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COMMUNICATION

Streamlined concept towards spatially resolved photoactivation of dynamic transesterification in vitrimeric polymers by applying thermally stable photolent bases

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David Reisinger,^a Kurt Dietliker,^b Marco Sangermano^c and Sandra Schlögl^{*a}

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Herein, we describe a convenient approach for a locally controllable photoactivation of vitrimeric properties in a covalently crosslinked thiol-epoxy network. In contrast to previous work, the applied photolent catalysts benefit from superior solubility properties, adequate curing characteristics in the non-activated state (the addition of a supplementary catalyst is not required) and an excellent thermal stability.

Vitrimers exhibit a covalently crosslinked network structure comparable to common thermosetting polymers. Nevertheless, they are able to reorganise their topology by dynamic associative exchange reactions, when the onset temperature for the underlying rearrangement mechanism, termed topology freezing transition temperature (T_v), is exceeded.^{1,2} Macroscopically visible as a glass-like fluidity according to the Arrhenius law, vitrimers are malleable, weldable and recyclable like thermoplastic polymers in spite of their permanent organic network structure. Inspired by Leibler et al., various vitrimeric polymers capable of rearranging their three-dimensional covalently crosslinked network structure by thermally triggerable dynamic transesterification were developed.^{3,4} On account of the diverse occurrence of ester links along with hydroxy moieties and different options for catalysis, thiol-ene, thiol-epoxy, thiol-acrylate, acrylate homopolymerised and polylactide based network structures are reported in the literature.^{5,6} However, a controlled and moreover spatially resolved onset of the exchange reactions at elevated temperatures, i.e. well above T_v , is challenging to achieve. One of the first concepts for realising a spatially resolved onset of dynamic transesterification was developed by Ji et al. in 2014. Using a carboxylic acid-cured epoxy composite, they exploited

the photothermal effect of carbon nanotubes for local heat generation by means of an IR laser evoking localised healing and welding.⁷ Although in such a system, controllability is lost at application temperatures above T_v .^{7,8}

Bowman and coworkers demonstrated a convenient approach for the light-mediated activation of elastomeric thioester-based vitrimers through the introduction of a photolent base (PLB) catalyst. By means of stress relaxation studies carried out at room temperature, they were able to show the controlled photoactivation of base-catalysed thiol-thioester exchange reactions.⁹

Recently, our research group extended this approach to the far more versatile transesterification mechanism.^{10,11} In one of our studies, we were able to locally control topological rearrangements at elevated temperatures, i.e. 90 °C, through the UV-mediated photocleavage of a thermally stable PLB catalyst. However, in its non-activated state, the photolent catalyst was suffering from a low solubility and was not able to catalyse the curing reaction in thiol-epoxy resins. Thus, the addition of a free base was required to accelerate the curing reaction, but after curing had to be removed again from the thiol-epoxy network under vacuum.¹⁰

Herein, two new photolent transesterification catalysts are introduced, which overcome these disadvantages, and allow an undoubtedly straightforward manufacturing strategy for covalently crosslinked polymers suited for spatially resolved photoactivation of vitrimeric properties. Furthermore, we will highlight that an undesired purely thermal cleavage of the new PLB can be entirely avoided.

Results and discussion

Regarding network formation, we decided to take advantage of the so-called click chemistry. This set of reactions is characterised by high chemical yields, even under mild reaction conditions, and an insensitivity against water and oxygen.¹²

In particular, we selected the amine base-catalysed nucleophilic ring-opening reaction of epoxides with thiols resulting in the

^a Polymer Competence Center Leoben GmbH, Roseggerstrasse 12, 8700 Leoben, Austria. E-mail: sandra.schloegl@pccl.at

^b SCD Dr. Sommerlade Chemistry Design GmbH, Rheinfeldener Straße 27, 79395 Neuenburg am Rhein, Germany.

^c Politecnico di Torino, Department of Applied Science and Technology, Corso Duca degli Abruzzi 24, 10124 Torino, Italy.

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formation of β -hydroxythioether links (Scheme S1 in ESI).¹³ Since no ester moieties are generated during this process, it is crucial to introduce them by an appropriate selection of the monomeric building blocks. The presence of both functionalities, i.e. hydroxy and ester groups, is a fundamental requirement for a network rearrangement by dynamic transesterification (Fig. 1).^{3,4} We used bisphenol A diglycidyl ether (DGEBA) as the epoxy monomer while ethylene glycol bis-mercaptoacetate (EGMA) and pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) were used as thiol components (chemical structures are shown in Fig. 2a). All resin formulations in this study were prepared with a stoichiometric ratio of epoxy to thiol functions. Beyond that, the thiol functionalities were distributed evenly between EGMA and PETMP.

As photolabile catalysts two derivatives of the strong amidine base 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, pK_a of the conjugate base in water is 13.4)¹⁴ were examined. One compound, SCD-PLB 090, was kindly provided by SCD Chemistry Design GmbH, the other derivative has been used in our previous work.¹⁵ The chemical structures of these photolabile compounds, termed PLB-090 and PLB-1193 in this study, are shown along with the corresponding UV-mediated cleavage mechanism in Fig. 2b.^{16,17}

However, it must be noted that these photolabile catalysts suffer from a relatively poor spectral sensitivity due to the absence of chromophores absorbing in the near UV-A/Vis part of the spectrum. Consequently, 2-isopropyl thioxanthone (ITX) exhibiting a distinct absorption band from 325 to 410 nm was added as photosensitizer (Fig. 2c), which is a common approach for shifting the absorption window of PLBs or other photoinitiators to the visible light region.^{10,17,18}

The thiol-epoxy resin formulations, termed TE-PLB-090 and TE-PLB-1193, contain 5 mol% of the respective PLB relative to the epoxy functions. If additionally ITX is incorporated

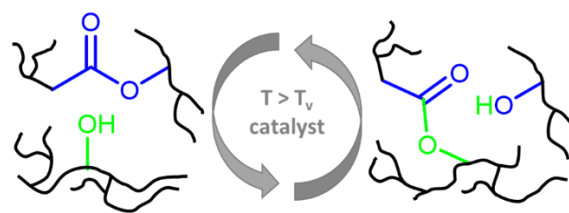


Fig. 1 Topological rearrangement of a covalently crosslinked network by dynamic transesterification.

(equimolar to the concentration of the PLB), the sample names are extended to TE-PLB-090-ITX and TE-PLB-1193-ITX, respectively. Under dark conditions, pot-lives of about 90 min can be obtained at room temperature. The nucleophilic ring-opening reaction of epoxides with thiols, catalysed by the tertiary amine in the uncured PLBs, however, is significantly accelerated at elevated temperatures. FTIR-ATR measurements were performed to follow the curing kinetics of unirradiated TE-PLB-090-ITX and TE-PLB-1193-ITX formulations at 70 °C (Fig. S1a and b in ESI). In compliance with the desired formation of β -hydroxythioether links, a broad hydroxy band (3425 cm^{-1}) arises simultaneously with the disappearance of the thiol (2565 cm^{-1}) and the epoxy band (915 cm^{-1}). Already after 8 to 10 minutes the thiol groups are entirely consumed, while the hydroxy peak reaches its maximum.

Compared to the photolabile quaternary ammonium salt composed of N-protonated 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as the cationic and tetraphenylborate as the anionic part deployed in our preceding study, PLB-090 and PLB-1193 provide considerable advantages in terms of sample preparation and curing. Caused by the low basicity of the quaternary ammonium borate salt, pyridine had to be added in the previous experiments as an additional base catalyst to gain reasonable curing times even at elevated temperatures.¹⁰ In addition, the

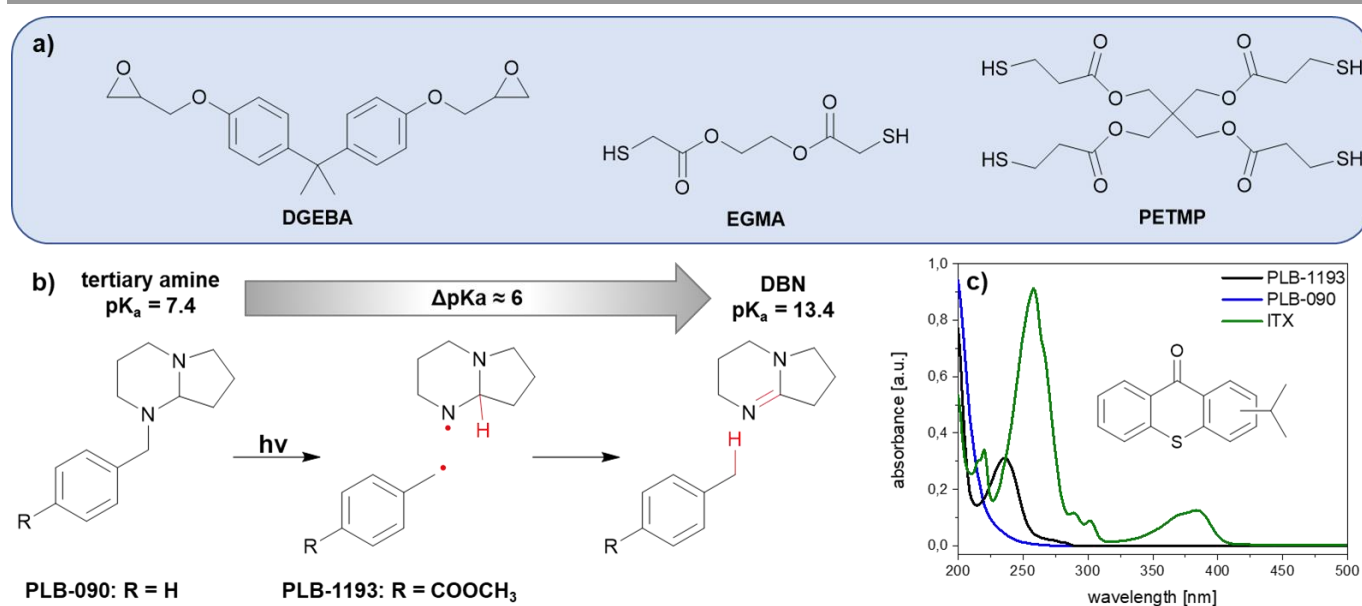


Fig. 2 a) Chemical structures of the monomers used for the preparation of covalently crosslinked thiol-epoxy cured networks containing both hydroxy and ester moieties. b) UV-mediated cleavage mechanism of the photolabile base catalysts PLB-090 and PLB-1193 including the related change in pK_a . c) UV-Vis absorption spectra of PLB-090, PLB-1193 and ITX (chemical structure shown as an inset) recorded at a concentration of 2×10^{-5} mol/L from 200 to 500 nm.

pyridine served together with acetonitrile as a solvent, since quaternary ammonium salts containing tetraphenylborate are suffering from a low solubility in a wide variety of commonly used monomeric building blocks.^{10,19} To avoid bubble formation at elevated temperatures in the fully cured material, pyridine and acetonitrile had to be gradually removed during curing by a lengthy vacuum treatment before the partially cured sample could be brought into its final shape.¹⁰

In contrast to the non-basic borate salt, the photolabile tertiary amine of PLB-090 and PLB-1193 in its uncleaved initial, i.e. N-benzylated state, exhibits a pK_a of about 7.4.¹⁴ This degree of basicity is ideal to equip our thiol-epoxy resin formulations with an adequate thermal curing characteristic, i.e. a reasonable pot-life at room temperature as well as a short curing time at elevated temperatures (70 °C). Moreover, PLB-1193 and especially PLB-090 are well soluble in the employed thiol-epoxy system without the need of any additional solvents. Thermal curing yields a highly optically transparent network structure, which is crucial for the subsequent local activation of the PLB by UV exposure.

To investigate the controlled activation of the base-catalysed dynamic transesterification, i.e. the vitrimeric properties, at elevated temperatures, stress relaxation measurements were performed using thin free-standing foils cured in a 0.5 mm thick mould. First, the behaviour of TE-PLB-090-ITX and TE-PLB-1193-ITX was examined prior to and after UV irradiation (424 J/cm² applied at 60 °C) (Fig. 3). Detailed information on the irradiation source used, including spectral intensity distribution, is provided in the ESI. For the unexposed test specimens of both samples, only a minor relaxation to about 80 % of the initial normalised relaxation module ($G_{(t)}/G_0$) can be observed after 4000 s. This slight decrease can be mainly attributed to the residual basicity of the photolabile tertiary amine in its uncleaved state, which is already able to catalyse dynamic transesterification to some extent, although at a much lower rate compared to amidine bases. In contrast, UV-irradiated samples show a distinctive stress relaxation caused by the cleavage of the photolabile base, i.e. the release of DBN as a particularly active transesterification catalyst. Topological rearrangements against the applied force lead to an immediate drop in ($G_{(t)}/G_0$) to about 20 % after 4000 s. TE-PLB-1193-ITX

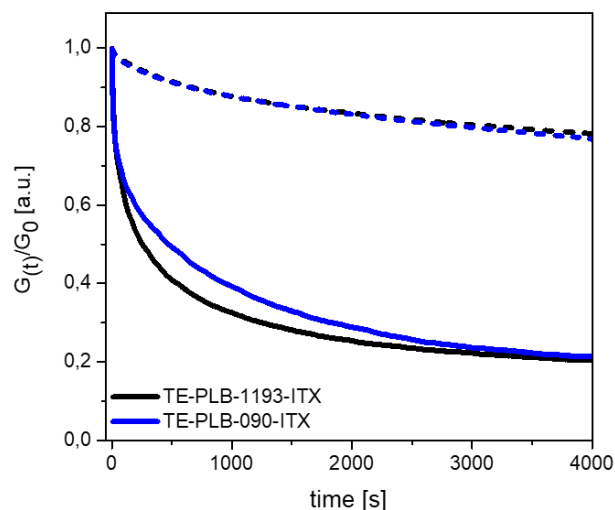


Fig. 3 Normalised stress relaxation curves conducted at 80 °C for TE-PLB-1193-ITX and TE-PLB-090-ITX before (dashed lines) and after UV irradiation with 424 J/cm² applied at 60 °C (solid lines).

reaches this plateau value faster because of the more pronounced sensitizing effect attributed to the larger overlapping area in the UV-Vis spectra (Fig. 2c).

In the following, stress relaxation measurements were performed in a temperature range from 70 to 100 °C on specimens of TE-PLB-090-ITX and TE-PLB-1193-ITX that had been UV-irradiated (424 J/cm² applied at 60 °C) in advance. Towards higher temperatures, generally an increase in the stress relaxation rate caused by an accelerated rearrangement process of the network against the applied force can be observed (Fig. 4a and b). Specifically, a temperature dependence of the characteristic relaxation time (τ) in agreement with the Arrhenius law represents one of the most distinctive features of vitrimers. In the associated equation, $\tau(T) = \tau_0 \exp(E_a/RT)$, E_a is the activation energy and R the universal gas constant. As the decrease in ($G_{(t)}/G_0$) can be described by a generic exponential behaviour, i.e. $G_{(t)}/G_0 = \exp(-t/\tau)$, the experimentally measured relaxation time at a decrease of ($G_{(t)}/G_0$) to $1/e$ (37 %) equals τ . Plotted against ($1/T$) in a semilogarithmic scale, the characteristic

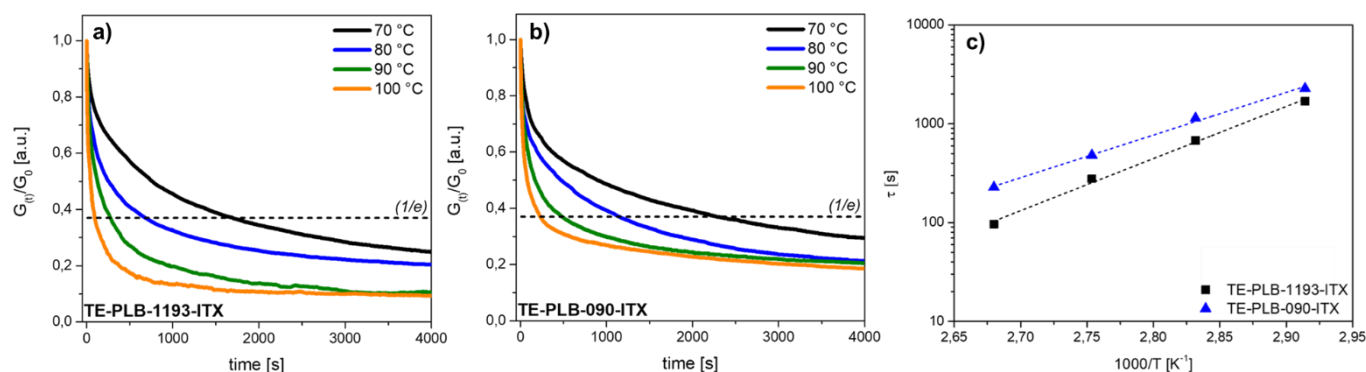


Fig. 4 Stress relaxation data collected from UV irradiated specimens (424 J/cm² applied at 60 °C) of a) TE-PLB-1193-ITX and b) TE-PLB-090-ITX in a temperature range from 70 to 100 °C in 10 °C increments. c) Arrhenius plots of the corresponding characteristic relaxation times obtained at a decrease of the respective normalised relaxation modulus to $1/e$.

relaxation times obtained in this way fit to a linear trend (Fig. 4c). Thus, an Arrhenius-type temperature dependence can be confirmed, which indicates a globally constant, i.e. temperature independent, network connectivity as it is typical for vitrimeric associative exchange mechanisms like dynamic transesterification.^{1,2,20}

The effect of ITX as a photosensitizer was studied by comparing the stress relaxation properties of a sensitised (TE-PLB-1193-ITX) and a non-sensitised (TE-PLB-1193) sample after different doses of UV irradiation (Fig. 5). For TE-PLB-1193, a decrease in $(G_{(t)}/G_0)$ to about 75 % is observed at a UV irradiation dose of 85 J/cm², which corresponds to an additional relaxation of only about 5 % compared to the reference. A fivefold increase in the UV irradiation dose to 424 J/cm² affects the behaviour of $(G_{(t)}/G_0)$ to a minor extent (decrease to 65 % after 4000 s). This points to the fact that the penetration depth of the short-wave UV light required for activation (Fig. 2c) is severely limited. The sensitised sample, containing 5 mol% ITX relative to the epoxy functions (TE-PLB-1193-ITX), however, already shows at a UV irradiation dose of 85 J/cm² a decrease in $(G_{(t)}/G_0)$ to about 45 % after 4000 s. In this case, a UV-irradiation dose of 424 J/cm² significantly enhances the stress relaxation (decrease in $(G_{(t)}/G_0)$ to about 20 % after 4000 s). The results confirm that ITX is able to improve the activation properties of our material substantially by extending the absorption window to the visible light region. Thus, considerably more photons can be absorbed and the penetration depth can be increased.

Beside the efficient UV-mediated release of a strong base, a high thermal stability of the PLB catalyst is crucial to avoid an undesired onset of dynamic transesterification at elevated temperatures. On that account, thermogravimetric analysis (TGA) under nitrogen atmosphere was performed. The onset temperature for thermal decomposition (defined as a mass loss of 5 %) can be determined for PLB-1193 and PLB-090 at 240 and 210 °C, respectively, which confirms a fundamentally high thermal stability (Fig. S2 in ESI).

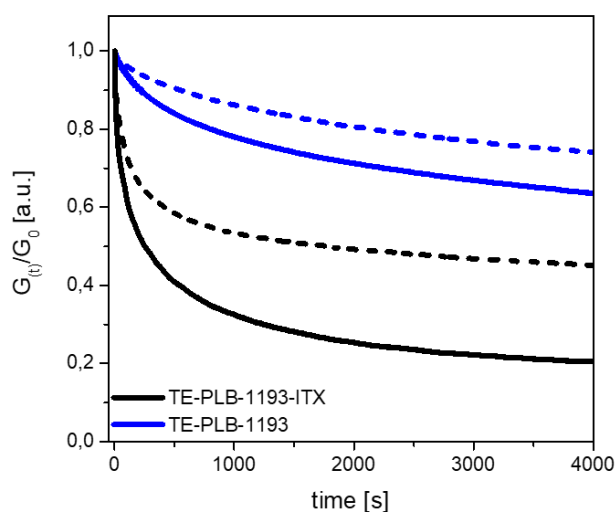


Fig. 5 Stress relaxation measurements performed at 80 °C for investigating the effect of ITX on the UV-mediated base release in TE-PLB-1193-ITX and TE-PLB-1193 at UV irradiation doses of 85 J/cm² (dashed lines) and 424 J/cm² (solid lines).

Moreover, stress relaxation measurements at 80 °C were performed with unirradiated but heat-treated specimens of TE-PLB-090-ITX and TE-PLB-1193-ITX to confirm the thermal stability also within a polymeric thiol-epoxy matrix (Fig. 6).

For heat treatment (10 min at 180 °C or 10 min at 250 °C), the specimens were clamped between two glass slides in order to prevent oxidation. Generally, no major differences can be observed between TE-PLB-090-ITX and TE-PLB-1193-ITX. The samples heat-treated for 10 min at 180 °C show a slight decrease in $(G_{(t)}/G_0)$ within the range of 80 to 85 % after 4000 s, which is comparable to the non-heat-treated reference samples (Fig. 3). On the other hand, the heat treatment for 10 min at 250 °C leads only to a limited stress relaxation, i.e. a decrease in $(G_{(t)}/G_0)$ to about 92 % after 4000 s. As indicated by TGA, this considerable reduction in the stress relaxation rate can be explained by the degradation of the photolabile tertiary amine at 250 °C. However, the degradation process takes place in a way impeding the release of free DBN. This behaviour represents a substantial add-on compared to the photolabile quaternary ammonium salt used in our last study that thermally decomposes categorically under release of the free base catalyst.^{10,19} By using the PLBs presented in this study, an undesirable thermally initiated onset of dynamic transesterification can be prevented at any temperature.

To determine the glass transition temperature (T_g) of our network, UV-irradiated TE-PLB-1193-ITX (424 J/cm² applied at 60 °C) was analysed by differential scanning calorimetry (DSC) (Fig. S3 in ESI). From the first heating cycle a T_g of 30 °C can be determined. The 10 °C higher T_g in the second heating cycle is common for transesterification-based vitrimers. During the topological rearrangement of the crosslinked network structure additional hydrogen bonds are formed leading to an overall increase in T_g .^{6,21} For demonstrating a locally controlled network rearrangement by the spatially resolved onset of vitrimeric properties, i.e. dynamic transesterification, a reshaping experiment was performed (Fig. 7). As a first step,

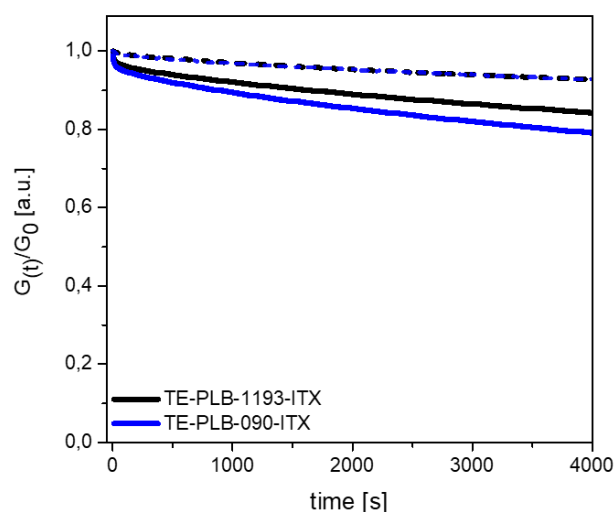


Fig. 6 Stress relaxation curves conducted at 80 °C using heat-treated specimens of TE-PLB-090-ITX and TE-PLB-1193-ITX. Comparison of two different heat treatment protocols: 10 min at 250 °C (dashed lines) and 10 min at 180 °C (solid lines).

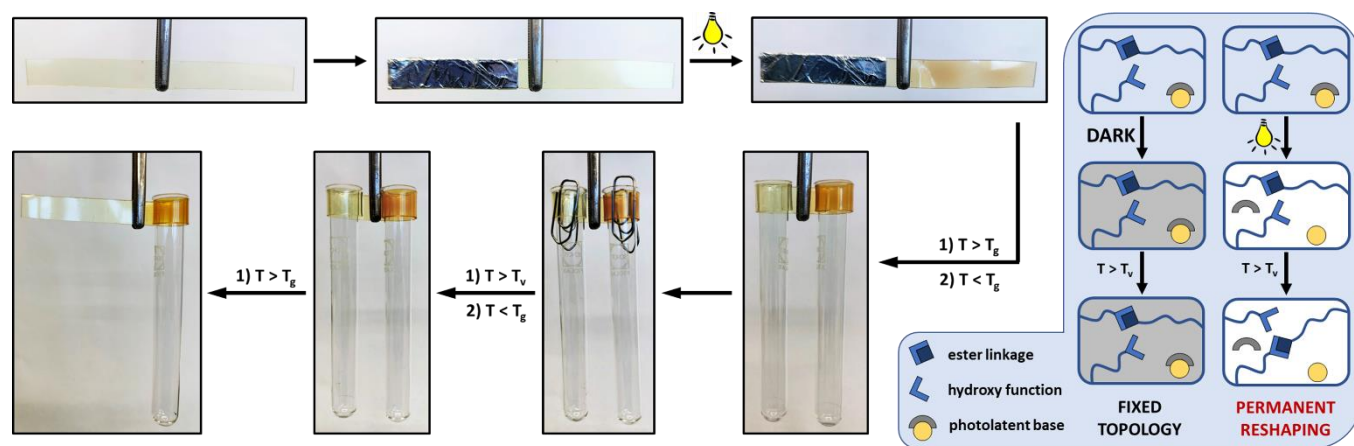


Fig. 7 Photographs monitoring the locally controlled permanent reshaping process of a rectangular test specimen by the spatially resolved onset of vitrimeric properties, i.e. dynamic transesterification, induced by the UV-mediated cleavage of a photolabile base catalyst.

one half of a rectangular TE-PLB1193-ITX test specimen was UV-irradiated (424 J/cm^2 applied at 60°C) to trigger the spatially resolved cleavage of PLB-1193 and the associated release of DBN as a highly active base catalyst. Subsequently, the test specimen was heated above T_g (45°C) to be able to grip two test tubes. The obtained circular shape of the gripping arms was fixed by four paper clips and the whole resulting setup was heated in an oven (65 min at 80°C). Throughout this heating step dynamic transesterification catalysed by DBN takes place in the UV-irradiated gripping arm, which leads to a reconfiguration of the network topology against the applied force, or rather into the circular shape. Once the test specimen cooled down to room temperature, i.e. below T_g , the paper clips were removed to obtain the gripper self-retaining in its closed state. By heating the specimen to 45°C for 10 min, i.e. above T_g , the unexposed gripping arm opened and returned to its flat position, since the stretched covalently crosslinked network moves back to the entropically more favourable initial state defined during curing. The UV-irradiated gripping arm, however, is able to retain its closed circular state due to a permanent rearrangement of the covalently crosslinked network by the base catalysed dynamic transesterification. This behaviour clearly illustrates the feasibility of activating vitrimeric properties locally in the material by UV irradiation.

Conclusions

In conclusion, an in several aspects optimised strategy for the efficient manufacturing of thiol-epoxy thermosets equipped with spatially resolved photoactivatable vitrimeric properties has been successfully demonstrated. The three-dimensional covalently crosslinked material is capable of undergoing dynamic transesterification in a controlled manner by the UV-mediated cleavage of a photolabile base catalyst, i.e. the release of a strong amidine base. Compared to our preceding study using an UV-cleavable ammonium borate salt, the photo-protected transesterification catalysts presented in this work offer several advantages in terms of excellent solubility properties

and adequate thermal curing characteristics in the non-activated state due to their covalently attached non-bulky protection groups maintaining a moderate basicity. Even at temperatures well above the topology freezing transition temperature, the controlled and spatially resolved UV-mediated onset of base-catalysed dynamic transesterification is confirmed by stress relaxation studies and the introduction of local permanent shape changes in a free-standing test specimen. Moreover, it has been highlighted that an undesired purely thermally induced release of the base catalyst can be entirely excluded. The commercial availability of the employed photolabile catalysts further enables an important step towards the technical application of locally controlled photoactivatable vitrimer systems.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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