**1**) with five equivalents of compound (**2**), deuterated benzene was added to the reaction mixture and the kinetics of formation of N-3-phenoxypropan-

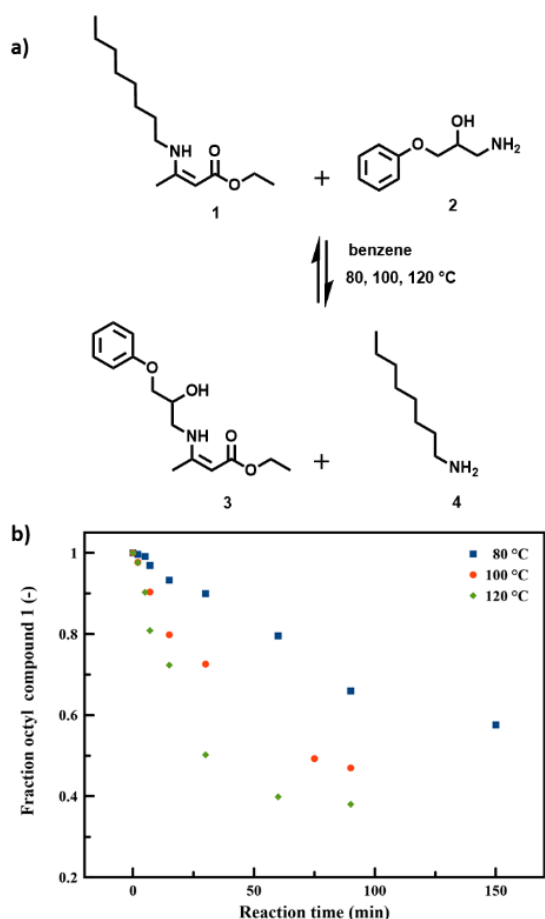


Figure 3. a) Reaction scheme showing the catalyst-free exchange of low-MW model compounds for the kinetic study. b) Disappearance of octyl VU compound (**1**) as a function of time at different temperatures.

2-ol VU (**3**) were conducted via $^1\text{H-NMR}$ at different temperatures being 80, 100 and 120 °C (Figure 3a). Two distinct proton signals at 1.48 and 1.53 ppm, corresponding to compounds (**1**) and (**3**), respectively, could be easily followed during the reaction (Fig. S3, ESI †). The decrease of the fraction of octyl VU (**1**) as a function of time and temperature is given in Figure 3b. By using an excess of compound (**2**), the system was shifted kinetically towards a pseudo-first-order reaction, whereby linearity during the first time points was maintained for 80, 100 and 120 °C, evolving in a shift towards chemical equilibrium at higher conversions. In the previously published model compound study by Denissen et al.⁴⁷, when APP (**2**) was replaced by benzylamine in the pseudo-first-order reaction, a slower transamination was observed in the same reaction conditions. While the transamination of β -hydroxy-amine APP reaches 40 % at 120 °C after 60 minutes (Figure 3b), only 50 % of benzylamine was transaminated. Thus, as expected, the relatively close proximity of the OH-group to the dynamic centre, results in an increased nucleophilicity of the primary amine and thus slightly enhances the transamination reaction rate.⁷

Synthesis and properties of the bio-based dynamic materials

The gained insights of the built-in protic handle on the dynamic exchange in the model compound study helped us to design vinyllogous urethane vitrimers with an increased

dynamic character. Similar to APP used in the model compound study, DHAP-MHQ was reacted with a readily available bifunctional acetoacetate (CDM-AA) and a crosslinker to prepare the network. The bulk condensation reaction between the CDM-AA, DHAP-MHQ and TREN crosslinker resulted in a range of β -hydroxy-amine vinyllogous urethane networks with varying DHAP-MHQ to TREN ratio, further referred to as HA-VU X, with X indicating the molar equivalents of DHAP-MHQ (see Table 2). By altering this ratio, materials with varying mechanical properties, T_g -values and exchange dynamics can be obtained. In addition to the HA-VU networks, a fully bio-based epoxy network (HA-VU-EP) was prepared with a renewable carbon content of 86 %, by replacing TREN with DGE-MHQ, which is the synthesised bi-functional epoxy. It should be noted that in this latter case, the primary amine can react twice with the epoxy unit to form the network.

All materials were prepared at 90 °C, homogenised by mixing in a Speedmixer, further cured at 100 °C and post-cured at 120 °C. The prepared dynamic materials had 5 mol % excess of primary amines with respect to the formed vinyllogous urethane moieties, so that a sufficient amount of amines could enable the fast network rearrangement. For all networks, the acetoacetate was consumed, as observed by ATR-FTIR with the disappearance of the vibration bands of the acetoacetate at 1720 and 1700 cm^{-1} and the appearance of the vinyllogous urethane ones at 1640 and 1600 cm^{-1} (Fig. S4, ESI †).

The material properties can be tailored by using different stoichiometric ratios. A more bio-based and faster relaxing material can be obtained by decreasing the amount of trifunctional crosslinker, whereas a higher thermal degradation temperature and storage modulus is observed when the crosslinking density, thus the amount of TREN crosslinker is higher (Table 2).

The thermal properties of the materials are displayed in Table 2 and Fig. S5-6, ESI † . DSC-analysis showed T_g 's ranging between 50 and 85 °C, linked to the stoichiometry of the material. The most densely crosslinked HA-VU 0.15 exhibits the highest T_g of 85 °C, yet is the least bio-based in the HA-VU series. Although a decreasing trend in T_g was expected for HA-VU 0.20, HA-VU 0.25 and HA-VU 0.30 related to the decrease in crosslinking density, HA-VU 0.30 showed a slightly higher T_g . This might be attributed to the higher DHAP-MHQ content of this material, compared to the other ones, resulting in other interactions such as π - π stacking. A T_g of 50 °C is obtained for the epoxy-based network (HA-VU-EP) with 50 % reversible and 50 % permanent crosslinks. This lower T_g value might be associated with homopolymerisations of epoxy molecules at elevated temperatures and the absence of the trifunctional crosslinker TREN. Additionally, relatively broad transitions in the DSC thermograms were observed (Fig. S5, ESI †), which might be attributed to hydrogen bonding interactions, related to the aforementioned β -hydroxy-amine group.

The thermal stability of the materials, on the contrary, is only slightly affected by the amount of DHAP-MHQ. Yet, a slower decrease in onset degradation can be visualised for higher crosslinking densities as expected (Figure S6, ESI †). HA-VU 0.15 has a higher onset degradation with a mass loss of 5 %

at 254 °C compared to HA-VU 0.20 (240 °C). For the HA-VU-EP, a different degradation profile was observed. Isothermal analysis of HA-VU 0.25 at 150 °C for 1h (Fig. S7, ESI†) demonstrates the stability under the aforementioned synthesis conditions, envisioning reprocessability (vide infra).

Table 2. Overview of the compositions and different properties of the vinylogous urethane-based materials including their renewable carbon content (RCC), relaxation time, swelling and solubility values, as well as mechanical and thermal properties.

Material	Eq. DHAP - MHQ	Eq. TREN (+5mol% NH ₂)	Eq. AA	RCC (%)	$\tau_{160^\circ\text{C}}^*$ ^a (s)	Swel. rat. (wt%) ^b	Sol. frac. (wt%) ^b	G' (MPa) ^c	ν' (mol m ⁻³) ^d	T _g (°C) ^e	T _{d,5%} (°C) ^f	Char yield (%) ^g
HA-VU 0.15	0.15	0.25	0.5	40	27	145	3	1.8	518.6	85	254	9.5
HA-VU 0.20	0.20	0.21	0.5	45	9	148	3.5	0.4	124.2	55	240	11.5
HA-VU 0.25	0.25	0.18	0.5	50	5	193	4	0.3	94.3	50	233	13.5
HA-VU 0.30	0.30	0.15	0.5	55	3	222	8	0.2	61.3	60	228	14.5
HA-VU-EP	0.44	-	0.28	86	119	70	6	1.1	345.9	50	239	25

^a Characteristic relaxation time obtained from stress relaxation experiments at 160 °C. ^b Swelling ratio and soluble fraction in THF for 24h at r.t. obtained from four sample measurements. ^c Apparent plateau storage modulus G' obtained from frequency sweep measurements at 160 °C and 1 rad s⁻¹. ^d Crosslinking density obtained using equation 3 ESI[†]. ^e Glass transition temperature obtained from second heating (rate 10°C/min). ^f TGA onset-degradation temperatures for 5% weight-loss. ^g Char yield derived from remaining mass % at 600 °C.

Next to the thermal degradation, different char yields in connection to their stoichiometry are obtained for the materials (Table 2 and Figure S6, ESI[†]). For example, for HA-VU-EP with the highest amount of DHAP-MHQ, a char yield of 25 % is present, which is relevant for applications targeting flame retardancy.⁴⁸

The resistance to creep is a recurring problem in the design of dynamic materials. In order to minimize this phenomenon, one strategy is to restrain molecular motion of polymeric fragments at service temperature, e.g. by increasing the T_g, and thereby suppressing macroscopic material flow.⁹ When the usage temperature is below T_g (e.g. 30 °C), the material is

showing limited creep as seen by the resulting strain being constant as a function of time (Figure 4). However, the material starts to exhibit more creep behaviour around and above its T_g (e.g. 55 °C for HA-VU 0.25).

Swelling experiments of the HA-VU(-EP) vitrimers have been conducted in THF to assess the resistance of the network materials to solvent and the corresponding ratios are reported in Table 2. The highest soluble and swelling fraction in THF are obtained for weaker network structures, yet no sample integrity was lost. Besides a solubility and swelling test in THF, HA-VU 0.25 has also been submerged in aqueous ammonia (25 %) for one week to verify the stability and resistance in an aqueous, yet basic solvent. A similar soluble fraction of 4 wt.% is observed in comparison to the solubility test in THF, yet a lower swelling ratio of 170 wt.% is found. Overall a good stability could be observed, despite the sensitivity of vinylogous urethane bonds to hydrolysis. Moreover, comparable soluble fractions to previously reported vitrimers are obtained.⁴⁷

The viscoelastic material properties were analysed by stress-relaxation and frequency sweep experiments and are reported in Table 2 and Figure 5. For the stress relaxation experiments, the relaxation modulus was followed as a function of time between 160 and 130 °C, after applying a constant strain of 1% in the linear viscoelastic region. For all materials, with the exception of HA-VU-EP, which is the partially permanent crosslinked network, full stress relaxation was revealed (Figure 5 and Fig. S8-11, ESI[†]). The most densely crosslinked network HA-VU 0.15 shows the slowest relaxation time in the HA-VU

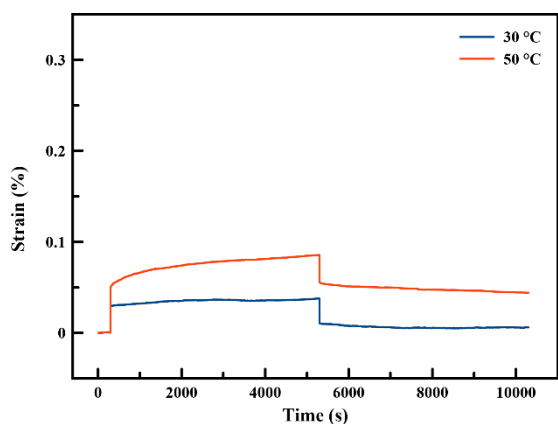


Figure 4. Creep experiment of HA-VU 0.25 with an applied stress of 2000Pa for 5000 seconds at 30 °C and 50 °C.

series range from only 3 seconds (for HA-VU 0.30) to 27 seconds (for HA-VU 0.15) at 160 °C, which is remarkably short taking into account the absence of an external catalyst.³¹ This result is foremost related to the protic nature of the β -hydroxy-amine incorporated into the dynamic network and the varying crosslinking density (Fig. S12, ESI[†]). Albeit 50% permanent crosslinks were incorporated in the HA-VU-EP network, the material showed a relaxation time at 160 °C of only 119 seconds.

At temperatures ranging from 160 °C to 140 °C, the material flow and consequently stress relaxation are dominated by chemical exchange, however, below 140 °C, effects resulting from the T_g -region come into play, resulting in a second distinct relaxation (Fig. S8-11, ESI[†]). Nevertheless, the characteristic exponential decay over the temperature range from 160-140 °C, following a Maxwell behaviour, allows to extract relaxation times at $G_t/G_0 = 1/e$ to the Arrhenius law. From the relationship between $\ln(\tau^*)$ and $1000/T$, subsequently the activation energy was calculated to be 162 kJ mol⁻¹ (Fig. S13, ESI[†]). To correlate the dynamicity of the networks and to obtain the mechanical properties, frequency sweep measurements of all materials were measured (Figure 5b, Fig. S14-17, ESI[†]). The crossover of the storage and loss modulus shifts to lower frequencies upon decreasing temperature. Likewise, the same trend as for the stress relaxation analysis of HA-VU networks is obtained: lower

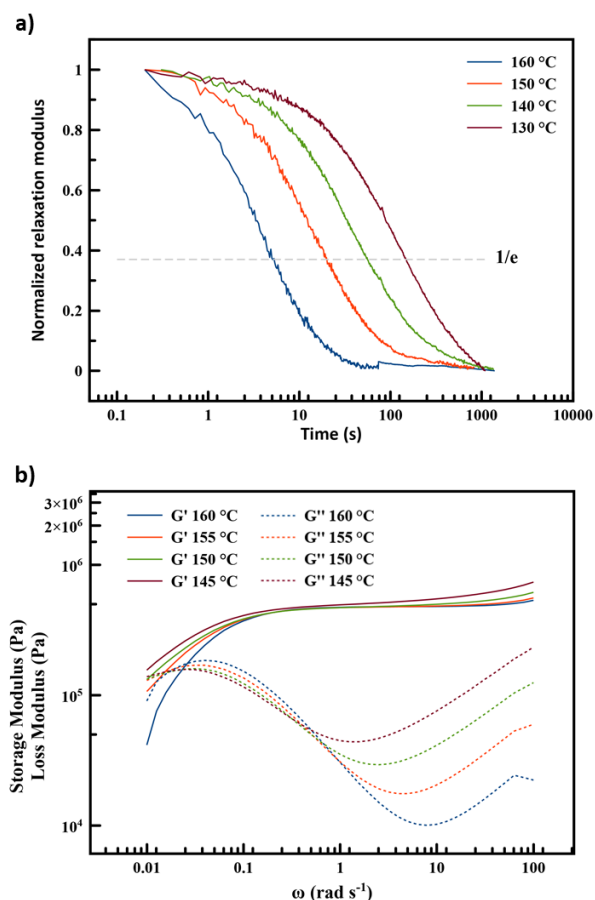


Figure 6. a) Normalised stress relaxation measurement and b) frequency sweep measurement of HA-VU 0.25.

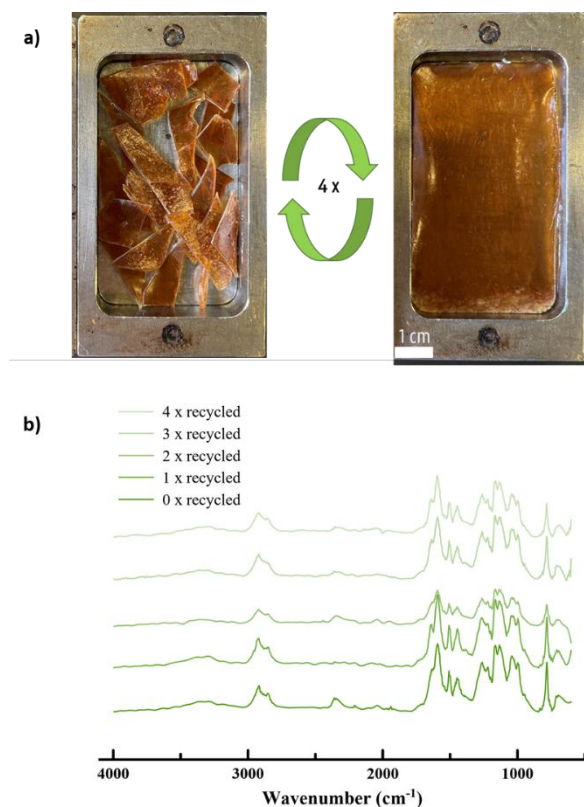


Figure 5. a) Recycling up to 4 times by compression moulding at 150°C for 15 minutes, starting from broken sample pieces. b) FT-IR of the recycled materials.

amounts of DHAP-MHQ result in crossover shifts moving to lower frequencies. The mechanical properties including the storage moduli can be obtained from frequency sweeps for 1 rad/s at 160 °C. The storage modulus G' increases with increasing crosslinking density from HA-VU 0.30 to HA-VU 0.15 (Fig. S18, ESI[†]). Moreover, the fully bio-based network HA-VU-EP was found to have good mechanical properties, which are similar to the ones of HA-VU 0.15. The corresponding crosslinking density could be derived from Equation 3, ESI[†] and, evidently, the same trend as the storage modulus is followed.

Recyclability

Recyclability is a key aspect for vitrimeric materials and CANS. Herein, reprocessability was assessed by breaking the sample into pieces, followed by remoulding for 15 min at 150 °C. It is observed that the sample properties, amongst which the T_g and degradation temperatures as well as FTIR bands, were merely unaltered after the 4th recycling step (Figure 6 a and b, Fig. S19-20, ESI[†]). The solubility tests after the 4th recycling of HA-VU 0.25 showed that the swelling ratio (from 192 to 211 wt.%) slightly increased. Nevertheless, the stress relaxation was only slightly altered after the 4th recycling step (from 5.1 to 7.1 s). (Fig. S21, ESI[†])

Conclusions

In this work, an optimised synthesis of a vanillin-based bifunctional compound with β -hydroxy-amine functionalities was shown, allowing to obtain and upscale relatively pure building blocks without the need of tedious purification techniques such as column chromatography. Next to this bio-based bifunctional aromatic amine compound, the applied acetoacetate can be readily obtained from a bio-sourced diol. The synthesised monomers were combined in bulk, with the formation of a bio-based vinylogous urethane network, with a renewable carbon content up to 86 %. Overall, greenness also implies the prevention of waste and thus indirectly, the recyclability of materials, a constitutional issue for thermoset materials that can be overcome by the formation of CANs. We reported fast relaxing vitrimers with good thermal properties and recyclability, without impairing in solvent resistance or mechanical properties. The networks were designed with higher T_g 's, to restrain molecular motions of polymeric fragments at room temperature and thus to prevent creep.

Conflicts of interest

There are no conflicts to declare.

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