Fast dynamic siloxane exchange mechanism for reshapable vitrimer composites

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Supporting Information Placeholder

ABSTRACT: In order to develop siloxane-containing vitrimers with fast dynamic characteristics, different mechanistic pathways have been investigated using a range of catalysts. In particular, one siloxane exchange pathway has been found to show a fast dynamic behavior in a useful temperature range (180-220°C) for its application in vitrimers. The mechanism is found to involve 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as an organic catalyst in the presence of hydroxyl groups. Using this new mechanistic approach, vitrimers with ultrafast stress-relaxation characteristics (relaxation times below 10s) have been prepared with a readily available epoxy resin and siloxane-amine hardener. Subsequently, the low viscosity siloxane-containing vitrimer resin enabled the preparation of glass fiber-reinforced vitrimer composites using an industrially relevant vacuum assisted resin infusion technique. The resulting composite was successfully thermoformed into a new shape, which makes it possible to envision a second life for such highly engineered materials.

INTRODUCTION

Fiber-reinforced composites (FRCs) typically consist of a polymeric matrix reinforced with glass or carbon fibers, used as a lightweight alternative to metals in aeronautics, wind power, and marine industries owing to their higher strength-to-weight ratio.[1] The choice for the polymer matrix can be both thermoplastics and thermosets. Because of their higher dimensional stability, thermosets are predominant in structurally demanding applications. Indeed, in contrast to thermoplastics, thermosets are three-dimensionally crosslinked networks that possess superior structural properties at the expense of malleability. These characteristics of thermosets limit their repair and recycling, and hence also for structural applications (e.g., FRCs) associated with it.[2, 3] Consequently, such highly engineered materials are often turned into waste, which is either incinerated or is ending up in landfills.[4] For instance, wind turbine blades composed of glass fiber reinforced polymer composites are often traded in for a new model with superior performance after only a decade because of economic reasons and despite their designed lifetime of 20-25 years.[5, 6] However, recently, the wind industry has called for a Europe-wide ban for landfilling of wind turbine blades[7] and with ever-increasing environmental concern, it is only a matter of time before other continents will follow this legislation.

Covalent adaptable networks[8-16] (CANs) have the potential for reusability of such aforementioned materials owing to the presence of dynamic covalent bonds. Vitrimers, coined by Leibler and coworkers in 2011,[17] are a particular type of CAN materials comprising of structural properties of thermosets with the malleability of thermoplastics. Vitrimers can be reshaped by a thermal trigger as a result of the presence of thermally activable dynamic chemical groups, and by definition, have a constant crosslink density over different temperatures, making them ideal candidates for the preparation of reshapable fiber-reinforced composites. Although vitrimers or CANs, in general, have been explored using a wide range of chemical functionalities as dynamic covalent bonds such as esters,[17, 18] imines,[19-22] disulfides,[23, 24] vinylogous urethanes,[11, 20, 25-28] siloxanes,[29-32] and many more,[13, 33-40] there are only a handful of examples for their application in FRCs.[10, 26, 41-44] Furthermore, techniques used in these reports are limited to simple lab-scale demonstrators because of the low viscosity requirement for vitrimer precursors, in combination with the desired high glass transition temperature (T_g > 80°C) for most applications. On the other hand, certain siloxane building blocks are known to be low viscous and inexpensive. Moreover, the corresponding siloxane-containing materials can exhibit a relatively high T_g.[30] In spite of their commercial availability, this dynamic chemistry has never been explored in the field of reshapable FRCs. Only FRCs based on a slow silyl ether-based exchange chemistry have been reported with a focus on the chemical recycling of the fibers.[45]

The first report on siloxane chemistry in the context of dynamic materials was published by McCarthy and coworkers in 2012,[29] followed by a number of studies with a focus on the use of both siloxane[30, 32, 46-48] and silyl ether[37, 49-51] chemistries in CANs. The studies on silyl ether chemistry explored the silyl ether metathesis reaction as well as the internal catalysis by a γ-NH functionality or hydroxyl groups to fabricate the corresponding materials. However, all these previously mentioned siloxane and silyl ether based materials exhibit a slow dynamic exchange, with relaxation times in the order of at least several hundreds of seconds, which hampers their processing and application. Recently, Terentjev and coworkers published two
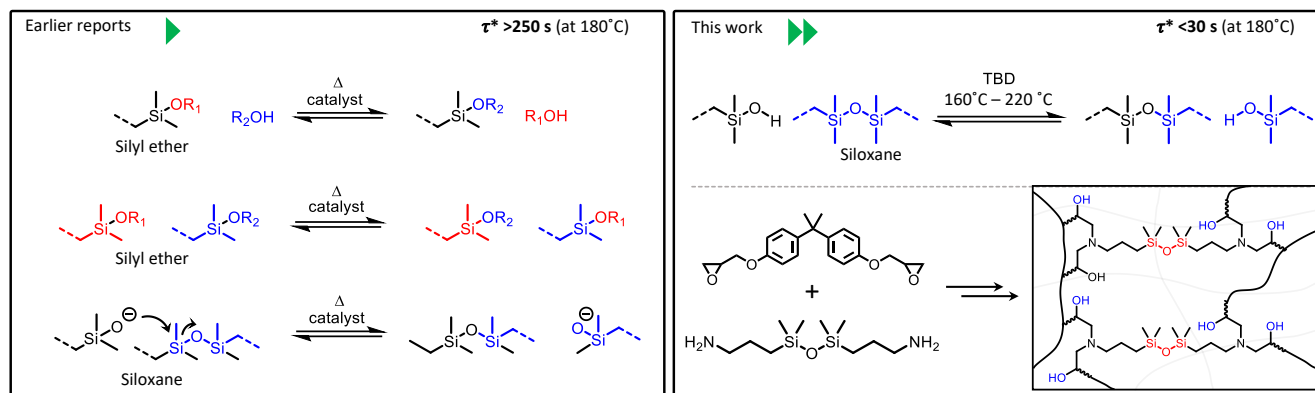
Figure 1. Graphical representation of the difference between previous reports and current work.

articles on siloxane-containing liquid crystals exhibiting fast dynamic exchange.[31, 32] However, since these materials also contained other dynamic bonds as a result of a thiol-acrylate reaction[52], it is difficult to assess the real contribution of the siloxane exchange chemistry on the dynamic nature of these liquid crystals.

In the present study, we will report a new pathway for a fast dynamic siloxane exchange, catalyzed by TBD, and demonstrate vitrimer synthesis starting from the readily available siloxane-containing amine hardener, i.e., 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyl disiloxane (BAS), and bis-phenol A diglycidyl ether (DGEBA) epoxy resin.

It will be demonstrated that the produced vitrimer materials exhibit much faster dynamic exchange in comparison to earlier investigated siloxane or silyl ether-based materials (**Figure 1**) with relaxation times in the order of seconds over at least three mechanical recycling cycles. Simultaneously, the aim of this study was to develop vitrimers with high enough T_g (> 80°C), suitable for potential application in FRC-based wind turbine blades as well as some parts in the automotive industry. Finally, it will be demonstrated that a glass fiber-reinforced composite could be prepared, using an industrially relevant vacuum-assisted resin infusion technique (VARI), and that the resulting FRC could be successfully reshaped and analyzed.

RESULT AND DISCUSSIONS

As the primary aim of this research was to develop a siloxane-containing dynamic material exhibiting fast dynamic exchange, the underlying siloxane exchange mechanism was first analyzed in detail. In the presence of a catalyst such as a siloxide, siloxane exchange occurs via a nucleophile attack on a silicon atom of a siloxane functionality in an S_N2-type fashion,[53] generating another nucleophile that continues the exchange. In this case, regardless of the applied nucleophile, the exchange dynamics of the siloxane are limited by the nucleophilicity of the produced siloxide (see Figure S22). Therefore, the slow dynamic exchange of the reported siloxane materials should be ascribed to the poor nucleophilicity of the participating siloxide.

To allow for a faster dynamic siloxane exchange and increase its applicability on a material level, a new siloxane exchange pathway had to be looked for. As mentioned above, recent publications from Terentjev and coworkers sparked our interest in TBD catalyzed, fast exchanging siloxane-containing liquid crystalline elastomeric materials.[31, 32] The addition of TBD as a catalyst led to a 100 times faster dynamic exchange, compared to the material prepared with tetramethylammonium

siloxanolate (TMAS), but we assume that this could also be associated to the retro-thiol Michael chemistry that is expected to occur in their materials. It is indeed known that a base, such as TBD, can catalyze the (retro)thiol-Michael reaction rapidly.[54, 55]

Scheme 1. Model study for chemical exchange between two different siloxane molecules.
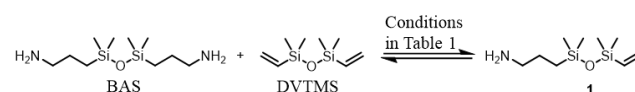
To investigate the siloxane exchange mechanism, only catalyzed by TBD, two different siloxane molecules, being 1,3-divinyltetramethyldisiloxane (DVTMS) and BAS were mixed in equimolar ratios (Scheme 1). The double bonds of DVTMS were expected to help for the NMR-analysis of the exchange reactions and are not supposed to have an impact on the mechanism.

As TBD-catalyzed polymerization of cyclic siloxanes is reported to involve a hydroxyl functionality,[56] the aforementioned siloxane molecules were heated in different conditions as reported in Table 1: in the presence of TBD and pentanol (entry 1), only pentanol (entry 2), without any additional compounds (entry 3), and only TBD (entry 4).

Table 1. Compositions for different entries during the investigation of the influence of various functionalities on the siloxane exchange mechanism.

Entry	DVTMS (eq)	BAS (eq)	TBD[a] (eq)	Pentanol[a] (eq)
1	1	1	0.05	0.05
2	1	1	0	0.05
3	1	1	0	0
4	1[b]	1[b]	0.05	0

[a]Molar equivalent with respect to BAS and DVTMS. [b]Dried over 4Å molecular sieves; the reaction vial was prepared in a glove box.

This set of conditions have been selected for an in-depth study of the siloxane exchange mechanism and to determine whether it is catalyzed by TBD in the presence of hydroxyl groups, relies on a siloxane metathesis, only involves hydroxyl groups or only uses TBD as catalyst, respectively. All these experiments were conducted in bulk while stirring at 120°C for 16 hours in septum sealed vials. This temperature was selected to have a high temperature for the reactions while having a safe margin between the reaction temperature and the boiling point

of DVTMS (139°C). [29]Si nuclear magnetic resonance (NMR) was performed for all reactions and the ^{29}Si NMR spectra of the reaction products are shown in **Figure 2**. Apart from the two peaks attributed to the BAS- (3.2 ppm) and DVTMS-compound (7.5 ppm), no additional peaks were observed, except for entry 1 and in a moderate way also for entry 4 (Table 1). This suggests that a metathesis-type siloxane exchange and alcohol catalyzed siloxane exchange did not occur under these conditions. In the case of entry 1, two new peaks (4.1 and 8.4 ppm) clearly emerged adjacent to the original two peaks, indicating the formation of a new siloxane product as a result of the exchange between DVTMS and BAS. 2D NMR (^{29}Si-^{1}H HMBC) (Figure S4, S5, S6) and liquid chromatography-mass spectrometry (LC-MS) (Figure S7) confirmed that this new product corresponds to the exchange product **1**. For entry 4 (only TBD but no addition of pentanol), both DVTMS and BAS were dried over 4Å molecular sieves for 72 hours prior to the reaction to avoid as much as possible undesired moisture acting as a potential source of hydroxyl groups. ^{29}Si NMR of this sample showed the peaks corresponding to the siloxane-exchange product, similar to entry 1 (with pentanol), but with much lower intensity. These small peaks could originate from remaining traces of moisture or from SiOH-groups at the glass surface of the reaction vial.
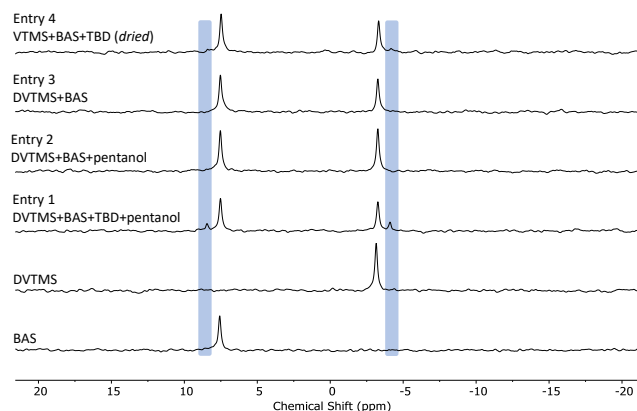

Figure 2. ^{29}Si NMR (in CDCl3) of different experiments conducted for the siloxane-exchange study as mentioned in Table 1. Blue lines are highlighting the region for newly formed peaks. The siloxane-exchange product **1** can be clearly observed in the NMR analysis of entry 1 and in a very small amount for entry 4.

All these experiments confirm that hydroxyl groups play a crucial role in the siloxane exchange mechanism, catalyzed by TBD. Scheme 2 shows the proposed pathway for the siloxane exchange in the presence of alcohol groups, which is similar to the TBD-catalyzed 'proton shuttling' polymerization mechanism of cyclic siloxanes, as reported by Shimada and coworkers.[56]

In the next step, the corresponding TBD-catalyzed siloxane-containing epoxy crosslinked polymer networks have been compared with ionic salt catalyzed siloxane materials (Scheme 3). For the straightforward synthesis of siloxane-containing materials, a DGEBA epoxy resin was cured at 120°C with BAS in the presence of a series of catalysts.

Scheme 2. Proposed pathway for TBD-catalyzed siloxane exchange mechanism.
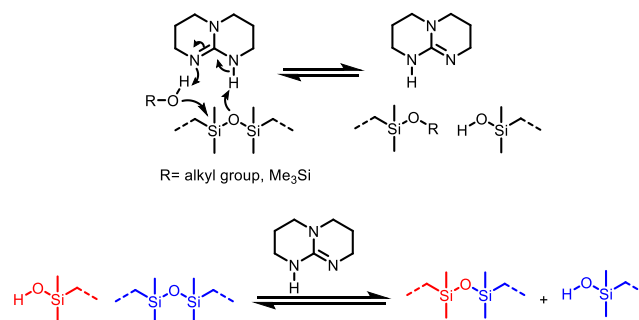
Following the literature,[29] TMAS was first investigated as a source of siloxide. The material obtained using this catalyst (entry 1, Table 2) showed slow dynamic characteristics upon compression molding (at 180°C) (Figure S2). However, TMAS is known to decompose thermally above 150°C, releasing trimethylamine.[29] Therefore, thermally more stable ionic bases such as potassium tert-butoxide (tBuOK), potassium trimethyl silanolate (SiMe3OK), and well-known non-ionic bases such as 7-methyl-1,5,7-triazabicyclo(4.4.0)dec-5-ene (MeTBD), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 4-dimethylamino-pyridine (DMAP), and TBD were explored in this study (Scheme 3). tBuOK is likely to deprotonate the secondary alcohol produced by the epoxy-amine reaction, creating an alkoxide to start the exchange, which is unlikely for siloxide.

Scheme 3. Exemplary network structure synthesized by DGEBA epoxy resin cured with BAS hardener (top). Different catalysts screened for the siloxane exchange (bottom)
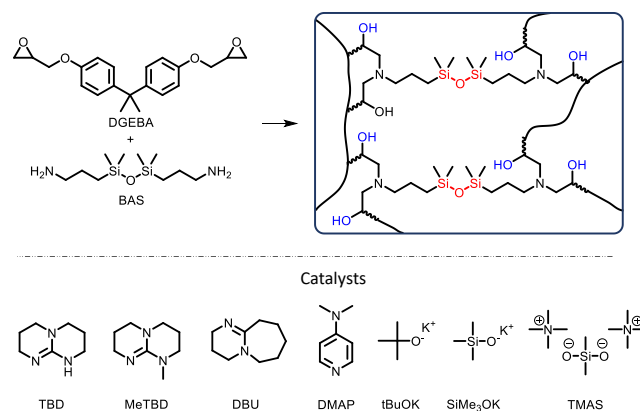
The synthesized crosslinked materials were typically ground and compression-molded in a temperature range between 180°C-220°C. This is much lower than the observed temperature for 5% weight loss (5% weight loss temperature, $T_{d-5\%}$ = 350°C), as determined by thermogravimetric analysis (TGA). Furthermore, the isothermal TGA exhibited only about 1% weight loss (for entry 13, Table 2) after one hour at 220°C under a constant flow of air or nitrogen (Figure S8). While the materials containing tBuOK, SiMe3OK, and TBD could be processed to transparent smooth plates, materials containing MeTBD, DMAP, and DBU showed no visible exchange during the compression molding process (powder was obtained after one hour). Interestingly, while TBD and MeTBD have similar basicity, MeTBD failed to catalyze the siloxane exchange. This further supports the proposed mechanism (Scheme 2) for TBD-catalyzed siloxane exchange, in which the N-H (of TBD) group is involved in the proposed pathway. While it has been

Table 2. Screening of different catalysts for the dynamic exchange in siloxane-containing materials.

Entry	Amine (eq)	Epoxy (eq)[a]	Catalysts	Catalyst (mol%)[b]	T_g[c] (°C)	Swelling degree[d] (%)	Soluble fraction[e] (wt%)	Processability[f]
1	1	1.5	TMAS	3	-[h]	-[h]	-[h]	Yes[i]
2	1	1.8	None	-[g]	-[h]	-[h]	-[h]	No[j]
3	1	1.5	None	-[g]	-[h]	-[h]	-[h]	No[j]
4	1	1.3	None	-[g]	-[h]	-[h]	-[h]	No[j]
5	1	1.5	tBuOK	3	-[h]	-[h]	-[h]	No[j]
6	1	1.5	tBuOK	6	68	-[h]	-[h]	Yes
7	1	1.5	SiMe₃OK	10	68	-[h]	-[h]	Yes[k]
8	1	1.5	MeTBD	6	-[h]	-[h]	-[h]	No[j]
9	1	1.5	DBU	6	-[h]	-[h]	-[h]	No[j]
10	1	1.5	DMAP	6	-[h]	-[h]	-[h]	No[j]
11	1	1.5	TBD	6	68	28	0.7	Yes
12	1	1.8	TBD	6	85	-[h]	-[h]	No[l]
13	1	1.8	TBD	10	85	15	1	Yes
14	1	2.0	TBD	10	95	-[h]	-[h]	No[l]

[a]One mole of siloxane amine can react with a maximum of two moles of DGEBA molecule. [b]With respect to the number of moles of the Si-O-Si functional group present in BAS. [c]Characterized by differential scanning calorimetry (DSC). [d]Swelling degree was measured in toluene over 24h. [e]Measured by Soxhlet extraction over 24 hours in toluene. [f]Compression molding for 1 hour at 220°C, except for entry 1 (180°C, 1h). [g]Not applicable. [h]Not characterized. [i]Minor cracks were present. [j]Samples did not heal during the typical compression molding time of 1h. [k]Minor surface cracks were present. [l]Samples had significant unhealed portions during the typical compression molding time of 1 hour.

reported that the temperature stability of TBD can be much improved by making use of protic ionic salts,[57] we could not observe a significant effect of potential TBD degradation at high temperatures on the material properties (*vide infra*).

Subsequently, we investigated the potential catalytic effect by the neighboring group participation for the siloxane exchange. Guan and coworkers reported a similar effect for the silyl ether chemistry, catalyzed by a γ-NH.[37] In our case, the BAS-compound, with two amino functionalities at the γ-position of the siloxane group, was strategically chosen as an amine hardener. Additionally, secondary hydroxyl groups, which were earlier shown to play a crucial role in the TBD catalyzed siloxane exchange, are formed after the reaction between amine groups and the epoxy resin. Upon compression molding, epoxy resins described under entries 2, 3, and 4, for which a catalyst was not used (Table 2), showed a lack of any dynamic exchange up to 220°C during compression molding (typically 1h). This is an indication that the internal catalysis by either amino or hydroxyl groups, as earlier observed for silyl ether-based materials,[37] is not significant for these siloxane-containing materials. This is again supported by the study on low molar mass compounds (entry 2, Table 1), which showed the absence of siloxane-exchange products when adding hydroxyl groups in the absence of TBD under the analyzed condition.

The epoxy materials exhibiting dynamic exchange, aided by different types of catalysts (entries 6, 7, 11, 13 of Table 2), were analyzed by rheology. Stress-relaxation measurements revealed that the TBD-catalyzed materials displayed the fastest exchange rate in comparison to epoxy materials containing tBuOK and SiMe₃OK (**Figure 3A**). Particularly, entry 13 (Table 2) with a TBD content of 10 mol% (with respect to the siloxane units) exhibited very fast stress relaxation, with a characteristic relaxation time τ* of only 5.6s at 220°C (fitted with Maxwell model of single exponential decay)[25] and activation energy of 87 ± 1 kJ/mol (**Figure 3B, 3C**). To the best of our knowledge, this is by far the fastest siloxane exchange ever reported.

To further characterize the proposed TBD-catalyzed exchange mechanism at the material level, frequency sweep experiments were conducted on entry 13 (Table 2). A constant shear storage modulus G' (at high frequencies), and a constant non-normalized relaxation modulus (at the start of measurements) are displayed at different temperatures (between 170°C and 220°C) during frequency sweep measurements and stress relaxation experiments respectively (Figure 4). These time sweep data (Figure S23) are consistent with a TBD catalyzed mechanism in which the total number of bonds remains constant during the exchange process and thus also strongly indicate that the siloxane material follows an associative pathway for the dynamic exchange in the investigated temperature window.

Then, we investigated if these materials hold the fast characteristic relaxation time over different mechanical recycling steps and thus if TBD continued to act as a catalyst after reprocessing. For this, the material (entry 13, Table 2.) was broken into pieces and compression-molded twice at 220°C (**Figure 4A**). After each step, the samples were characterized by stress relaxation experiments, differential scanning calorimetry (DSC), and dynamic mechanical analyses (DMA) (Figure S13). Besides the coloration of the materials over different recycling steps (see Figure S3), these materials displayed near-identical relaxation times of around 6 seconds (see Table 3, Figure S14, S15, S16) and showed similar T_g values around 85°C in DSC and DMA analysis (Figure S9). Additionally, DMA analysis (Figure S13) of the recycled samples showed a similar rubbery plateau,

meaning that no or minimal changes in crosslink density occurred after all reprocessing cycles at 220°C.
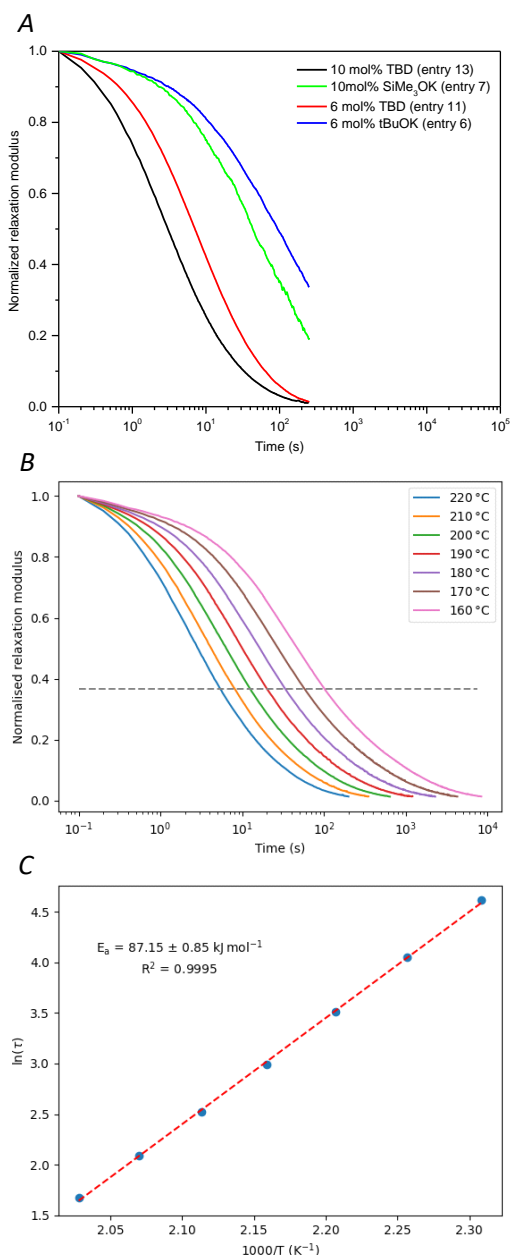

Figure 3. A) comparison of stress-relaxation times with different catalysts at 220°C. B) Normalized stress-relaxations of entry 13 (Table 2) at different temperatures. C) Arrhenius plot of entry 13.

Also the low soluble fraction (~1%, see Table 3) of these processed materials, an indication of a highly cured network, remained nearly identical, demonstrating again the stability of the material during the reprocessing cycles. The Soxhlet extraction, applied for the determination of the soluble fraction, was simultaneously used to check if TBD leaching could be observed. After an extraction experiment in toluene (30 hours), the ¹H NMR analysis of the evaporated sample did not show a detectable amount of TBD.
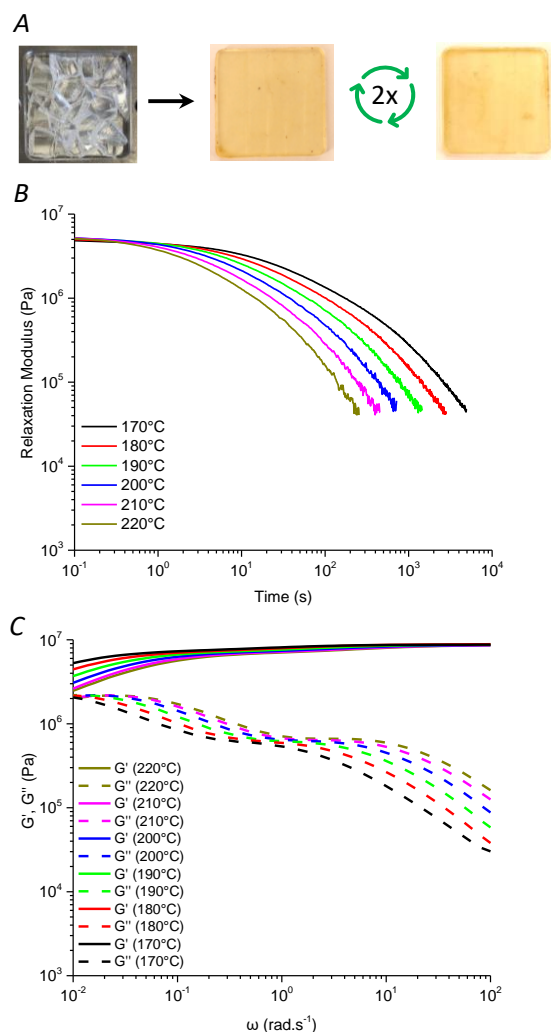

Figure 4. A) Mechanical recycling of siloxane- containing epoxy vitrimer (entry 13, Table 2) at 220°C through compression molding. B) Non-normalized stress-relaxation plot of R0 (Table 3) at different temperatures showing nearly constant relaxation modulus at early relaxation times. C) Frequency sweep experiments of R0 at different temperatures show nearly constant shear storage modulus (G') at higher frequencies.

Table 3. Mechanical recycling of a TBD-catalyzed vitrimer (entry 13) and material characterization after each reprocessing step.

Entry[a]	T_g^{DSC} (°C)	T_g^{DMA} (°C)	Soluble fraction[b] (wt%)	Swelling Degree[c] (%)	τ* (s)
1 (R0)	85	85	1	15	~ 6
2 (R1)	85	81	1	-[d]	~ 6
3 (R2)	85	83	1	11	~ 6

[a]Recycling steps [b]Measured by Soxhlet extraction over 24 hours in toluene. [c]Swelling degree was measured in toluene. [d]Not measured. All the samples were compression molded at 220°C for 40 min.

Fiber-Reinforced Vitrimer Composite

Because of those quite promising material properties in combination with the low viscosity of the used formulations, we

finally investigated the feasibility of FRC preparation using this vitrimer resin. Indeed, a very low viscosity resin, which remains low in viscosity throughout the manufacturing process, is a key factor for proper impregnation of the fibers in composite preparation using VARI, a widely used technique for the manufacturing of wind turbine blades for example. In fact, the vitrimer formulation chosen for the composite preparation (entry 13, Table 2) shows a low viscosity (300 mPa.s at 25°C, Figure S17), even after an hour of mixing. Such viscosity value is even lower compared to widely applied commercial regular epoxy resins yielding similar T_g values (see Figure S17). As larger composite components require a long production time (e.g., for larger composite wind turbine blades), having a low viscosity for a longer duration is even more interesting.[58]

This vitrimer resin mixture was used to impregnate a plain-woven glass fabric of 220g/m^2 (Interglas 92145, aero, FK144) in a [0°]$_8$ (8 layers of glass fabric with the main fabric direction (warp) parallel to the longitudinal direction of the specimens) stacking sequence using VARI (Figure S18).[59, 60] This resulted in a transparent vitrimer composite (8 layers) after curing at 120°C for 12 hours. Such an appearance allowed us to visually inspect the quality of the plate and successful impregnation of all fibers, proving the feasibility of manufacturing a fiber-reinforced vitrimer composite (FRVC) (**Figure 5**). As a proof-of-concept, small sections of the produced composite plate were cut and thermoformed, simply by heating the plates in a zigzag-shaped mold (Figure S19) at 180°C and 190°C with a pressure of 15 bar (Figure S20) and 30 bar (Figure S21) respectively for 20 minutes in the air. The absence of shear cracking through the thickness of the specimens after the 1st thermoforming cycle demonstrates the thermoforming capabilities of the vitrimer composite.
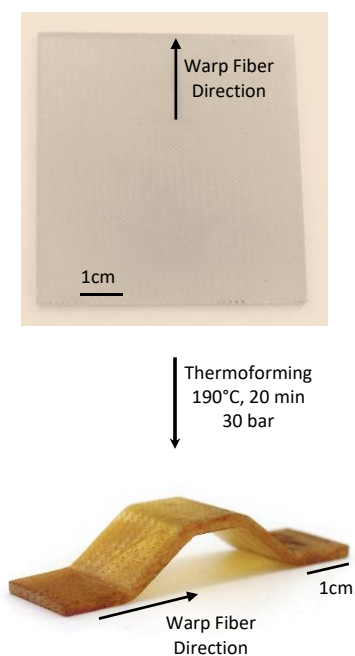

Figure 5. A small section of pristine siloxane-containing vitrimer composite (top). A thermoformed (190°C, 30 bar, in the air) section of siloxane-containing vitrimer composite (bottom).
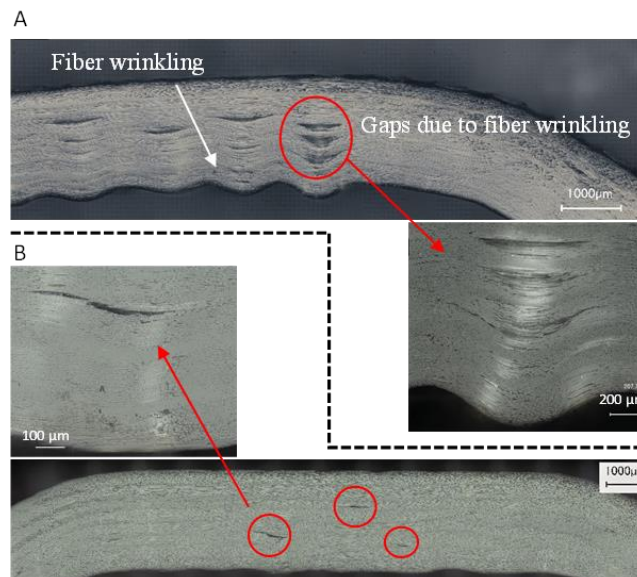

Figure 6. Microscopy images of a longitudinal section of thermoformed composite. A) A section of FRVC thermoformed at 180°C with 15 bar. B) A section of FRVC thermoformed at 190°C with 30 bar.

To further evaluate the quality of the thermoformed FRVC, microscopic images of a longitudinal section were analyzed (**Figure 6**). The composite specimen (A), thermoformed at 180°C with 15 bar of pressure, had quite a few microvoids and some fiber wrinkling was observed. Interestingly, the other specimen (B), thermoformed at 190°C with 30 bar of pressure, showed only very few minor microvoids, and the fiber wrinkling was greatly minimized. It should be noted that this fiber wrinkling is a general issue that was already observed when reshaping thermoplastic composites and can be affected by fabric weave patterns, as well as by lay-up sequence.[61-64] It is usually caused by the resistance of the reinforcement to take a given shape due to poor fabric drapability.[61, 62] Figure S24 shows the delamination and cracks of an epoxy-based thermoset composite that undergoes a similar treatment.

The avoidance of such fiber wrinkling and the full composite characterization will be part of an upcoming study. Nonetheless, this thermoforming experiment is already a first indication that the industrially compatible manufacturing of reshapable vitrimer composites is possible with this commercially available vitrimer formulation.

CONCLUSION

In this study, the siloxane exchange mechanism has been investigated with different catalysts and in the presence of hydroxyl groups. Interestingly, a siloxane exchange pathway catalyzed by TBD in the presence of a hydroxyl group was found. This exchange is much faster than siloxide or alkoxide catalyzed siloxane exchange routes reported so far. Utilizing this exchange pathway in combination with more than half-a-century old industrially relevant epoxy amine chemistry, TBD- catalyzed siloxane-containing epoxy vitrimers were synthesized. It has been demonstrated that the synthesized dynamic materials can be mechanically reprocessed at least three times while maintaining fast stress relaxation times in the order of seconds and T_g-values around 85°C. Furthermore, a low viscosity vitrimer resin formulation was obtained from commercially available compounds to prepare a glass fiber-reinforced vitrimer

composite. A section of the FRVC has been thermoformed into a new shape, which allows envisaging a second life for these composite materials instead of burying or incinerating them.

EXPERIMENTAL SECTION

Chemicals

Triazabicyclodecene (98%), Bisphenol A diglycidyl ether (DER332, epoxy equivalent weight 176 g/mol), was purchased from Sigma Aldrich. Potassium tert-butoxide (98%) and 1-pentanol (99%) was purchased from Acros Organics. 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyl disiloxane (95.0%) was purchased from Manchester Organics. 7-methyl-1,5,7-triazabicyclo(4.4.0)dec-5-ene (>95.0%), 4-dimethylaminopyridine (>99.0%), 1,8-diazabicyclo[5.4.0]-undec-7-ene (>98.0%), and 1,3-divinyltetramethyldisiloxane (>98%) was purchased from TCI Europe. Potassium trimethyl silanolate (95%), tetramethylammonium siloxanolate was purchased form Gelest. $CDCl_3$ (99.8%) was purchased from Eurisotop. Acetonitrile (99.9%) was purchased from Chem-Lab.

Instruments

Nuclear magnetic resonance (NMR) analyses were conducted on a Bruker DRX500 (500 MHz) NMR spectrometer. The NMR spectra were measured (unless specified otherwise) in $CDCl_3$, and chemical shifts (δ) are presented in parts per million (ppm) relative to $CDCl_3$ as the internal standard. Liquid chromatography-mass spectrometry (LCMS) data were measured on an Agilent Technologies 1100 series LC/MSD system equipped with a diode array detector and single quad MS detector (VL) with an electrospray source (ESI-MS). Acetonitrile solution of the compounds was used to record LCMS spectra and was analyzed using ACD/Spectrus software. Thermogravimetric analyses (TGA) were performed on a Mettler Toledo TGA/SDTA 851e instrument. Dynamic thermogravimetric measurements were performed under a nitrogen atmosphere with a heating rate of 10°C/min from 25°C to 800°C. All isothermal thermogravimetric measurements were performed under both a nitrogen and oxygen atmosphere at 220°C, and 190°C for 60 min with a heating rate of 10°C/min. A Mettler Toledo instrument 1/700 was used to perform differential scanning calorimetry (DSC) measurements under a nitrogen atmosphere with a heating rate of 10°C/min and a cooling rate of 10°C/min. Measurements were performed from −50°C to 200°C or 0°C to 200°C. Stress-relaxation tests were performed using an Anton-Paar MCR 302 rheometer with a plate diameter of 8 mm and on samples having a diameter of 8 mm and a thickness of about 2 mm. DMA analyses were performed using a TA Instrument Discovery DMA850 analyzer in an oscillation/tension mode with 0.1% strain and frequency of 1Hz. The samples were heated with a heating rate of 3 °C/min.

Synthesis of polymer networks (typical procedure)

First, the hardener (BAS) and the catalyst (powdered for solid catalyst) were mixed together using a speedmixer (DAC 150.1 FVZ) for two minutes at 3500rpm. In case these two compounds did not mix well, they were heated at 60°C for 5 minutes and then put back in the speedmixer for another 2 min at 3500rpm. In a second step, the epoxy resin was added to the speedmixer and mixed for 2 min at 3500rpm. Finally, the resulting sample was heated for a couple of hours at 60°C in a normal oven prior to post-curing at 120°C in a vacuum oven for 14 hours. See Table 2 for ratios of each compound.

Material reprocessing

To reprocess the network, the polymer sample was broken into pieces (ground by a grinder or cut into small pieces by a mechanical cutter tool) and placed into a two-piece square-shaped steel mold (50 mm x 50 mm) for compression molding. This mold was closed and placed in a preheated hydraulic press (hot press) for two minutes under 1 ton of weight. The usual processing temperature was 220°C (except for entry 1, Table 2 which was processed at 180°C). The weight was then increased to approximately 7t and kept constant, typically for an additional 40 min. TBD catalyzed samples (entry 13, Table 2) in Figure S1 were pressed in a mold (30 mm x 15 mm) at 220°C (4 ton) for 5 minutes and 10 minutes respectively, demonstrating that formulations with the fast dynamic exchange can be processed at a much shorter period of time than a typical compression molding time. The molds were allowed to cool down a bit and samples were removed.

Network characterization

Swelling degree

A piece of approx. 70-75mg of processed material was weighed, then immersed in 5 mL of toluene at room temperature for 48 hours. The swollen material was then weighed and the swelling degree was calculated as follows:

(Eq. 1) $Swelling\ degree\ (\%) = \frac{m_s - m_i}{m_i} \times 100$ in which m_s = swollen mass and m_i = initial mass.

Soluble fraction

Another piece of approx. 70-75mg material from the same processed sample was weighed, subjected for Soxhlet extraction in toluene for 24 hours, dried under vacuum at 110°C for 72 hours, and weighed again. The soluble fraction was then calculated as follows:

(Eq. 2) $Soluble\ fraction\ (\%) = \frac{m_i - m_d}{m_i} \times 100$ in which

m_d = mass after drying and m_i = initial mass.

TBD leaching experiment

This experiment was performed with 1.339g of processed material in a similar way as for the determination of the soluble fraction, except that toluene was concentrated under vacuum, and the concentrate was subjected to ^{1}H NMR analysis in $CDCl_3$.

Rheology

Unless specified, the stress relaxation experiments were performed using a normal force of 1N at a frequency of 1Hz, and a strain of 0.25% (determined by amplitude sweep experiments) under N_2. Amplitude experiments were carried out at a constant temperature (160°C) and constant normal force (1N) with variable shear strain from 0.01% to 10%. Time sweep measurements were performed with 0.25% of shear strain. Frequency sweep experiments were conducted with a normal force of 1.5N, a constant shear strain of 0.25%, and a variable angular frequency of 100Hz to 0.01Hz under N_2. Viscosity was measured using two parallel 25mm plates with 1mm gap at a shear rate of $100s^{-1}$.

Preparation of glass fiber-reinforced vitrimer composite

For the preparation of the composite plate, eight layers of the glass fabric reinforcement were stacked on a flat glass mold, all oriented with the warp direction parallel to the longitudinal direction of the plate. This layup sequence is referred to as $[0°]_8$ stacking sequence. After this, the necessary consumables of the VARI process, illustrated in Figure S18 A, were put in place. Once the stacking was completed and the bag was sealed, the

vacuum was applied on the set-up and was kept as such during the mixing of the vitrimer formulation (see Table S1). After mixing the vitrimer components, it was degassed for 10 mins prior to the infusion. The infusion process was completed in 3-5 mins as a result of the very low viscosity of the vitrimer formulation, making this process an ideal choice (infused plate Figure S17 B). After infusion, the plate was pre-cured under vacuum for 3h at 60°C, followed by a cure for 12h at 120°C, which ensured that the composite plate reached the targeted T_g of 85°C, as verified through DSC experiments (Figure S11).

Thermoforming of composites

The thermoforming of the composite samples was achieved by simply applying heat and pressure on the samples in a home-made, constricted mold shape. The desired mold shape, which in this case was a zigzag-shaped aluminum mold (Figure S18), was attached to an Instron 5800R tensile testing machine and was enclosed in a heating chamber. After this, the heating chamber and the mold were pre-heated at the desired temperature, and each specimen was positioned in the open mold and was held at the desired temperature for 10 mins to reach equilibrium, prior to initiating the thermoforming cycle. Through the machine software, the closing velocity of the mold and the applied force were controlled and recorded (Figure S19 and Figure S20 graph of thermoforming data). When the mold was fully closed, the full load selected for each specimen was applied. For each specimen after first contact, it took 10 mins for the mold to fully close and a full load and temperature were held for about another 10 mins. Taking into consideration the kinetics and stress relaxation data of the vitrimer matrix, the amount of time was estimated for the specimen to result in the given shape. During the 10 mins, the load value was slightly decreasing because the material was relaxing its stress. Thus, small adjustments were made in displacement to maintain the applied load constant, creating small spikes in the pressure graph over time shown in Figure S19 and Figure S20. Finally, in order to stabilize the specimens in this given shape, they were let to air-cool in a closed mold until 40°C, which was below the vitrimer's T_g value. Then the mold could be opened safely, and each specimen was removed.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. NMR spectra, calculations, DSC and TGA thermograms, LC-MS spectrum, DMA data, stress-relaxation data, viscosity data, and plot of thermoforming parameters data are included in the SI (PDF).

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

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

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TOC-figure

Fast reprocessable siloxane-based vitrimers and composites