# Suppressing Creep and Promoting Fast Reprocessing of Vitrimers with Reversibly Trapped Amines

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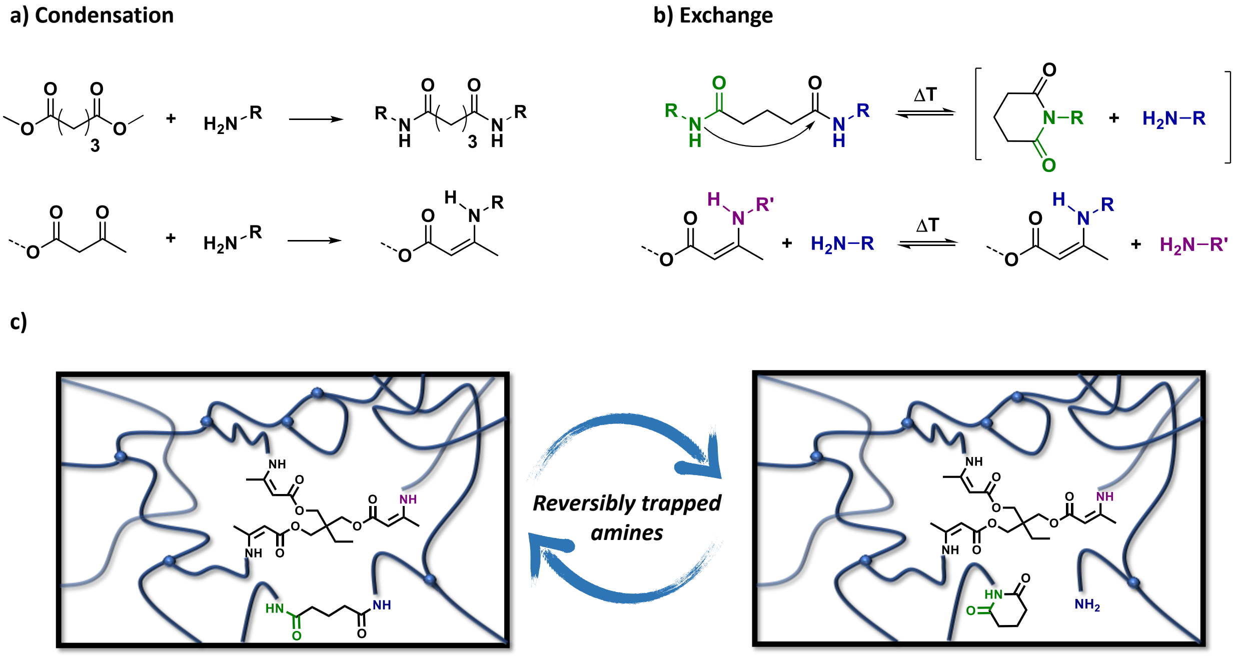
**Abstract:** We report a straightforward chemical strategy to tackle current challenges of irreversible deformation in low $T_g$ vitrimers at operating temperature. In particular, vinylogous urethane (VU) vitrimers were prepared where reactive free amines, necessary for material flow, were temporarily shielded inside the network backbone, by adding a small amount of dibasic ester to the curing mixture. The amines could be released as reactive chain ends from the resulting dicarboxamide bonds *via* thermally reversible cyclisation to an imide moiety. Indeed, (re)generation of the required nucleophilic amines as network defects ensured reprocessing and rapid material flow at higher temperature, where exchange dynamics are (re)activated. As a result, VU vitrimers were obtained with limited creep at service temperature, yet with good reprocessability at elevated temperatures. Thus, by exerting strong control on molecular level over the availability of exchangeable functional groups, a remarkable improvement of VU properties was obtained.

## Introduction

Vitrimers are cross-linked polymer networks, wherein chain mobility and plastic deformation is enabled by chemical exchange reactions of covalent bonds, without going through a depolymerized state.[1–3] Although allowing material flow when heated, vitrimers are characterised by a constant connectivity, rendering them solvent-resistant and assuring good mechanical properties and dimensional stability.[1,4–6] As such, processability is mainly controlled by the rate of dynamic rearrangements of the network architecture itself.[7,8] Therefore, an important design constraint to consider for vitrimers, is the fact that every reactive cross-linking moiety also requires the ready availability of a second reactive moiety.[9–11] Without exception, the rate determining step in vitrimer cross-link exchanges relies on the availability of *two* distinct reactive species, with at the one hand the reactive cross-link itself, and on the other hand a reactive side chain or chain-end that will receive the new cross-link after exchange.[12] In case of a metathesis bond transfer mechanism, the required reactant will be another cross-linking site. In terms of reactivity, this situation is in stark contrast to other dynamic or reversible polymer networks (*i.e.* dissociating covalent or supramolecular networks), where pre-association of a reactive chain-end, cross-link or network defect is not at all crucial for the overall bond exchange process. Moreover, this 'bimolecular' (or bisegmental) nature of covalent bond exchanges in vitrimers renders bond exchange rates much more context-dependent with dynamics that can strongly vary according to cross-linker structure,[13] catalyst selection,[14–16] polymer backbone[17,18] and adjacent chemical environment.[19,20]

To understand how cross-link exchanges in vitrimers can be retarded or even stopped at service temperature, while retaining high exchange rates at elevated temperatures, a more profound understanding of their chemical reactivity is required. For this purpose, several strategies have been applied with the main focus on phase separation,[21–23] cross-linking density,[4,24–28] and the combination of permanent and transient bonds in order to hinder low temperature material deformation.[29–33] However, from a more general material design point of view,[34] a (theoretically) defect-free vitrimer should show only elastic behaviour upon deformation.[35] Especially when considering that for most known vitrimer chemistries, it was experimentally demonstrated that viscous flow relies on the presence of reactive chain ends or side chains. With the only exception to this experimental and theoretical observation being metathesis-based vitrimers.[36,37] Most probably, this viscous behaviour arises from a combined effect of availability of exchangeable functional groups and non-elastic defects.[7]

One of the vitrimer chemistries that has rapidly become a benchmark system to design and study viscous flow within polymer networks is the transamination of vinylogous urethanes (VU),[2] where it is well understood that the dynamic exchange relies on the presence of pendent amines. For example, Leibler and co-workers were able to strongly suppress material flow in PDMS-based VU vitrimers by trapping most free amines with a monofunctional capping agent.[38] We hypothesised that, in contrast to irreversibly shutting down exchangeable groups, the thermoreversible (re)generation of pendent amines would lead to the recovery of exchange dynamics with temperature.



**Scheme 1.** a) Condensation reaction resulting in a dicarboxamide or vinylogous urethane bond, respectively; b) Dicarboxamide dissociation to an imide and amine pendent group. The free chain-end amine is subsequently used for transamination exchange; c) Modified vinylogous urethane network with thermoreversibly trapped amines in a dicarboxamide bond.

In this work, we report our highly encouraging findings in this area of arresting low temperature deformation while keeping reprocessability, by adopting a very recently developed reversible covalent amide linkage within VU vitrimers (**Scheme 1**).[39] By adding a small amount (0.2 to 4 wt%) of a dibasic ester co-monomer, amines can be fully reacted and trapped into the polymer matrix, resulting in creep-resistant VU vitrimers (**Scheme 1a**). In essence, by adding a second covalent dynamic exchange, a *dissociative* connection is incorporated in associative VU networks (**Scheme 1b**). As long as these dissociative bonds only make up a small fraction of the vitrimer, decross-linking will be negligible for the overall network connectivity and integrity when heating. On the other hand, they can become quite significant kinetically speaking, through the combined effect of releasing reactive amines required for the *associative* transamination of VUs, and introducing network defects, both of which lead to an increase in viscous flow (Scheme 1c). With respect to VU vitrimer design, a thorough analysis of stress-relaxation and creep experiments was conducted, in order to allow the identification of the factors that drive relaxation dynamics, both from a chemical and a network connectivity perspective. For this, a varying concentration of glutarate-type co-monomers was added to classical VU formulations.

## Results and Discussion

To study the effect of synergistic dicarboxamide dissociation and VU transamination on material flow, several reprocessable networks were prepared. First, benchmark materials were synthesised by mixing trifunctional 1,1,1-trimethyl-propane trisacetoacetate (**1**) and bifunctional Priamine 1074 (**2**) in different stoichiometric ratios, *i.e.* with 5 mol% excess acetoacetate groups (VU-95), equimolar conditions (VU-100) and 5 mol% excess amine groups (VU-105) (**Figure 1a**). Generally, VU-100 and VU-105 are characterised by an increased concentration of exchangeable groups $[-RNH_2]$ compared to VU-95, resulting in an increase in exchange dynamics. For VU-95 and VU-100, the presence of free chain-end amines could only be ascribed to imperfect network formation.[40] Importantly, it was previously determined that VU transamination relies on proton transfers, resulting in the prevalence of one exchange mechanism over the other based on the availability of protonated amines (Scheme S1).[4,17,38,40–42] This resulted in an increase of exchange dynamics when adding a strong acid (e.g. *para*-toluenesulfonic acid, *p*TsOH) and a decrease when adding a strong base (e.g. triazabicyclodecene, TBD).[41] To have a better understanding of the effect of the availability of (protonated) pendent amines, the same benchmark materials were prepared, but with the addition of 0.75 mol% of TBD, further referred to as VU-95 + TBD, VU-100 + TBD and VU-105 + TBD. From all the aforementioned benchmark materials, the high and low temperature exchange 'limits' could be determined, which would serve as a reference to the modified VU materials (*vide infra*).

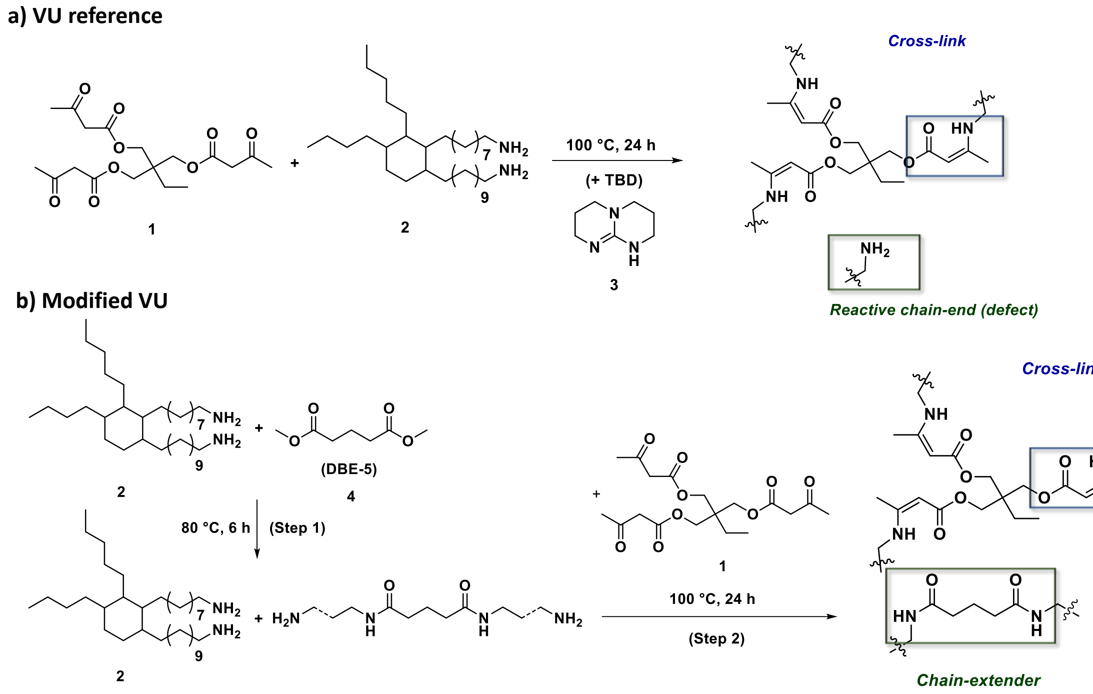


**Figure 1.** a) Reaction scheme for the formation of vinylogous urethane vitrimers with and without TBD additive. b) Reaction scheme for the synthesis of modified vinylogous urethane vitrimers, whereby 1-20 mol% of dibasic ester is first reacted with the excess amines and later cured with acetoacetates.

In a second step, some modified VU materials were designed whereby (protonated) chain-end amines could be released by the previously established dissociation equilibrium between dicarboxamides and imide-amines.[39] This was achieved by adding dimethyl glutarate (DBE-5, **4**) to an excess of amine **2** and further curing with acetoacetate **1** (**Figure 1b**). To ensure that the presence of pendent amines is minimised, a similar composition to VU-95 was targeted, whereby the amount of amine **2** was adjusted to account for the reaction with the dibasic ester **4** prior to the VU formation. Moreover, by increasing the concentration (in mol%) of **4**, the probability to thermally release pendent amines will also increase, resulting in modified VU materials, further referred to as VU-95 + 1%, VU-95 + 5%, VU-95 + 10%, and VU-95 + 20 %.

After network formation, the conversion of acetoacetate and ester functions was assessed *via* ATR-FTIR (**Figure S1-S2**), in which the decrease of carbonyl vibrations could be qualitatively monitored around 1720 $cm^{-1}$ and 1730 $cm^{-1}$, respectively. Moreover, all polymer networks were swollen in a ninhydrin solution (1.5 g of ninhydrin in 100 mL THF) for 24 h to show if any free chain-end amines still remained. As expected, a significant change in colour could be observed with a higher percentage of exchangeable amine moieties (**Figure S3**).

For all networks, the possibility for (fast) reprocessing was tested *via* compression moulding at 150 °C. Different reprocessing times were used ranging from 5 to 90 min, depending on the availability of pendent amines (**Table S1**). All networks were reprocessable within a reasonable time frame (15 min to 120 min), except for VU-95 + TBD and VU-100 + TBD and, therefore, they were not considered for further analysis (**Figure S4**).

Next, the thermal properties of the materials were investigated by DSC (**Figure S5-S6**) and TGA analysis (**Figure S7-S8**) and the results are summarised in **Table 1**. The obtained values for the glass transition ($T_g$) were situated between -16 and -1 °C, with a decrease arising from a higher amount of free chain-end amines. Additionally, TGA analyses also showed near-identical thermal stability (above 300 °C) for all materials. Moreover, isothermal TGA analyses at 150 °C (*i.e.* reprocessing temperature) revealed no significant mass loss (< 1 %) after a period of 120 min, under air (**Figure S9-S10**). These results were promising, considering that the dibasic ester co-monomer had no significant influence on the thermal properties compared to the reference samples.

We hypothesised that the reduction of the fraction of pendent amines, through reaction with the dibasic ester co-monomer, would have a positive effect on the elasticity and the overall connectivity of the vitrimer network.[43] To experimentally validate this, the network integrity was investigated *via* swelling experiments. As expected, a lower concentration of pendent amines resulted in both a significant decrease in swelling ratio and soluble fraction, when comparing the VU-105 network to the other (modified) vitrimers.

Since most literature examples regarding creep reduction in vitrimers also impede material flow at reprocessing conditions,[7,38] stress-relaxation experiments were conducted to determine whether good reprocessability would not be significantly hampered by capping free chain-end amines (**Figure S11-S12**). For the reference VU materials, a clear increase in characteristic relaxation time ($\tau^*$) at 160 °C could be observed as expected from VU-105 to VU-95 (~100-200 fold, **Figure 2a** and **Table 1**). Additionally, when assessing the relaxation behaviour of VU-105 + TBD, a reduction in exchange dynamics was observed (~33 fold) confirming that proton transfers are essential to achieve fast exchange rates. As expected, these results indicated that by theoretically leaving out all exchangeable groups, a significant decrease in exchange

**Table 1.** Overview of composition and physical properties of (modified) vinylogous urethane vitrimers.

| Vitrimer | $T_g$[a] (°C) | $T_{d5\%}$[b] (°C) | Swel. Rat.[c] (%) | Sol. Frac.[c] (%) | $E_a$[d] (kJ.mol$^{-1}$) | $\tau^*_{160\,°C}$ (s) | $\tau^*_{110\,°C}$ (s) | $\dot{\varepsilon}_{rel,80\,°C}$[e] | $\dot{\varepsilon}_{rel,50\,°C}$[e] |
|---|---|---|---|---|---|---|---|---|---|
| VU-95 | - 5 | 315 | 124 ± 5 | 8.4 ± 0.9 | 68 ± 8 | 4660 | 54 210 | 12 | 6 |
| VU-100 | - 1 | 316 | 132 ± 1 | 7.1 ± 0.7 | 75 ± 6 | 3650 | 37 120 | 12 | 5 |
| VU-105 | -15 | 315 | 329 ± 35 | 12.7 ± 1.6 | 91 ± 2 | 20 | 640 | 400 | 100 |
| VU-105 + TBD | -16 | 318 | 155 ± 3 | 6.4 ± 0.6 | 75 ± 7 | 740 | 9860 | 12 | 5 |
| VU-95 + 1% | -4 | 317 | 128 ± 9 | 5.9 ± 0.8 | 47 ± 11 | 960 | 44 120 | 0.008 | 0.006 |
| VU-95 + 5% | -3 | 317 | 130 ± 1 | 5.1 ± 0.6 | 56 ± 4 | 500 | 33 050 | 12 | 4 |
| VU-95 + 10% | -5 | 317 | 147 ± 2 | 3.7 ± 0.6 | 63 ± 2 | 240 | 23 010 | 26 | 5 |
| VU-95 + 20% | -2 | 315 | 181 ± 2 | 5.2 ± 0.5 | 107 ± 19 | 20 | 10 420 | 68 | 10 |

[a] Determined from the second heating in DSC analysis (10 °C.min-1) [b] TGA onset temperatures after 5% weight loss ($T_{d5\%}$), [c] obtained after swelling for 24 h in THF. [d] Determined in low temperature region (110 °C to 130 °C if a dual viscosity profile present) otherwise full temperature region. [e] Determined from slope of steady-state region in creep curve relatively to VU-105.

kinetics at all temperatures could be observed. The temperature dependency (*i.e.* slope in Arrhenius curve), on the other hand, is very similar for all materials with $E_a$ values below 100 kJ.mol$^{-1}$ (**Figure S13**), indicative of a similar bond exchange mechanism. Notably, the acceleration effect of the thermal release of free chain-end amines could clearly be observed at 160 °C for the modified VU materials (**Figure 2b**). Indeed, a sharp drop in relaxation time (4660 s *vs* 960 s, respectively) can be observed when comparing the reference network VU-95 to VU-95 + 1%. A further increase of the concentration of dicarboxamide moieties, which dissociate into an imide and amine functionality, resulted in an even faster exchange rate with VU-95 + 20% showing similar fast exchange dynamics in comparison to the benchmark vitrimer VU-105 (~ 20 s). In contrast, at 110 °C, all modified VU networks displayed τ* values within the same order of magnitude as the VU-95 network (**Figure S12**). Even when a higher concentration of dicarboxamide was present, *i.e.* VU-95 + 20%, exchange kinetics at lower temperatures only increased with a factor 4, while increasing with a factor 40 at higher temperatures by releasing additional pendent amines. As a consequence, a deviation from a linear decrease in viscosity could be observed with temperature, resulting in viscosity profiles that show a positive curvature, or even two distinct viscoelastic regimes (**Figure 3 and Figure S14**). In essence, a more sudden decrease in viscosity is indeed expected as soon as sufficient amine moieties are released at higher temperature. Additionally,

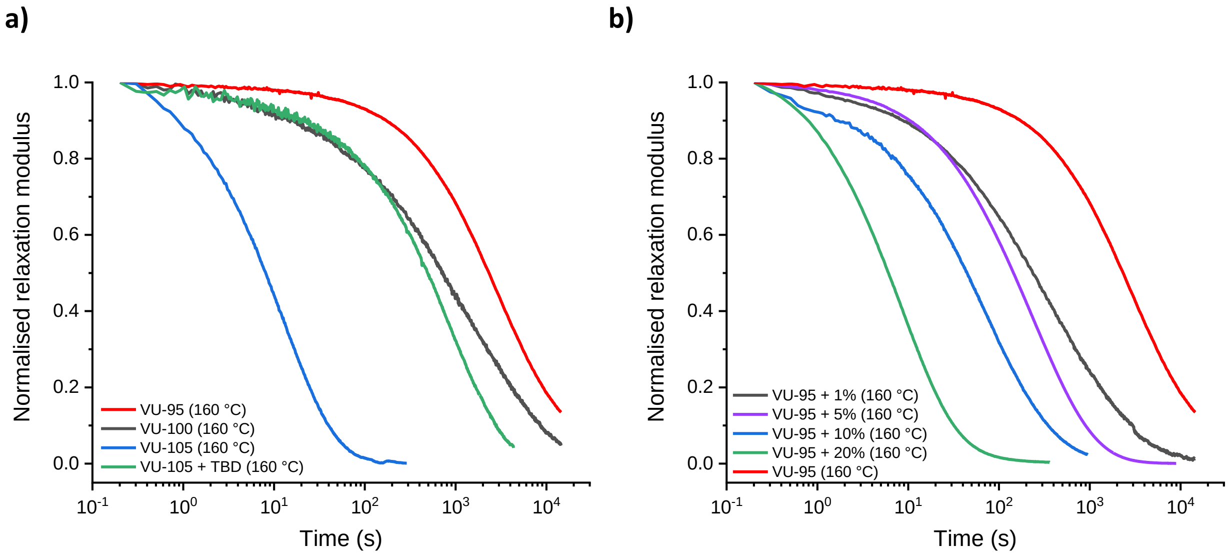


**Figure 2.** Stress-relaxation data of a) reference VU (+ TBD) and b) modified VU vitrimers at 160 °C. Note the accelerated stress decay when increasing the concentration of dicarboxamide.

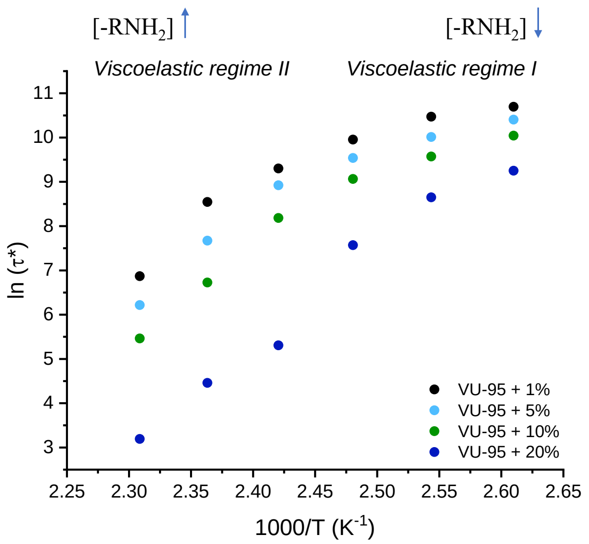


**Figure 3.** Arrhenius plot of the modified VU vitrimers indicating two distinct viscoelastic regimes depending on the availability of exchangeable pendent amines.

the sharpness of this 'downward shift' in Arrhenian plots should depend on the concentration and association constant of the dicarboxamide bonds. This effect can indeed be seen in Figure 3, as the acceleration becomes more pronounced as a function of the amount of DBE comonomer that was added to the formulations.

When taking a closer look to the shape of the relaxation curves for the modified VU networks at lower temperatures (**Figure 4** and **Figure S12**), the significant impact of adding a second dynamic covalent exchange chemistry on the overall viscoelastic behaviour can be understood. From 110 °C to 140 °C, built-up stresses in the VU-95 + 5% network could not be relaxed to zero, even after a long time. This was attributed to a decrease in the availability of exchangeable groups, caused by the temperature dependent (re)trapping of free chain-end amines (see rate equations in **Figure 4**). More specifically, in this temperature range the small amount of released amines do not exchange fast enough within a reasonable time frame, yielding an apparent more elastic response to deformation. The strong reduction in viscous behaviour was ascribed to the relatively thermally demanding dissociation of a glutaramide-type structure to a six-membered glutarimide and amine.[39] Note that this apparent liquid to solid behaviour is similar to that of hybrid networks containing both dynamic and non-dynamic covalent bonds,[44,45] although residual stresses can still relax for the modified VU system by simply heating to higher temperatures.

Next, frequency sweep experiments were conducted to determine whether the introduction of a small amount of dynamic dicarboxamide bonds would result in partial decrosslinking (Figure **S15-S16**). For all modified materials, no significant changes in the shear storage modulus (G') could be detected as a function of temperature and frequency. However, the substantial variation of shear loss modulus (G'') indicated that mechanical energy could be efficiently dissipated. This observation of G' and G'' as a function of temperature and frequency supported the hypothesis that decrosslinking was negligible, but the release of a small fraction of amine groups still had an important effect on the overall exchange kinetics.

The final aim of this study was to investigate the low temperature deformation behaviour of the modified VU vitrimers compared to the reference materials. To evaluate the changes in the viscosity profile at lower temperatures (< 100 °C) and further support our findings, creep experiments were conducted. When using a generalised Kelvin-Voight model to describe strain formation as a function of time (see SI for **Equations S1-S10** and Figure **S17-S18**), overall creep rates ($\dot{\varepsilon}$) can be determined to give an indication of how fast permanent deformation will occur in the polymer network. However, an often overlooked condition for such an analysis is that the recorded creep curve must be evaluated in a time range where so-called steady-state behaviour occurs (*i.e.* see **Figure S19** for sufficiently large time scales where **Equation S9** is valid).[46]

For the investigated materials, a constant shear stress of 2 kPa was applied for 5000 s in the range of 30 °C to 80 °C and the resulting strain was monitored as a function of time (**Figure S20-S21**). Next, $\dot{\varepsilon}$ values were plotted as a function of temperature for all (modified) VU vitrimers (**Figure 5**). At a first glance, a large reduction in irreversible deformation with a factor 10 to 30 can be observed at 50 °C when removing the availability of free chain-end amines from VU-105 to VU-95 (see **Figure 5a** and **Table S2**). A similar reduction was obtained for VU-105 + TBD, in good agreement with stress-relaxation data. Moreover, since there is no significant change in $\dot{\varepsilon}$ below 50 °C for VU-95, VU-100 and VU-105, any irreversible deformation can mainly be

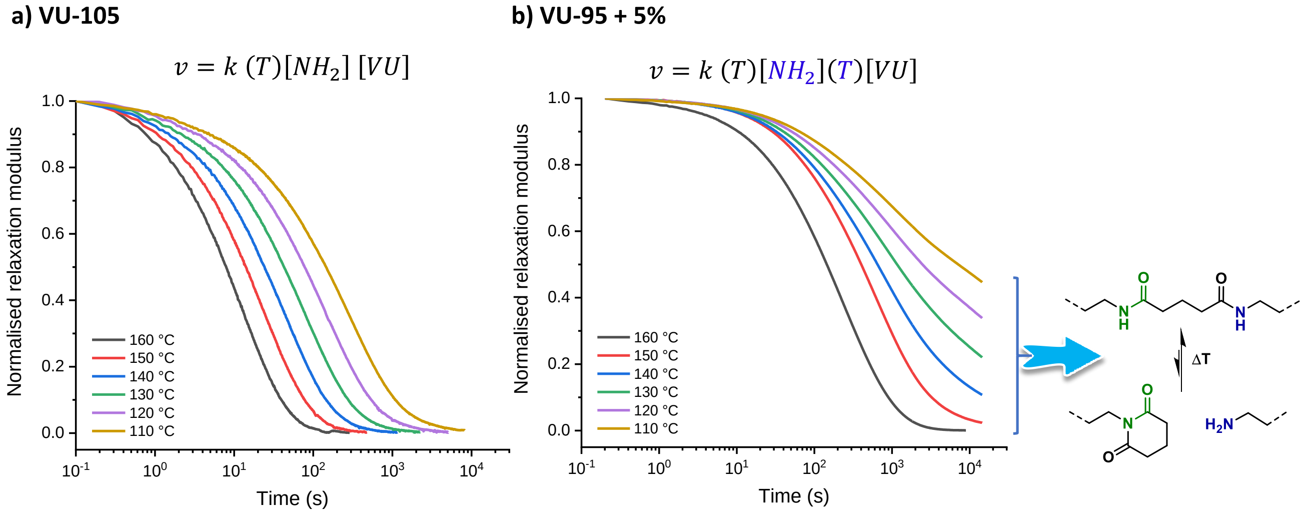


**Figure 4.** Representative stress relaxation data of a) VU-105 and b) VU-95 + 5% obtained between 110 °C and 160 °C. For the modified VU vitrimer, the concentration of chain-end amines becomes temperature dependent, resulting in a decrease of the exchange rate and absence of full relaxation within the investigated time frame.

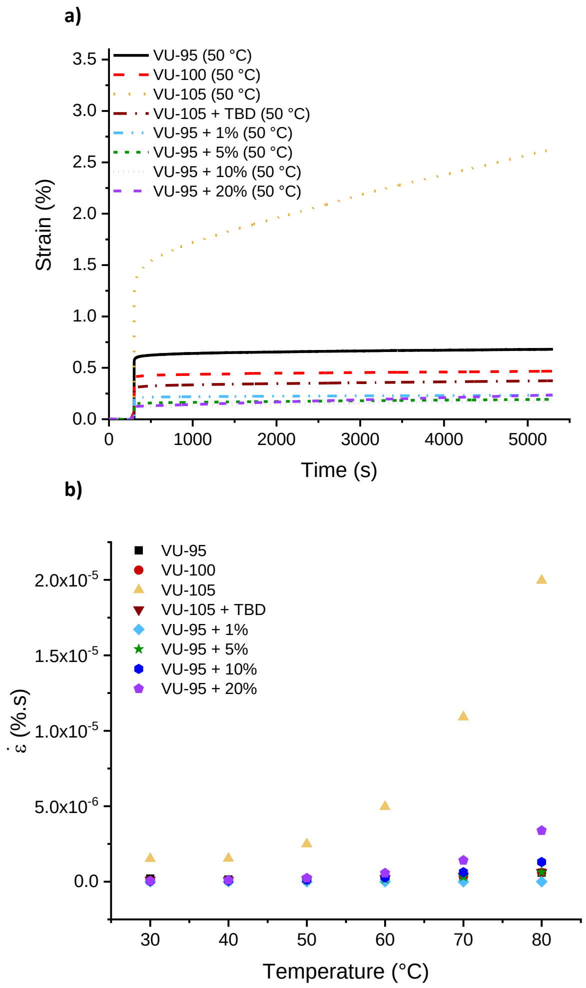


**Figure 5.** Creep data of all (modified) VU vitrimers with a) creep experiment without recovery at 50 °C and b) creep rate ($\dot{\varepsilon}$) as a function of temperature, highlighting the creep reduction when lowering the probability for free chain-end amines (Note that some data points might overlap in the figure).

attributed to network defects that are intrinsically non-elastic or viscous parts present within the vitrimer material (see **Figure 5b**).[43]

For the modified VU materials, the most drastic decrease in $\dot{\varepsilon}$, compared to network VU-105, could be observed for the VU-95 + 1% material, with no significant changes over the complete temperature interval. This is ascribed to the combined effect of a lower probability for network defects and exchangeable functional groups. Interestingly, the extensively decreased creep rate, combined with the relatively fast relaxation rate at 160 °C, unambiguously confirmed our hypothesis of (re)trapping reactive amines. Moreover, these experimental observations also showed that potential 'side-reactions' with an excess of acetoacetate groups are minimal and therefore negligible. When increasing the concentration of dicarboxamide bonds, the same decreasing trend in $\dot{\varepsilon}$ can be observed, but with a creep onset from 60 °C onwards. Not surprisingly, creep increases with increasing amounts of dicarboxamide bonds, and thus a higher probability for pendent amines, but still with a factor 6 to 32 times slower at 80 °C compared to VU-105. Considering the relationship between -ln ($\dot{\varepsilon}$) and temperature (1000/T) for the modified VU vitrimers, a viscous flow $E_a$ could be calculated from the slope of the Arrhenius curve (**Figure S22**), with values ranging from 30 to 82 kJ.mol$^{-1}$, which are in relatively good agreement with stress-relaxation data (*i.e.* $E_a$ in **Table 1**). Again, the apparent rise in temperature dependency was attributed to the availability of exchangeable amine moieties. Finally, to verify the reproducibility and significance of this viscoelastic behaviour, synthesis, reprocessing, stress-relaxation and creep experiments were repeated for the VU-95 + 1% formulation. Arrhenius plots of those experiments clearly indicate the same data could be retrieved within error (**Figure S23**).

## Conclusion

In summary, we report a straightforward chemical method to prepare creep-resistant vitrimers by combining dicarboxamide *dissociation* with the *associative* transamination of vinylogous urethanes. Elastomers were synthesised by the addition of commercially available dibasic ester co-monomers to an amine-acetoacetate curing mixture. The co-monomer appeared to have a negligible effect on the thermal properties and connectivity of the resulting modified vitrimers compared to their benchmarks because of the limited fraction of dicarboxamide bonds. On the other hand, when assessing rheology measurements, a drastic difference in exchange kinetics was observed caused by the reversible generation of pendent chain-end amines, required for the exchange, at elevated temperatures.

From stress-relaxation data, a gradual acceleration of exchange rate was observed through the simultaneous activation of transamination and introduction of network defects with increasing temperature, which resulted in an apparent double viscosity profile. As such, activation energies were determined from 47 to 107 kJ.mol$^{-1}$ for low dicarboxamide dissociation, while a sharper change in viscosity was detected for high dissociation. Moreover, with respect to the relaxation profile, this specific viscoelastic behaviour resulted in a change in relaxation rate with temperature, dictated by the (re)generation rate of pendent amines. In addition, creep experiments revealed that a significantly better performance in terms of long-term dimensional stability could be achieved by the introduction of reversible dicarboxamide bonds with the best system, showing the absence of significant creep up to 80 °C. In short, we can conclude that this straightforward approach allowed to limit irreversible deformation for low $T_g$ vitrimers without hampering reprocessability and thus greatly improves the applicability of reprocessable polymer networks. In addition, such strategies should in principle be applicable to a wide range of vitrimer chemistries.

## Experimental Section

See SI.

## Acknowledgements

F.D.P. and J.W. thank BOF-UGent for GOA-funding. F.V.L. and Y.S. acknowledge the Research Foundation-Flanders (FWO) for Ph.D. (FWO.3F0.2016.0039.01) fellowships. We would like to thank Bernhard De Meyer and Jan Goeman for technical support and Dr. Nezha Badi for fruitful discussions.

**Keywords:** Vitrimers • Creep-resistance • Transamination • Vinylogous urethane • Recyclable thermoset

1 D. Montarnal, M. Capelot, F. Tournilhac and L. Leibler, *Science*, 2011, **334**, 965–968.
2 W. Denissen, G. Rivero, R. Nicolaÿ, L. Leibler, J. M. Winne and F. E. Du Prez, *Adv. Funct. Mater.*, 2015, **25**, 2451–2457.
3 M. K. McBride, B. T. Worrell, T. Brown, L. M. Cox, N. Sowan, C. Wang, M. Podgorski, A. M. Martinez and C. N. Bowman, *Annu. Rev. Chem. Biomol. Eng.*, 2019, **10**, 175–198.
4 C. Taplan, M. Guerre, J. M. Winne and F. E. Du Prez, *Mater. Horizons*, 2020, **7**, 104–110.
5 P. Taynton, K. Yu, R. K. Shoemaker, Y. Jin, H. J. Qi and W. Zhang, *Adv. Mater.*, 2014, **26**, 3938–3942.
6 K. Yu, P. Taynton, W. Zhang, M. L. Dunn and H. J. Qi, *RSC Adv.*, 2014, **4**, 10108–10117.
7 M. Guerre, C. Taplan, J. M. Winne and F. E. Du Prez, *Chem. Sci.*, 2020, **11**, 4855–4870.
8 O. Anaya, A. Jourdain, I. Antoniuk, H. Ben Romdhane, D. Montarnal and E. Drockenmuller, *Macromolecules*, 2021, **54**, 3281–3292.
9 S. Ciarella, F. Sciortino and W. G. Ellenbroek, *Phys. Rev. Lett.*, 2018, **121**, 058003.
10 W. Denissen, J. M. Winne and F. E. Du Prez, *Chem. Sci.*, 2016, **7**, 30–38.
11 J. Han, T. Liu, C. Hao, S. Zhang, B. Guo and J. Zhang, *Macromolecules*, 2018, **51**, 6789–6799.
12 H. Yang, K. Yu, X. Mu, X. Shi, Y. Wei, Y. Guo and H. J. Qi, *Soft Matter*, 2015, **11**, 6305–6317.
13 B. M. El-Zaatari, J. S. A. Ishibashi and J. A. Kalow, *Polym. Chem.*, 2020, **11**, 5339–5345.
14 W. Liu, D. F. Schmidt and E. Reynaud, *Ind. Eng. Chem. Res.*, 2017, **56**, 2667–2672.
15 M. Capelot, M. M. Unterlass, F. Tournilhac and L. Leibler, *ACS Macro Lett.*, 2012, **1**, 789–792.
16 J. L. Self, N. D. Dolinski, M. S. Zayas, J. Read de Alaniz and C. M. Bates, *ACS Macro Lett.*, 2018, **7**, 817–821.
17 Y. Spiesschaert, C. Taplan, L. Stricker, M. Guerre, J. M. Winne and F. E. Du Prez, *Polym. Chem.*, 2020, **11**, 5377–5385.
18 F. I. Altuna, U. Casado, I. E. dell'Erba, L. Luna, C. E. Hoppe and R. J. J. Williams, *Polym. Chem.*, 2020, **11**, 1337–1347.
19 S. K. Schoustra, J. A. Dijksman, H. Zuilhof and M. M. J. Smulders, *Chem. Sci.*, 2021, **12**, 293–302.
20 F. Van Lijsebetten, J. O. Holloway, J. M. Winne and F. E. Du Prez, *Chem. Soc. Rev.*, 2020, **49**, 8425–8438.
21 R. G. Ricarte, F. Tournilhac, M. Cloître and L. Leibler, *Macromolecules*, 2020, **53**, 1852–1866.
22 R. G. Ricarte, F. Tournilhac and L. Leibler, *Macromolecules*, 2019, **52**, 432–443.
23 J. J. Lessard, G. M. Scheutz, S. H. Sung, K. A. Lantz, T. H. Epps and B. S. Sumerlin, *J. Am. Chem. Soc.*, 2020, **142**, 283–289.
24 R. L. Snyder, D. J. Fortman, G. X. De Hoe, M. A. Hillmyer and W. R. Dichtel, *Macromolecules*, 2018, **51**, 389–397.
25 S. Zhao and M. M. Abu-Omar, *Macromolecules*, 2019, **52**, 3646–3654.
26 J. P. Brutman, D. J. Fortman, G. X. De Hoe, W. R. Dichtel and M. A. Hillmyer, *J. Phys. Chem. B*, 2019, **123**, 1432–1441.
27 M. Hayashi and R. Yano, *Macromolecules*, 2020, **53**, 182–189.
28 R. Hajj, A. Duval, S. Dhers and L. Avérous, *Macromolecules*, 2020, **53**, 3796–3805.
29 L. Li, X. Chen, K. Jin and J. M. Torkelson, *Macromolecules*, 2018, **51**, 5537–5546.
30 J. J. Cash, T. Kubo, D. J. Dobbins and B. S. Sumerlin, *Polym. Chem.*, 2018, **9**, 2011–2020.
31 R. Martin, A. Rekondo, A. Ruiz de Luzuriaga, G. Cabañero, H. J. Grande and I. Odriozola, *J. Mater. Chem. A*, 2014, **2**, 5710.
32 S. Wang, S. Ma, Q. Li, X. Xu, B. Wang, K. Huang, Y. Liu and J. Zhu, *Macromolecules*, 2020, **53**, 2919–2931.
33 Y. Liu, Z. Tang, D. Wang, S. Wu and B. Guo, *J. Mater. Chem. A*, 2019, **7**, 26867–26876.
34 Y. Gu, J. Zhao and J. A. Johnson, *Trends Chem.*, 2019, 1, 318–334.
35 S. P. O. Danielsen, H. K. Beech, S. Wang, B. M. El-Zaatari, X. Wang, L. Sapir, T. Ouchi, Z. Wang, P. N. Johnson, Y. Hu, D. J. Lundberg, G. Stoychev, S. L. Craig, J. A. Johnson, J. A. Kalow, B. D. Olsen and M. Rubinstein, *Chem. Rev.*, 2021, **121**, 5042–5092.
36 C. A. Tretbar, J. A. Neal and Z. Guan, *J. Am. Chem. Soc.*, 2019, **141**, 16595–16599.
37 Y.-X. Lu and Z. Guan, *J. Am. Chem. Soc.*, 2012, **134**, 14226–14231.
38 T. Stukenbroeker, W. Wang, J. M. Winne, F. E. Du Prez, R. Nicolaÿ and L. Leibler, *Polym. Chem.*, 2017, **8**, 6590–6593.
39 F. Van Lijsebetten, Y. Spiesschaert, J. M. Winne and F. E. Du Prez, *J. Am. Chem. Soc.*, 2021, **143**, 15834–15844.
40 M. Guerre, C. Taplan, R. Nicolaÿ, J. M. Winne and F. E. Du Prez, *J. Am. Chem. Soc.*, 2018, **140**, 13272–13284.
41 W. Denissen, M. Droesbeke, R. Nicolaÿ, L. Leibler, J. M. Winne and F. E. Du Prez, *Nat. Commun.*, 2017, **8**, 14857.
42 Y. Spiesschaert, J. Danneels, N. Van Herck, M. Guerre, G. Acke, J. Winne and F. Du Prez, *Macromolecules*, 2021, **54**, 7931–7942.
43 H. Zhou, E. M. Schön, M. Wang, M. J. Glassman, J. Liu, M. Zhong, D. Díaz Díaz, B. D. Olsen and J. A. Johnson, *J. Am. Chem. Soc.*, 2014, **136**, 9464–9470.
44 F. Meng, M. O. Saed and E. M. Terentjev, *Macromolecules*, 2019, **52**, 7423–7429.
45 Z. Song, H. Zhan and Y. Zhou, *Angew. Chemie Int. Ed.*, 2010, **49**, 8444–8448.
46 H. Münstedt, *J. Rheol. (N. Y. N. Y).*, 2014, **58**, 565–587.

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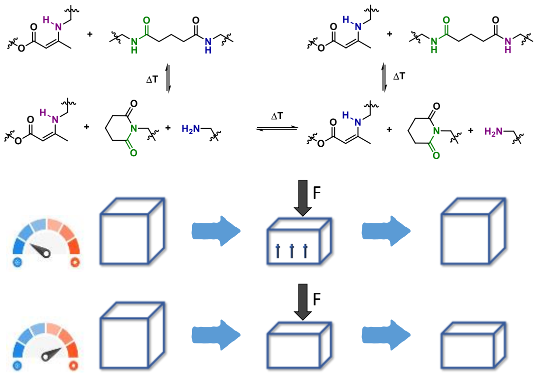

Viscous deformation in elastomeric vitrimers is suppressed by temporarily trapping a reactive side chain in the polymer backbone. Upon heating, the network defect is recovered allowing for fast exchange. This offers a versatile strategy to simultaneously achieve fast reprocessing, while maintaining strong dimensional stability of vitrimers.

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