Supporting information

Dynamic curing agents for amine-hardened epoxy vitrimers with short (re)processing times

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1. Processability formulas

Two different methods to calculate if processability will be possible in the obtained networks can be followed.

The first calculation method is taken and adjusted from Li et al.\textsuperscript{1}

**Parameter definitions**

$N_{A0}$, $N_{B0}$ and $N_{D0}$ are the total numbers of A, B and D functional groups, respectively.

$f$ is the functionality crosslinker $A_f$.

$r$ is the initial mole ratio between $A$ functional groups and $B + D$ functional groups:

$$r = \frac{N_{A0}}{N_{B0} + N_{D0}}$$

$\rho$ is the fraction of $A$ groups that initially belong to cross-linkers:

$$\rho = \frac{f N_{A0}}{f N_{A0} + 2 N_{A0}}$$

$S_B$ is the probability of $A$ reacting with $B$ if an $A$ reacts.

$$S_B = \frac{k}{k + 1}$$

Where $\beta$ is a function of reactivity ratio and conversion; $\beta = 1$ when $B$ and $D$ groups are equally reactive with $A$ groups or when $B$ and $D$ groups are completely reacted.

$k$ is the initial mole ratio between $B$ and $D$ functional groups:

$$k = \frac{N_{B0}}{N_{D0}}$$

$p$ is the fractional conversion of $A$.

$N_{Ar}$ is the amount of $A$ groups reacted:

$$N_{Ar} = N_{A0} p$$

$p_B$ is the fractional conversion of $B$.

$$p_B = \frac{N_{Br}}{N_{B0}}$$

**Derivations**

$$\alpha_p = \frac{rp^2 \rho S_B^2 k + 1}{1 - rp^2 (1 - \rho) S_B^2 k + 1}$$

In the utilized reactions presented here:
A stands for the NH$_2$ functional group  
B stands for the epoxide functional group  
D stands for the acetoacetate functional group

**Assumption:** only primary amines react with the epoxides. Note that this assumption is used here only for simplifying calculations, even if in reality also a percentage of secondary amines will react with epoxides.

In the case presented here $r > 1$ because an excess of NH$_2$ in the network is necessary for transamination.

$$ r = \frac{N_A}{N_B + N_D} > 1 $$

Therefore, at full conversion of $B$ and $D$ functional groups $p \neq 1$, but $p = \frac{1}{r}$ since

$$ N_{Ar} = N_B + N_D $$

$$ p = \frac{N_{Ar}}{N_A} = \frac{N_B + N_D}{N_A} = \frac{1}{r} $$

$N_{Br}$ is the total number of $B$ groups reacted.

$$ N_{Br} = N_A p S_B $$

According to the defined parameters above, we know that

$$ N_{B0} = \frac{N_A}{r \cdot k + 1} $$

Therefore, $S_B$ can be obtained via $p_B$

$$ p_B = \frac{N_{Br}}{N_{B0}} = \frac{N_A p S_B}{N_A k} = \frac{rpS_B(k + 1)}{k} $$

$$ S_B = \frac{p_B k}{rp(k + 1)} $$

Since we assume full conversion: $p_B = 1$ and $p = \frac{1}{r}$

$$ S_B = \frac{k}{k + 1} $$

Implementing this in the formula of $\alpha_p$ presented by Li et al.:

$$ \alpha_p = \frac{1}{p^2 \rho \left(\frac{k}{k + 1}\right)^{2k + 1}} $$

$$ 1 - \frac{1}{p^2(1 - \rho)\left(\frac{k}{k + 1}\right)^{2k + 1}} $$
\[ \alpha_p = \frac{p^k}{k + 1} \]

\[ 1 - p (1 - \rho) \frac{k}{k + 1} \]

\[ \alpha_c \text{ is the critical value of gelation:} \]

\[ \alpha_c = \frac{1}{f - 1} \]

Therefore, to avoid a percolated permanent network:

\[ \alpha_p < \alpha_c \]

\[ \frac{p^k}{k + 1} \frac{k}{1 - p (1 - \rho) \frac{k}{k + 1}} < \frac{1}{f - 1} \]

Equation S1. Used formula to calculate processability for the here utilized compositions.

Table S1. Results of the calculations using Equation S1 for different compositions.

<table>
<thead>
<tr>
<th></th>
<th>20-80*</th>
<th>30-70*</th>
<th>42-58*</th>
<th>60-40*</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_p )</td>
<td>0,53</td>
<td>0,42</td>
<td>0,32</td>
<td>0,20</td>
</tr>
<tr>
<td>( \alpha_c )</td>
<td>0,5</td>
<td>0,5</td>
<td>0,5</td>
<td>0,5</td>
</tr>
</tbody>
</table>

*mol% dynamic bonds – mol% permanent bonds

These values state that materials containing at least 30% vinylogous urethane bonds should be processable in the used composition. However, the values given here are just indicative, since they do not take into account the possible reaction of secondary amines and is thus an underestimation of necessary dynamic bonds. Therefore, the threshold value of gelation of a permanent network will most likely be lower than 0.5 and the obtained value of \( \alpha_p \) will be higher.

The second calculation method that can be followed, is based on two different assumptions, namely that the amine – acetoacetate reaction occurs before any epoxy moiety reacts and that the relative reactivity of primary and secondary amines is the same towards epoxy moieties (which is not true). While this calculation method will lead to an overestimation of necessary dynamic bonds for processability, the first calculation method leads to an underestimation. Here, the classical equations for obtaining the critical gelation ratio to produce a permanent epoxy-amine network can be used. As an example, this calculation method is used for the investigated ratio of 42-58 mol%VU-mol%epoxy.

As a first step, the functionality-average functionality (f) needs to be calculated: in this case a tris-functional amine has a functionality of 6 (6NH moieties) and a bis-functional amine has a functionality of 4 (4NH moieties). The used molar ratio was 3.5 bis-functional amine to 1 tris-functional amine, leading to the following f value.

\[ f = \frac{4 \times 3.5 + 6 \times 1}{3.5 + 1} = 4.44 \]
From this value, the critical ratio to avoid gelation of the permanent network can be calculated based on the formula for the gel conversion in a stepwise polymerization.

\[ \alpha_c = \frac{1}{f - 1} = 0.29 \]

This means that in order to avoid gelation, the ratio of epoxy functionalities to NH functionalities (1/r) needs to be lower than 0.29 (assuming full conversion of the epoxy functionalities).

\[ \frac{Epoxy\, functionalities}{NH\, functionalities} = \frac{1}{r} < \alpha_c = 0.29 \]

In this case, there is a 5% excess of primary amines for both OPN and WFN methods. In the OPN method, there are thus 10 NH (5 NH\(_2\)) functionalities (1.75 molar ratio BAC + 0.5 molar ratio TREN) present for 2.75 epoxide functionalities. However, 2 acetoacetate functionalities will ‘block’ 4 of these NH-functionalities. Thus, a ratio of 6NH to 2.75 epoxides is obtained, which is the same for the WFN method. From this, r can be calculated based on the ratio of epoxy functionalities to reactive NH functionalities.

\[ \frac{1}{r} = \frac{2.75}{6} = 0.458 \]

According to this formula, the used 42-58 composition would not be processable since 1/r > \( \alpha_c \).

Note: Both calculation methods each represent ‘extreme’ cases based on either the assumption of ‘full selectivity’ or ‘no selectivity’. However, the assumption made in the first calculation method is more supported by two small molecule studies, in which 1,2-epoxyhexane, 2-ethyl-1-hexylamine and ethyl acetoacetate were mixed in the same ratios as for WFN and OPN and heated to 100 °C. Since NMR measurements showed that only 18% (for WFN) and 17% (for OPN) of the epoxides were opened by a secondary amine.

Processability test

Figure S1. OPN\(_{42/5}\) network reprocessed in 6 minutes (1 minute heating of the mold and 5 minutes compression using 1 metric tons pressure).
Figure S2. Processability test of epoxy vitrimers with different weight (and mol) percentages of vinylogous urethane matrix. These materials were obtained following the OPN method. (Wt%VU:Wt%Epoxy) A) 15:85; B) 24:76; C) 35:65; D) 52:48. (mol%VU:mol%Epoxy) A) 20:80; B) 30:70; C) 42:58; D) 60:40.

2. Material Characterization

Figure S3. Isothermal TGA at 150 °C for 120 minutes of the different obtained materials.
Figure S4. DSC thermograms of WFN₄₂/₅, OPN₄₂/₅, ER 1, ER 2 and VUR with a heating and cooling rate of 10 °C/min.

Figure S5. FT-IR spectrum of WFN₄₂/₅, OPN₄₂/₅, ER 1, ER 2 and VUR.

3. Reaction mechanisms
4. Viscoelastic behavior characterization

a. Amplitude sweep
Figure S8. Amplitude sweep of WFN$_{42/5}$ Rx0 to determine its linear viscoelastic region (LVER) at 160 °C with a force of 5 N.

Figure S9. Amplitude sweep of OPN$_{42/5}$ Rx0 to determine its LVER at 160 °C with a force of 5 N.
Figure S10. Amplitude sweep of VUR to determine its LVER at 160 °C with a force of 5 N.

b. Stress-relaxation

Figure S11. Stress relaxation experiments of VUR from 115-160 °C. The dashed line corresponds to the value 1/e, which defines the characteristic relaxation time τ. A constant strain of 1% was applied, which was within the linear viscoelastic region (LVER).

c. Arrhenius plot

Table S2. Activation energy of the obtained vinylogous urethane vitrimers via stress-relaxation experiments.

<table>
<thead>
<tr>
<th>Networks</th>
<th>Equation</th>
<th>E_s (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WFN_{42/5}</td>
<td>12.74x – 27.69</td>
<td>106 ± 0.5^a</td>
</tr>
<tr>
<td>OPN_{42/5}</td>
<td>12.02x – 26.45</td>
<td>100 ± 0.8^a</td>
</tr>
<tr>
<td>VUR</td>
<td>14.81x – 30.77</td>
<td>123 ± 15.4^b</td>
</tr>
</tbody>
</table>
This value was calculated using the data points between the temperature range of 115 °C – 160 °C.

b. This value was calculated using the data points between the temperature range of 140 °C – 160 °C.

**Figure S12.** Arrhenius plot of the obtained relaxation times for VUR with a linear trendline.

d. Creep experiments

**Figure S13.** Creep experiments of VUR at different temperatures with an applied stress of 5000 Pa for 20 minutes.

**Figure S14.** Creep experiments of ER 1 at different temperatures with an applied stress of 5000 Pa for 20 minutes.
Figure S15. Creep experiments of ER 2 at different temperatures with an applied stress of 5000 Pa for 20 minutes.

5. Recyclability

Figure S16. TGA of the original and the four times recycled samples of WFN_{42/5} and OPN_{42/5} with a temperature ramp from 25 °C to 800 °C at 10 °C/min.
Figure S17. Isothermal TGA of the original and the four times recycled samples of WFN_{42/5} and OPN_{42/5} at 150 °C for 120 minutes.

Figure S18. DSC thermograms of WFN_{42/5} and the four recycling steps of WFN_{42/5} with a heating and cooling rate of 10 °C/min.
Figure S19. DSC thermograms of OPN$_{42/5}$ and the four recycling steps of OPN$_{42/5}$ with a heating and cooling rate of 10 °C/min.

Figure S20. FT-IR spectrum of WFN$_{42/5}$ and the four recycling steps of WFN$_{42/5}$. 
**Figure S21.** FT-IR spectrum of OPN\textsubscript{42/5} and the four recycling steps of OPN\textsubscript{42/5}.

**Figure S22.** Amplitude sweep of WFN\textsubscript{42/5} Rx4 to determine its LVER at 160 °C with a force of 5 N.
Figure S23. Amplitude sweep of OPN_{42/5} Rx4 to determine its LVER at 160 °C with a force of 5 N.

Figure S24. Stress relaxation experiments of WFN_{42/5} Rx4 from 115-160 °C. The dashed line corresponds to the value 1/e, which defines the characteristic relaxation time τ. A constant strain of 1 % was applied, which was within the linear viscoelastic region (LVER).
**Figure S25.** Stress relaxation experiments of OPN42/5 Rx4 from 115-160 °C. The dashed line corresponds to the value 1/e, which defines the characteristic relaxation time $\tau$. A constant strain of 1% was applied, which was within the linear viscoelastic region (LVER).

**Figure S26.** Arrhenius plot of the obtained relaxation times for WFN42/5 Rx4 with a linear trendline.

**Figure S27.** Arrhenius plot of the obtained relaxation times for OPN42/5 Rx4 with a linear trendline.

**Table S3.** Activation energy of the recycled vinylogous urethane vitrimers via stress-relaxation experiments.

<table>
<thead>
<tr>
<th>Networks</th>
<th>Recycling Steps</th>
<th>Equation</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WFN42/5</td>
<td>Rx4</td>
<td>$12.26x - 26.49$</td>
<td>$102 \pm 0.4$</td>
</tr>
<tr>
<td>OPN42/5</td>
<td>Rx4</td>
<td>$11.55x - 25.38$</td>
<td>$96 \pm 1.3$</td>
</tr>
</tbody>
</table>
Figure S28. Creep experiments of WFN_{42/5} Rx4 at different temperatures with an applied stress of 5000 Pa for 20 minutes.

Figure S29. Creep experiments of OPN_{42/5} Rx4 at different temperatures with an applied stress of 5000 Pa for 20 minutes.

6. Vinylogous urethane containing curing agent

Figure S30. A picture of the obtained vinylogous urethane curing agent.
Figure S31. Molecular structure of the vinylogous urethane curing agent.

Figure S32. FT-IR spectrum of the dried vinylogous urethane curing agent.

Figure S33. Viscosity profile at 25 °C of the vinylogous urethane curing agent.
Figure S34. Viscosity profile at 50 °C of the dried vinylogous urethane curing agent.

Figure S35. Viscosity profile at 80 °C of the dried vinylogous urethane curing agent.
Figure S36. Viscosity profile at 25 °C of the mixture of dried vinylogous urethane curing agent and Epikote™ Resin MGS LR 135.

Figure S37. Viscosity profile at 35 °C, 40 °C and 45°C of the mixture of dried vinylogous urethane curing agent and Epikote™ Resin MGS LR 135.
Figure S38. Viscosity profile at 50 °C and 80 °C of the mixture of dried vinylogous urethane curing agent and Epikote™ Resin MGS LR 135.
7. Fiber reinforced polymer composite

a. Thermogravimetric analysis (TGA)

![Graph of TGA for 4-layer composite](image1)

Figure S39. TGA of the four layered composite with a temperature ramp from 25 °C to 800 °C at 10 °C/min.

![Graph of TGA for 1-layer composite](image2)

Figure S40. TGA of the one layered composite with a temperature ramp from 25 °C to 800 °C at 10 °C/min.

Table S4. Fiber volume fraction calculation of the four and one layer composites.

<table>
<thead>
<tr>
<th></th>
<th>Volume sample (^a) (mm(^3))</th>
<th>(m_{\text{glass fiber}}) (^b) (mg)</th>
<th>Density (\text{glass} ) (mg/mm(^3))</th>
<th>Volume (\text{fibers} ) (^c) (mm(^3))</th>
<th>Fiber volume fraction (^d) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Four-layer</td>
<td>25.15</td>
<td>33.26</td>
<td>2.5</td>
<td>13.30</td>
<td>53</td>
</tr>
<tr>
<td>One-layer</td>
<td>5.13</td>
<td>4.91</td>
<td>2.5</td>
<td>1.97</td>
<td>38</td>
</tr>
</tbody>
</table>

\(^a\) Measured before start of the TGA experiment. \(^b\) Weight after the TGA measurement. \(^c\) Calculated by dividing \(m_{\text{glass fiber}}\) through the density of glass. \(^d\) Calculated by dividing Volume \(\text{fibers} \) through Volume sample.
a. Thermal foldability of the composite

In order to reshape the composite, the sample was first placed in a pre-heated press for 5 minutes. Then, the sample was bended as shown in Figure S41B. However, only a slight bend (Figure S41 C&D) could be obtained this way without damaging the fibers. Therefore, the sample was placed in a pre-heated oven at 150 °C for 10 minutes together with the weights used for reshaping. After those 10 minutes the sample was gradually deformed as shown in Figure S41E. Once the desired deformation was reached, the sample was kept in its new shape for 15 minutes to ensure full stress release due to reorganization of the vinylogous urethane matrix. Following this, the weights were removed and the sample was left to cool down. The sample maintained its new shape without visible damage to the matrix (Figure S41F).
Figure S41. A) One-layer composite before reshaping. B) Reshaping set-up in the press at 150 °C. C&D) Slightly bended one-layer composite. E) Reshaping set-up at 150 °C in an oven. F) Highly reshaped one-layer composite without damage to the fibers.
8. Transesterification experiments

Transesterification experiments (Figure S42-47) were performed in order to ensure that the observed processability and stress-relaxation were the result of the vinylogous urethane transamination and not because of transesterification. For this, propyl-3-(butylamino)but-2-enoate was mixed with an excess (2 equivalents) of an alcohol (benzyl alcohol or 2-hexanol) at different temperatures and with or without catalyst.

Benzyl alcohol was first investigated because of its higher reactivity and easier visualization by NMR (Figure S42-43). Here it was found that transesterification can occur on vinylogous urethanes in the presence of Zn(acetate)$_2$ as catalyst. Following this, transesterification with 2-hexanol was investigated, since it better mimics the polymer matrix. In a first test at 120 °C, in the absence of any catalyst, no transesterification was observed (Figure S44). When Zn(acetate)$_2$ was added in the mixture, transesterification was observed after 1h at 120 °C and the transesterification product increased over time (Figure S45).

Furthermore, to better mimic the investigated materials, an experiment with DIPEA, a tertiary amine, as catalyst was also performed. In Figure S46, no transesterification can be observed at 120 °C in the presence of DIPEA. As a final experiment, the temperature was increased to 160 °C, in the absence of a catalyst, and only a minimal amount of transesterification was observed (Figure S47).

All these results indicate that in the investigated timeframe, the processability and stress-relaxation in the materials are mostly governed by transamination, and thus not by transesterification, of vinylogous urethanes.

![Diagram](image)

*Figure S42. NMR-spectra as a function of time of the transesterification reaction at 100 °C between propyl-3-(butylamino)but-2-enoate and benzyl alcohol. After 24 h, no change was observed in the spectra, indicating that no transesterification occurs during the investigated time period.*
Figure S43. NMR-spectra as a function of time of the transesterification reaction at 100 °C between propyl-3-(butylamino)but-2-enoate and benzyl alcohol in the presence of Zn(acetate)$_2$ as catalyst (5 mol%). After 1 h, a signal at 5.09 ppm (B) can be seen, which is linked to the transesterification product and this signal increases over time. This is a clear indication that transesterification can occur at elevated temperatures with Zn(acetate)$_2$ as catalyst.

Figure S44. NMR-spectra as a function of time of the transesterification reaction at 120 °C between propyl-3-(butylamino)but-2-enoate and 2-hexanol. After 3 h, no change was observed in the spectra, indicating that no transesterification occurs during the investigated time period.
Figure S45. NMR-spectra as a function of time of the transesterification reaction at 120 °C between propyl-3-(butylamino)but-2-enoate and 2-hexanol in the presence of Zn(acetate)$_2$ as catalyst (5 mol%). After 1 h, a signal at 4.80 ppm (B) can be observed, which is linked to the transesterification product, and this signal increases over time. This is a clear indication that transesterification can occur at elevated temperatures with Zn(acetate)$_2$ as catalyst.

Figure S46. NMR-spectra as a function of time of the transesterification reaction at 160 °C between propyl-3-(butylamino)but-2-enoate and 2-hexanol in the presence of DIPEA. DIPEA was added to observe the influence of a tertiary amine on the transesterification of the vinylogous urethane. After 3 h, no change was observed in the spectra, indicating that no transesterification occurs during the investigated time period.
Figure S47. NMR-spectra as a function of time of the transesterification reaction at 160 °C between propyl-3-(butylamino)but-2-enoate and 2-hexanol. After 1 h, a signal at 4.80 ppm (B) can be observed, which is linked to the transesterification product, and this signal increases over time. This is a clear indication that transesterification can occur at elevated temperatures without the presence of a catalyst.

Reference