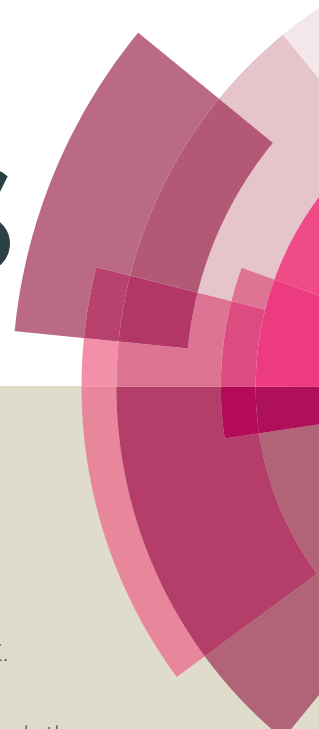


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Shape memory epoxy vitrimers based on DGEBA crosslinked with dicarboxylic acids and their blends with citric acid

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Thermosetting polymers were synthesized from a commercial epoxy resin (diglycidyl ether of bisphenol A, DGEBA) and a tricarboxylic (citric, CA) and different dicarboxylic (sebacic, SA and glutaric, GA) acids. Crosslinking of DGEBA-SA and DGEBA-GA systems was achieved by using an epoxy excess that was homopolymerized after consuming all the acid groups. It was found that the material properties depend on the diacid length and on the epoxy excess and that, with the proper formulation, vitrimers with T_g values ranging from 51°C to 62°C, and a high rate of stress relaxation (less than 1 h at 160°C to achieve 63% of relaxation) could be obtained. Notably, using a mixture of tri-functional CA with SA allowed to reduce the epoxy excess while keeping a high T_g value and speeding up the stress relaxation. Three of the formulations were selected and their shape memory performance was studied. Good shape fixity and shape recovery ratios (>99%) were obtained, indicating a good shape memory performance overall. These properties can be used to create different permanent and temporary shapes on a thermosetting polymer obtained from widely available and affordable raw materials.

Introduction

Shape memory epoxies and their nanocomposites are receiving increasing interest due to their excellent mechanical and thermal properties, very good shape fixing and recovery and their versatility to place the glass transition temperature (T_g) in a convenient temperature range.^{1–29} In a typical case, a temporary shape is produced at temperatures above T_g by exerting a force. This shape is fixed by cooling below T_g while keeping the force. The initial shape is recovered by removing the force and heating again above T_g . Alternatively, keeping the temporary shape during the second heating stage enables the material to behave as a force actuator. Several practical applications were devised for both types of responses. In recent years, new formulations were developed including blends and nanocomposites of different nature that expanded the potential applications of shape memory epoxies. Examples are the possibility to produce remote activation by alternating magnetic fields, electrical currents or light irradiation,^{6,13–16,18} materials with multiple shape memory behavior,^{14,16,17,21,26} or materials exhibiting desired combinations of high strengths and elongations.^{5,9,24,25,23}

Leibler and co-workers recently introduced the concept of vitrimers

as a new class of cross-linked polymeric materials exhibiting an interchange of covalent bonds above a temperature T_v (located above T_g).^{30–32} The importance of this new type of cross-linked polymers is that the behaviour above T_v makes it possible their self-healing and recycling, and the relaxation of residual stresses. Shape memory materials based on vitrimers enable producing complex temporary shapes outside a mould. This is simply achieved by generating the permanent shape at a suitable temperature above T_v for the necessary period of time to erase the stress.^{30,31,33} This permanent shape is fixed by cooling below T_v and can be used as the starting point to generate temporary shapes in the temperature range located between T_g and T_v . The use of vitrimers can also provide a flexible strategy to achieve multishape memory effect. Layers of premade epoxy vitrimers with different thermal transitions self-assemble through covalent bonds by hot-pressing at a temperature above T_v . This provides an easy way to get spatial control of the shape memory of 3D structures.³⁴ Although many different chemistries were developed to generate vitrimers,³⁵ the focus of this study is placed on the same chemistry explored by Leibler and co-workers.^{30–32} Specifically, they showed that epoxies containing 2-hydroxyester groups produced by the epoxy-carboxylic acid reaction (Figure 1a), exhibit a fast interchange of these covalent bonds (Figure 1b) above a characteristic temperature (T_v), in the presence of Zn salts. Although the fast transesterification of 2-hydroxyester bonds produced by the epoxy-carboxylic acid had been reported in the literature,^{36,37} the group of Leibler was the first to use this chemistry to develop the concept of vitrimers. Vitrimers based on this chemistry are receiving increasing attention in the literature using different formulations and catalysts.^{34,38–43} Our specific aim was to develop formulations based

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† Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: Complete vitrimers formulations, details on the calculation of R_f and R_r , network parameters, and calculation of activation energy and T_v . See DOI: 10.1039/x0xx00000x

on DGEBA (diglycidyl ether of bisphenol A), the most used epoxy monomer for practical applications and commercial, easily available and cheap poly(carboxylic acids).

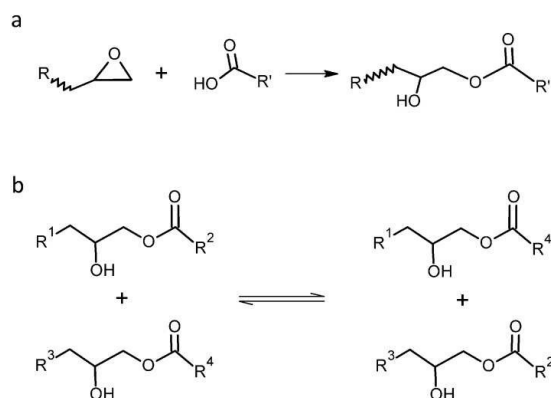


Figure 1. (a) 2-hydroxyester formation through the reaction between an epoxy and a carboxylic acid groups (b) transesterification reaction between two 2-hydroxyester links.

In order to use the resulting vitrimer for shape memory applications, it is desirable to develop a network with a T_g located above room temperature (RT) in order to employ a cooling to RT to fix the temporary shape. If there are no extra requirements for the use of the material, a T_g located somewhere in the range of 50–80°C would have the advantage of minimizing the heat needed to produce the temporary shape. This also decreases the temperature gap between the high and the low (RT) temperature of the thermal cycle, a factor that enables to increase the fixity ratio by decreasing the shrinkage of the material during the cooling step. Several fatty acids were reported in the literature to cure DGEBA in order to produce vitrimers. However, all of them presented T_g values significantly lower than 40°C. The use of a commercial blend of di- and tri-carboxylic fatty acids (Pri pol 1040) led to a material with a T_g close to RT.^{30–32,41} Among the family of typical fatty diacids, only adipic acid (C6) enabled obtaining a material with a T_g close to 40°C when employed in a stoichiometric ratio with respect to epoxy groups.⁴⁰ Sebacic acid (C10) has also been employed to cure DGEBA (1:1 stoichiometry) to produce epoxy vitrimers for shape memory applications.^{34,39} The glass transition temperature of the cured material is about 30°C which requires a temperature of 0°C to set the temporary shape.³⁴ Another problem that has not been paid enough attention is that the use of a fatty diacid (A2) in stoichiometric proportion with DGEBA (B2) would ideally produce a linear polymer through the epoxy-acid reaction. Transesterification reactions lead to gelation and formation of a polymer network.³⁶ However, a significant sol fraction is present at the end of polymerization that is not desirable for practical applications.³⁶ An increase in the crosslinking density, and hence in the T_g value can be achieved by employing an excess of epoxy groups and producing their homopolymerization subsequently to the epoxy-acid reaction. Tertiary amines are efficient catalysts/initiators to produce both reactions in series.^{9,37}

Another possible crosslinker of DGEBA is citric acid, a tricarboxylic acid present in lemon, lime and orange juices, which is nowadays produced from sugars through a microbiological process.⁴⁴ It was already employed as an aqueous solution to crosslink epoxidized soybean oil (ESO),^{38,42} and an epoxidized sucrose soyate.⁴⁵ The 2-hydroxyesters generated by the reaction of citric acid with ESO showed an acceptable transesterification rate in the absence of any catalyst.^{38,42} Citric acid is not soluble in DGEBA but homogeneous solutions can be prepared in the presence of a fatty acid as is reported in this study.

In this work, we present two different strategies to synthesize shape memory epoxy vitrimers based on DGEBA and polycarboxylic acids, with T_g located at temperatures high enough to enable setting the temporary shape at 20°C. The first strategy consisted in dissolving citric acid in melted sebacic acid (in a 50:50 ratio of carboxylic groups), followed by addition of DGEBA (10 % over stoichiometry) to enable formation of a homogeneous solution that was thermally cured. An imidazole (1-methylimidazole, 1MI) was added with the aim of catalyzing the transesterification reactions, necessary to relax the stress when converting the temporary shape into a permanent one. 1MI also proved to be a good catalyst for the epoxy-acid reaction. The second strategy was based on preparation of DGEBA-sebacic acid and DGEBA-glutaric acid blends with an excess of epoxy groups. This produced two sequential reactions in the presence of a tertiary amine (1MI in our case): in the first place the epoxy-acid reaction and then the homopolymerization of the epoxy groups in excess.⁶ By selecting an adequate epoxy excess it was possible to convey both T_g and the rate of transesterification reactions to convenient values. Shape memory properties of the resulting vitrimers are reported with particular emphasis on the possibility of transforming temporary shapes into permanent ones.

Experimental

Materials

A diglycidyl ether of bisphenol A (DGEBA) based diepoxy monomer (D.E.R. 332 from Dow Chemical; epoxide equivalent weight EEW = 174 g/eq), citric acid (CA) monohydrate (C₆H₈O₇·H₂O; >98%; acid equivalent weight AEW = 70 g/eq), glutaric acid (GA, C₅H₈O₄; >98%; AEW = 94 g/eq) and 1-methylimidazole (1MI; 99%) were purchased from Sigma-Aldrich. Sebacic acid (SA; C₁₀H₁₈O₄; >98%; AEW = 101 g/eq) was kindly supplied by Castor Oil (Buenos Aires, Argentina). All reagents were used as received without any further purification. Figure 2 shows their chemical structures.

Synthesis of epoxy-acid vitrimers

The formulations to obtain the networks are detailed in Table 1 (see Table S1 in ESI for further details). The experimental procedure carried out in every case is described below.

DGEBA/CA-SA/1MI. CA·H₂O and SA powders were mixed together in a glass vial and heated in a convection oven at 140°C. Once the SA melted, the vial was manually agitated several times until complete dissolution of CA, and the oven temperature was lowered to 125°C. At this time, the required amount of DGEBA was placed in

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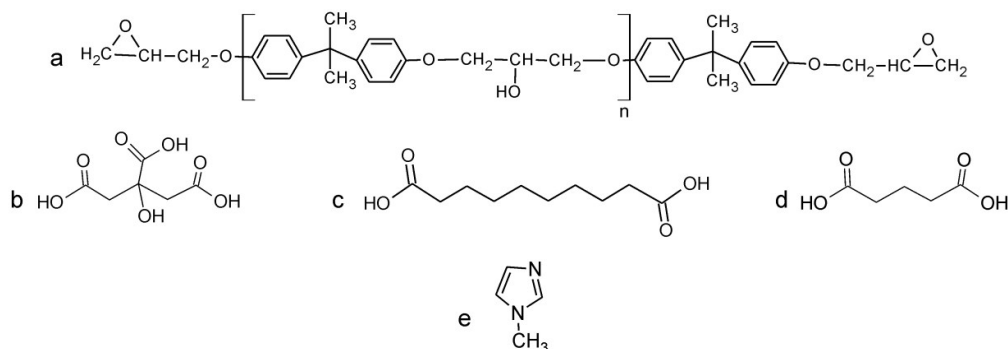


Figure 2. Chemical structure of the reagents. (a) DGEBA, $n=0.028$; (b) citric acid; (c) sebacic acid; (d) glutaric acid; (e) 1-methylimidazole.

the oven. After 10 min, the pre-heated DGEBA was added to the CA-SA solution, and the mixture was manually mixed to obtain a clear solution. The DGEBA/CA-SA blend was allowed to react at 125°C for 4 minutes before adding the 1MI, and 4 minutes later the clear, pale yellow mixture was casted in a disposable aluminium mould and cured for 3h at 120°C and 6h at 160°C.

Table 1. Formulations used to synthesize the epoxy-acid vitrimers. Base: 1.0 acid milliequivalents.

Label	DGEBA meq	CA.H ₂ O meq	SA meq	GA meq	1MI mmol	R
CS11	1.10	0.50	0.50	0	0.055	1.1
S12	1.20	0	1.00	0	0.060	1.2
S15	1.50	0	1.00	0	0.075	1.5
S20	2.00	0	1.00	0	0.100	2.0
G15	1.50	0	0	1.00	0.075	1.5

DGEBA/SA/1MI and DGEBA/GA/1MI. DGEBA and SA (or GA) were heated separately in aluminium disposable beakers placed in an oven at 140°C (105°C), until the diacid melted completely. The oven temperature was subsequently lowered to 130°C (100°C), and DGEBA and the diacid were mixed together with a glass rod. The blend was allowed to react for 4 minutes, and then 1MI was added and manually mixed. Finally, the system was cured for 3h at 120°C and 6h at 160°C.

Methods

DMTA. Dynamic-mechanical thermal analysis (DMTA) was performed in dynamic mode, employing a TA Instruments Q800 Dynamic Mechanical Analyzer with a three-point bending geometry, at a frequency of 1 Hz. Specimens of rectangular cross-section (1.5 mm x 5 mm) were tested, with a 20 mm span. Tests were carried out at a heating rate of 2 °C/min, from 20 °C to 180 °C, following the evolution of the storage modulus (E') and loss modulus (E'').

Alpha relaxation temperatures (T_{α}) were defined as the maxima of $\tan \delta (= G''/G')$ peaks.

DSC. Dynamic scanning calorimetry (DSC) tests were performed in a Shimadzu DSC 50 calorimeter under a nitrogen atmosphere, at a heating rate of 10 °C/min, from room temperature to 170 °C. Glass transition temperature (T_g) values were measured at the onset of the transition.

Stress relaxation. Shear stress relaxation was determined with an AntonPaar Physica MCR 301 rheometer, using specimens with a rectangular cross section (1.5 mm x 5 mm) and a distance of 18 mm between the dampers. Isothermal tests were carried out at different temperatures in the range comprised between 120 °C and 160 °C. When the sample reached the desired temperature, a torsion deformation $\gamma = 5\%$, corresponding to a deflection angle (θ) of about 30° was applied and the stress relaxation, expressed as a relaxation modulus, $G(t)$, was recorded.

Shape memory. Shape memory performance was studied with an AntonPaar Physica MCR 301 rheometer, using specimens with the same dimensions as those used for stress relaxation experiments. In these tests, the materials' behaviour during several cycles of temporary shape fixation and shape recovery were analyzed, each cycle comprising the following steps:

- A constant $\gamma = 5\%$ was applied at 100°C and maintained upon cooling to 20°C.
- After equilibrating at 20°C for 5 min, the specimen was released by setting a torque $\tau = 0$, and the evolution of γ was measured for the following 10 min.
- Temperature was raised keeping $\tau = 0$ to recover the permanent shape, and the evolution of γ was measured until 10 min after reaching $T = 100^\circ\text{C}$.

In order to characterize the shape-memory behaviour of the networks, shape fixity (R_f) and shape recovery (R_r) ratios were

calculated from these tests. A detailed explanation of the calculations is given in the ESI.

Additionally, tests with higher deformation values ($\gamma = 10, 15, 20, 25, 30$ and 40% , corresponding to $\theta = 60, 90, 120, 150, 180$ and 240° approximately) and one single cycle were also performed to evaluate the same parameters.

Results and discussion

Thermal and dynamic-mechanical properties

The dynamic-mechanical properties of the epoxy-acid networks are shown in Figure 2. Curves of E' vs. T display the typical shape for thermosetting polymers, with a high modulus at low temperatures corresponding to the glassy state, followed by the α relaxation and a rubber region characterized by a lower E' value. All formulations

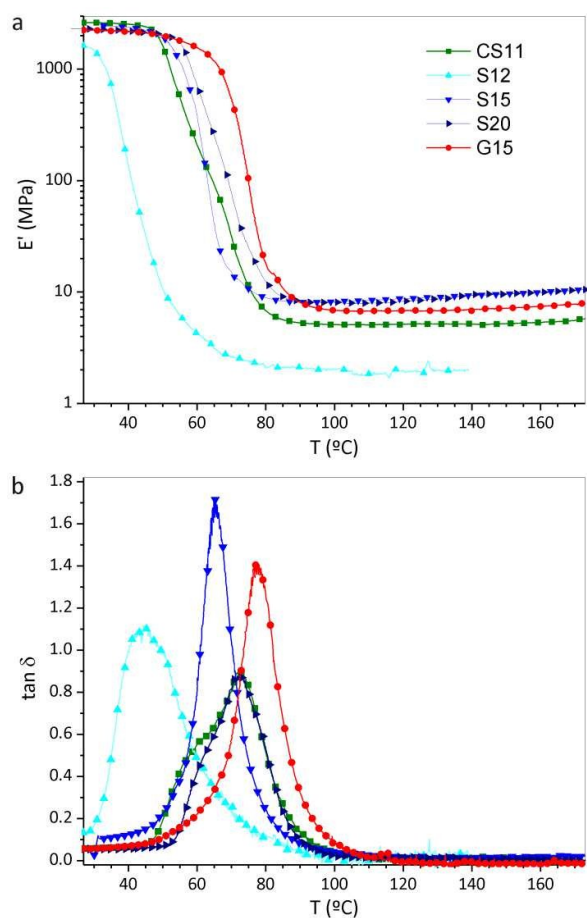


Figure 3. (a) Storage modulus (E') and (b) damping factor ($\tan \delta$) of the vitrimers as a function of temperature.

have high flexural storage moduli in the glassy state (1.5–3.0 GPa), which is a characteristic of epoxy networks.^{46,47} The plateau in the rubbery state, with E' value increasing with T also indicates the presence of covalent crosslinks, demonstrating that the epoxy excess effectively underwent homopolymerization. Significant

differences in T_{α} values were measured in the DMA tests, ranging from 45°C for S12 to 78°C for G15. The variations of T_{α} can be explained by differences in the concentration of phenyl groups, hydroxyl moieties, crosslink points and aliphatic long chains (particularly from the SA). It is known that an increment in the former three factors leads to an increase in T_{α} while the fourth has the opposite effect.⁴⁶ An analysis of SA cured networks shows that T_{α} increases from 45°C for $R=1.2$ to 66°C for $R=1.5$, and to 73°C for $R=2.0$. It can be shown (Table S2 in ESI) that the concentration of phenyl groups increases, and that of SA aliphatic chains decreases in the same way, while the crosslinking density is an increasing function of R , since in these materials all the crosslinking points can only be created by the homopolymerization of the epoxy excess. The effect of shortening the aliphatic chain length can be inferred from the comparison of S15 and G15 networks, and provides clear evidence that the presence of long SA chains enhances the local mobility and lowers down significantly the T_{α} value. Finally, it was also evidenced that the addition of CA increased T_{α} up to 73°C for a R value as low as 1.1, due mainly to the higher crosslinking density and $-\text{OH}$ concentration. It is also worth to mention that CS11 presents a broader transition, with the $\tan \delta$ peak showing a shoulder at lower temperatures, probably originated by heterogeneities at the molecular level due to the use of a mixture of acids as crosslinker.

DSC curves (Figure 4) show a very similar trend for T_g values, ranging from 30°C for S12 to 62°C for G15 and being 15–20°C lower than T_{α} values measured by DMTA. S15, S20 and CS11 showed intermediate values of 51°C , 54°C and 53°C , respectively, confirming the DMTA analysis results. With the exception of S12, the T_g values found enable the temporary shape setting at RT.

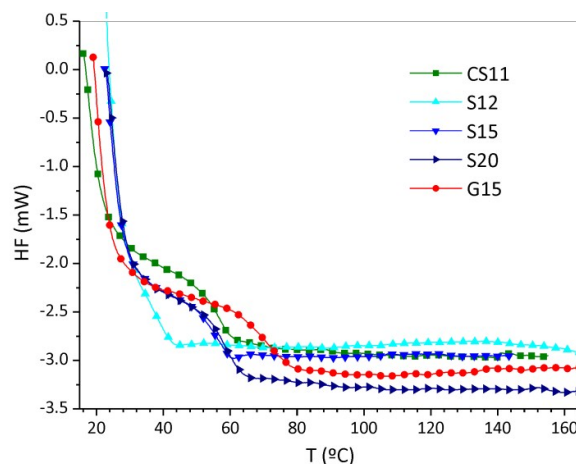


Figure 4. DSC thermograms of the vitrimers (exothermic heat flows point upwards).

Stress relaxation

Stress relaxation behaviour of the vitrimers was assessed to evaluate the transesterification reaction rate, which is responsible for reshuffling the network topology and setting a new permanent shape.^{30–32,38–42,48} The stress relaxation properties measured at

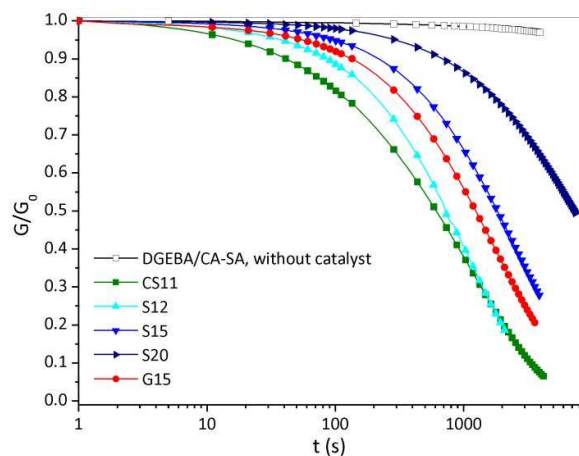


Figure 5. Stress relaxation of the vitrimers at 160°C. A stress relaxation test carried out on a stoichiometric DGEBA/SA-CA network without 1MI is shown here for comparison purposes.

160°C for every formulation are shown in Figure 5. A comparison of the uncatalyzed DGEBA/CA-SA network ($R=1.0$) with the CS11 vitrimer shows the strong effect of the 1MI catalyst, that enhances the transesterification rate by around three orders of magnitude enabling the permanent re-shaping of the vitrimer in about 1h.

Besides the use of a transesterification catalyst, there are other network parameters that can affect the relaxation rate, and they were also analyzed. In the first place, when DGEBA-SA-1MI systems are compared the results show that stress relaxation proceeds slower for higher values of R . This is a direct consequence of the lower ratio of 2-hydroxyester groups to non-reversible ether links (generated by homopolymerization) for higher R values. It should be noted that the concentration of 1MI increases with R (Table S2). However experimental evidence shows that the effect of the 2-hydroxyester concentration is much stronger than that of a slight increase in catalyst concentration.

The comparison between G15 and S15 shows that the latter takes about 45% more time to achieve the same level of relaxation ($G/G_0=0.37$). In this case, the higher concentrations of 1MI and 2-hydroxyester groups in G15 can be one of the reasons, but a complementary explanation for differences between relaxation rates could be found in the distance between adjacent reacting groups (2-hydroxyesters). Since the length of the GA aliphatic chain is about one half of that of SA, the 2-hydroxyester linkages in the G15 network are much closer to each other, hence less hindered to react. These two effects add up, but they cannot be distinguished and quantified individually from these experiments.

The CS11 vitrimers showed the fastest relaxation rate of the series at 160°C, as a result of the combined effects of a higher concentration of 2-hydroxyester moieties and the proximity between them. The contribution of $-OH$ concentration is quite dear here, since CS11 has a lower 1MI concentration than S15 and G15. It is important to stress that CA provides not only three $-COOH$ groups (yielding three 2-hydroxyesters) within less than 6 carbon atoms of distance, but also an additional hydroxyl group. It is known that $-OH$ concentration plays a substantial role in the

transesterification reaction,^{31,38} and hence it can be assumed that these additional $-OH$ groups contribute to increase the reaction rate. The higher functionality of CA allows obtaining a highly crosslinked material without the need of using a high value of R , keeping a convenient ratio of 2-hydroxyester groups to ether links generated through the homopolymerization reaction.

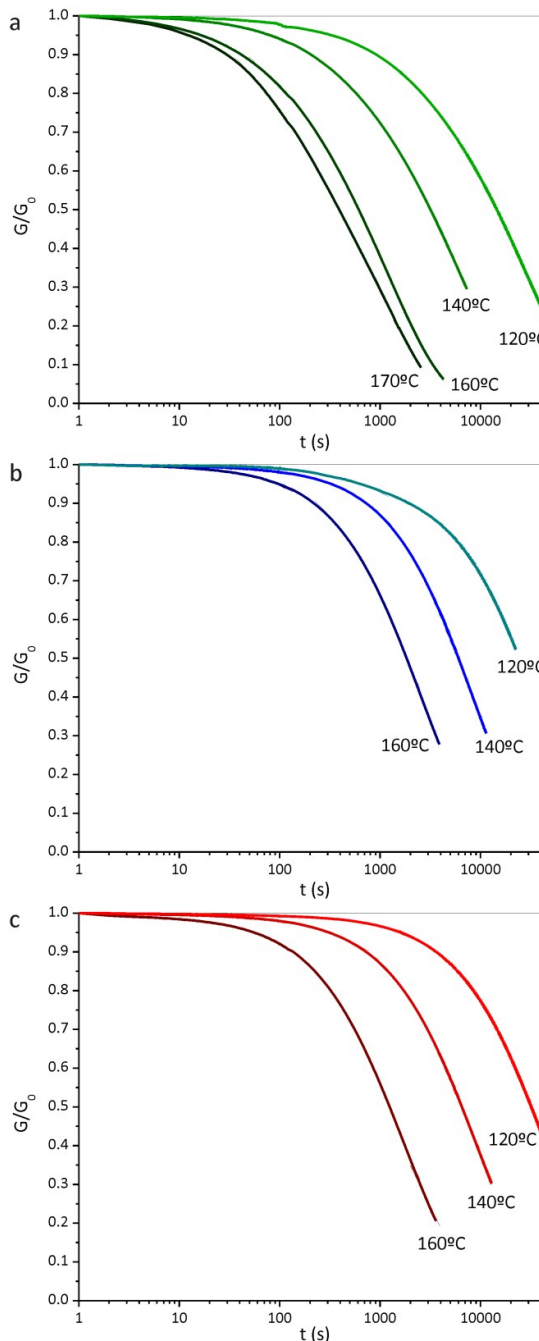


Figure 6. G/G_0 vs time at different temperatures for CS11 (a), S15 (b) and G15 (c) vitrimers.

DMTA, DSC and stress relaxation tests at 160°C showed that CS11, S15 and G15 networks have adequate combinations of properties

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(i.e. fast relaxation rates and T_g values above 50°C). Hence, further characterization of the transesterification reactions was carried out for these vitrimers by measuring the stress relaxation at different temperatures (Figure 6), and obtaining the activation energy (E_a) at two different relaxation values. E_a values were calculated from the relaxation time-temperature relation for each vitrimer, using an Arrhenius-type equation (Eq. 1):

$$\ln \tau = E_a / (R \cdot T) - \ln A \quad \text{Eq. 1}$$

where τ is the time needed to attain a given stress relaxation value, A is a pre-exponential factor and R is the gas constant.

Eq. 1 provides an excellent fitting of experimental data (ESI, Figure S2). Activation energies can be used to predict the relaxation stress rate within a temperature range, and also indicate the sensitivity of the transesterification reaction rate to a change of temperature. E_a values are shown in Table 2, and range from about 90 kJ/mol for S15 to around 120 kJ/mol for G15, with CS11 showing an intermediate value of ~107 kJ/mol. The values for CS11 and G15 are somewhat higher than those reported for other catalyzed vitrimers³² and those of uncatalyzed ESO-CA networks,³⁸ and significantly lower than that reported for polylactide vitrimers with stannous octoate as transesterification catalyst.⁴³ Additionally, T_v values of CS11, S15 and G15 were determined as 105°C, 107°C and 117°C, respectively.

Table 2. Activation energy (E_a) for the transesterification reactions and topology freezing temperature (T_v), calculated with Eq. 1 from the tests shown in Figure 6.

	E_a	E_a	E_a	T_v
	($G/G_0 = 0.6$)	($G/G_0 = 0.37$)	(average)	
	kJ/mol	kJ/mol	kJ/mol	°C
CS11	107.7	106.0	106.9	105
S15	91.2	87.5	89.3	107
G15	115.1	122.6	118.8	117

Shape memory

Figure 7 shows the strain- and temperature-time curves obtained in the shape memory experiments for CS11, S15 and G15 formulations, and Table 3 summarizes the fixity ratio (R_f) and recovery ratio (R_r) for each individual cycle. In general, fixity ratios above 99% were measured for all the vitrimers, which is a very good result. Recovery ratios were also very high, demonstrating the ability of these polymers to go back to their permanent shape.

Table 3. R_f and R_r for CS11, S15 and G15 vitrimers, for $\gamma=5\%$ and $N = 1$ to 5.

	N	1	2	3	4	5
		$R_f(\%)$	100.0	100.0	100.0	100.0
CS11	$R_r(\%)$	98.4	99.2	99.3	99.3	99.4
	$R_f(\%)$	99.6	99.6	99.7	99.6	99.5
S15	$R_r(\%)$	99.0	99.7	98.7	100.0	99.8
	$R_f(\%)$	99.8	99.8	99.8	99.8	99.8
G15	$R_r(\%)$	99.5	99.7	99.8	99.7	99.8

It is worth to mention the repeatability of the results, showing no significant variation for different cycles. Differences among formulations are also very low.

Tests with higher deformation levels were also performed, and are shown in Figure 8. Fixity and recovery ratios calculated for these tests are summarized in Table 4. These tests show that R_f and R_r values are very high regardless the deformation applied to the material. An X indicates the material failure with the corresponding

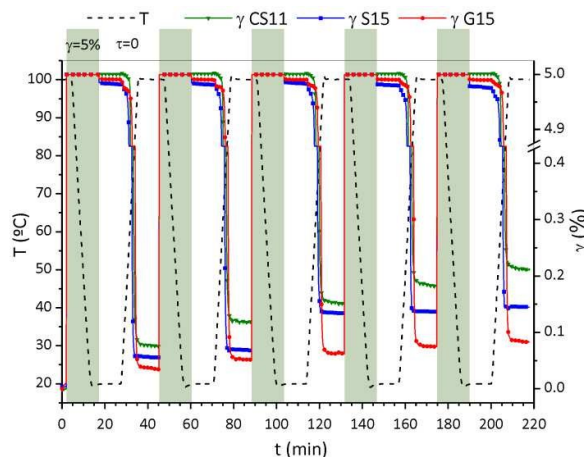


Figure 7. Deformation (γ) and temperature vs. time curves for the 5-cycle shape memory tests for CS11, S15 and G15, with $\gamma = 5\%$.

applied strain at 100 °C. Decreasing this temperature could enable to extend the deformation range without failure.⁵ Overall, these materials show excellent fixity and recovery ability when compared to other epoxy shape memory polymers.^{1-5,7-13,17,18,24-29} It should be recalled, however, that shape memory experiments were carried out in torsion mode; hence, the deformation values cannot be directly compared with other experiments where only uniaxial tensile or compressive stresses are applied.

Table 4. R_f and R_r for CS11, S15 and G15 vitrimers for different values of γ and $N = 1$. An X symbol means that the specimen broke when the deformation was applied. Shape memory test with $\gamma = 25\%$ were not performed on S15 and G15, since tests with $\gamma = 30\%$ could be performed.

	γ (%)	5	10	15	20	25	30	40
		$R_f(\%)$	100.0	100.0	100.0	100.0	100.0	X
CS11	$R_r(\%)$	98.4	98.5	99.6	99.2	99.0	X	-
	$R_f(\%)$	99.6	99.5	99.6	99.6	-	99.7	X
S15	$R_r(\%)$	99.0	99.0	99.0	99.3	-	100.0	X
	$R_f(\%)$	99.8	99.9	99.9	99.9	-	99.9	X
G15	$R_r(\%)$	99.5	99.4	98.7	98.4	-	98.8	X

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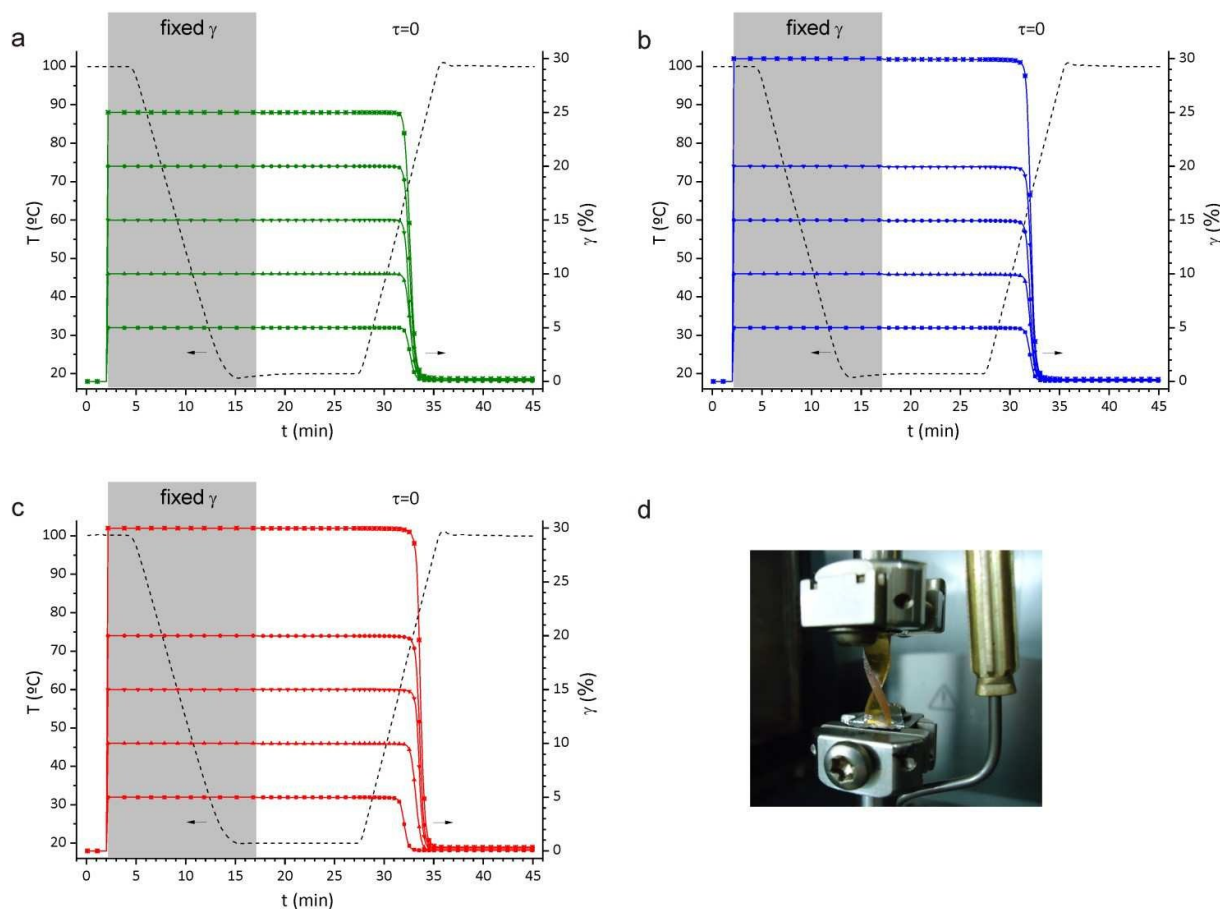


Figure 8. Shape memory tests with different deformation values: (a) CS11; (b) S15; (c) G15. (d) G15 sample with an applied deformation of 30%, corresponding to a deflection angle of more than 180°.

Temporary and permanent shape changes

Combination of temporary and permanent shape changes for CS11 vitrimer was evaluated both qualitatively and quantitatively. For the qualitative test (Figure 9; a movie clip showing this experiment is also available as ESI), the temporary shape was set by heating the sample at 90–100°C using hot water and manually twisting it before cooling to RT (a, b). Afterwards, the permanent shape #1 was recovered by submerging the sample in hot water again (c, d). To set the permanent shape #2 (e), the sample was twisted in the same way as described for the temporary shape setting, but it was subsequently subjected with damps to preserve the shape, and placed in a convection oven at 160°C for 1h. After the thermal treatment, it was no longer possible to recover the permanent

shape #1 by heating the sample above T_g . Instead, a new temporary shape (f) could be obtained by manually applying a stress before the specimen cooled below T_g . Finally, a new immersion in hot water (g) led to the permanent shape #2 again (h).

The quantitative demonstration of both temporary and permanent shape changes is shown in Figure 10. In a first step, a temporary shape with a deformation $\gamma=5\%$ was programmed at 100°C, and then the specimen was cooled to 20°C. This shape was retained upon releasing the specimen ($\tau=0$), but when temperature was raised above T_g , the permanent shape #1 (corresponding to $\gamma=0\%$) was recovered. The next step involved the modification of the permanent shape. For this purpose, a deformation of 5% was fixed for 1h at a temperature of 160°C, and then the sample was cooled again maintaining $\gamma=5\%$. The deformation corresponding to the

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permanent shape #2 was measured as 4.7% when the sample was heated to 100°C without applying any torque (τ). The discrepancy between the new permanent γ and the fixed value of 5% is due to incomplete stress relaxation for the temperature and time used, and is in agreement with a stress relaxation of 91% at 1h for the same temperature (Figures 5 and 6). Finally, a new temporary shape ($\gamma=0\%$) was fixed at 100°C. This shape was maintained at 20°C when the sample was released, and when temperature surpassed T_g the sample went back to the permanent shape #2.

Conclusions

The results presented herein show the possibility of synthesizing thermosetting vitrimers from affordable and commercially available raw materials such as DGEBA, inexpensive poly(carboxylic acids), and an imidazole as a catalyst for both the epoxy-acid reaction and the homopolymerization of the epoxy excess. Interestingly, the imidazole was an excellent catalyst for the transesterification reaction, speeding up the re-shuffling of the polymeric networks and enabling permanently re-shaping the material within a reasonable timeframe. The shape memory properties of these vitrimers were evaluated through shape fixity and recovery ratios, and overall excellent results were obtained. Regarding the differences between formulations, the network synthesized with

glutaric acid has better properties than that obtained using sebacic acid, though the latter is more environmentally friendly due to the renewable origin of sebacic acid. Moreover, the use of citric acid (dissolved in sebacic acid) is very advantageous, since it leads to highly crosslinked networks, decreasing the need of an epoxy excess and accelerating the stress relaxation.

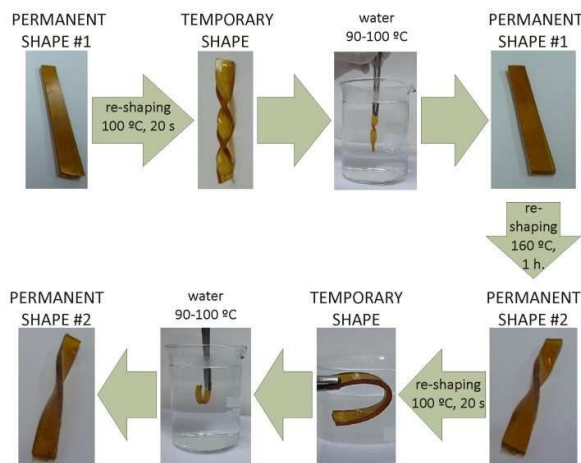


Figure 9. Qualitative assessment of shape memory and permanent shape changing for CS11 vitrimer.

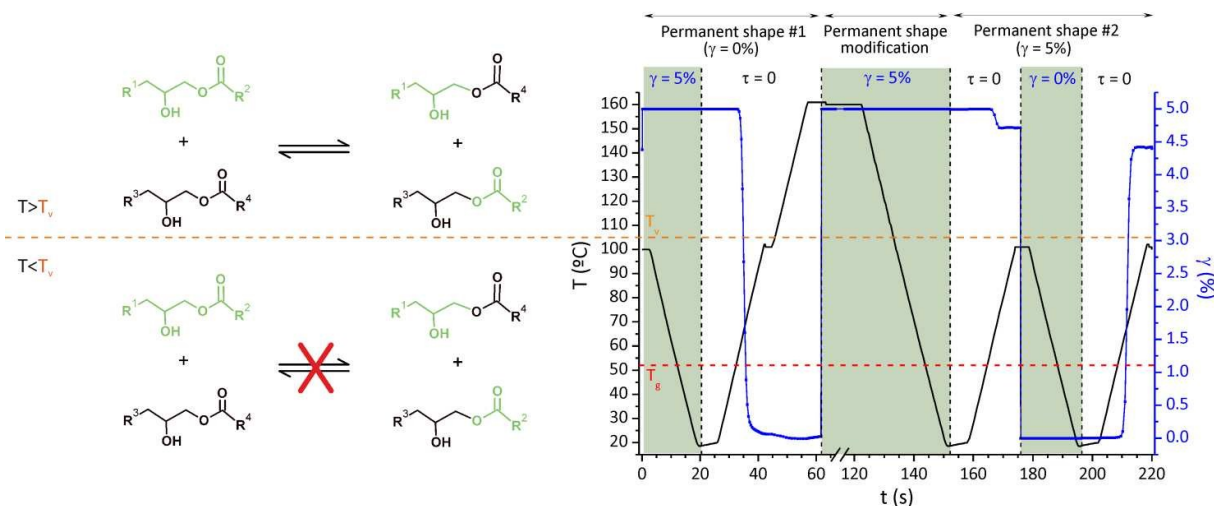


Figure 10. Combined shape memory and stress relaxation experiment for CS11 vitrimer. The scheme at the left illustrates that at the rate of transesterifications becomes negligible below T_g .

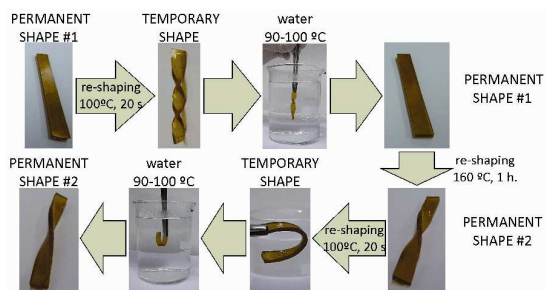
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Notes and references

- 1 T. Xie and I. A. Rousseau, *Polymer*, 2009, **50**, 1852–1856.
- 2 I. A. Rousseau and T. Xie, *J. Mater. Chem.*, 2010, **20**, 3431.
- 3 D. M. Feldkamp and I. A. Rousseau, *Macromol. Mater. Eng.*, 2010, **295**, 726–734.
- 4 Y. Liu, C. Han, H. Tan and X. Du, *Mater. Sci. Eng. A*, 2010, **527**, 2510–2514.

- 5 A. B. Leonardi, L. A. Fasce, I. A. Zucchi, C. E. Hoppe, E. R. Soulé, C. J. Pérez and R. J. J. Williams, *Eur. Polym. J.*, 2011, **47**, 362–369.
- 6 J. Puig, C. E. Hoppe, L. A. Fasce, C. J. Pérez, Y. Piñeiro-Redondo, M. Bañobre-López, M. A. López-Quintela, J. Rivas and R. J. J. Williams, *J. Phys. Chem. C*, 2012, **116**, 13421–13428.
- 7 S. Pandini, F. Bignotti, F. Baldi and S. Passera, *J. Intell. Mater. Syst. Struct.*, 2013, **24**, 1583–1597.
- 8 Y. Dong, Q.-Q. Ni, L. Li and Y. Fu, *Mater. Lett.*, 2014, **132**, 206–209.
- 9 N. Zheng, G. Fang, Z. Cao, Q. Zhao and T. Xie, *Polym Chem*, 2015, **6**, 3046–3053.
- 10 M. Fan, X. Li, J. Zhang and J. Cheng, *J. Therm. Anal. Calorim.*, 2015, **119**, 537–546.
- 11 Y. Dong, Q.-Q. Ni and Y. Fu, *Compos. Part Appl. Sci. Manuf.*, 2015, **72**, 1–10.
- 12 D. Santiago, X. Fernández-Francos, F. Ferrando and S. De la Flor, *J. Polym. Sci. Part B Polym. Phys.*, 2015, **53**, 924–933.
- 13 W. Wang, D. Liu, Y. Liu, J. Leng and D. Bhattacharyya, *Compos. Sci. Technol.*, 2015, **106**, 20–24.
- 14 Y. Wu, J. Hu, C. Zhang, J. Han, Y. Wang and B. Kumar, *J Mater Chem A*, 2015, **3**, 97–100.
- 15 X. Liu, H. Li, Q. Zeng, Y. Zhang, H. Kang, H. Duan, Y. Guo and H. Liu, *J Mater Chem A*, 2015, **3**, 11641–11649.
- 16 L. Yu, Q. Wang, J. Sun, C. Li, C. Zou, Z. He, Z. Wang, L. Zhou, L. Zhang and H. Yang, *J Mater Chem A*, 2015, **3**, 13953–13961.
- 17 H. Guo, Y. Li, J. Zheng, J. Gan, L. Liang, K. Wu and M. Lu, *RSC Adv*, 2015, **5**, 67247–67257.
- 18 A. B. Leonardi, J. Puig, J. Antonacci, G. F. Arenas, I. A. Zucchi, C. E. Hoppe, L. Reven, L. Zhu, V. Toader and R. J. J. Williams, *Eur. Polym. J.*, 2015, **71**, 451–460.
- 19 T. Tanpitaksit, *Express Polym. Lett.*, 2015, **9**, 824–837.
- 20 T. Tsujimoto, *Express Polym. Lett.*, 2015, **9**, 757–763.
- 21 Y. Dong, H. Xia, Y. Zhu, Q.-Q. Ni and Y. Fu, *Compos. Sci. Technol.*, 2015, **120**, 17–25.
- 22 J. Karger-Kocsis and S. Kéki, in *Multifunctionality of Polymer Composites*, Elsevier, 2015, pp. 822–841.
- 23 Y. Liu, J. Zhao, L. Zhao, W. Li, H. Zhang, X. Yu and Z. Zhang, *ACS Appl. Mater. Interfaces*, 2016, **8**, 311–320.
- 24 S. Ponyrko, R. K. Donato and L. Matějka, *Polym Chem*, 2016, **7**, 560–572.
- 25 A. Arnebold and A. Hartwig, *Polymer*, 2016, **83**, 40–49.
- 26 X. Kuang, G. Liu, X. Dong and D. Wang, *Polymer*, 2016, **84**, 1–9.
- 27 X. Wu, X. Yang, Y. Zhang and W. Huang, *J. Mater. Sci.*, 2016, **51**, 3231–3240.
- 28 L. Chen, W. Li, Y. Liu and J. Leng, *Compos. Part B Eng.*, 2016, **91**, 75–82.
- 29 C. Li, J. Dai, X. Liu, Y. Jiang, S. Ma and J. Zhu, *Macromol. Chem. Phys.*, 2016, **217**, 1439–1447.
- 30 D. Montanari, M. Capelot, F. Toumilhac and L. Leibler, *Science*, 2011, **334**, 965–968.
- 31 M. Capelot, D. Montanari, F. Toumilhac and L. Leibler, *J. Am. Chem. Soc.*, 2012, **134**, 7664–7667.
- 32 M. Capelot, M. M. Unterlass, F. Toumilhac and L. Leibler, *ACS Macro Lett.*, 2012, 789–792.
- 33 Q. Zhao, W. Zou, Y. Luo and T. Xie, *Sci. Adv.*, 2016, **2**, e1501297–e1501297.
- 34 Z. Pei, Y. Yang, Q. Chen, Y. Wei and Y. Ji, *Adv. Mater.*, 2016, **28**, 156–160.
- 35 W. Denissen, J. M. Winne and F. E. Du Prez, *Chem Sci*, 2016, **7**, 30–38.
- 36 K. Dušek and L. Matějka, in *Rubber-Modified Thermoset Resins*, eds. C. K. Riew and J. K. Gillham, American Chemical Society, Washington, D.C., 1984, vol. 208, pp. 15–26.
- 37 C. E. Hoppe, M. J. Galante, P. A. Oyanguren and R. J. J. Williams, *Macromol. Mater. Eng.*, 2005, **290**, 456–462.
- 38 F. I. Altona, V. Petta rin and R. J. J. Williams, *Green Chem.*, 2013, **15**, 3360–3366.
- 39 Z. Pei, Y. Yang, Q. Chen, E. M. Terentjev, Y. Wei and Y. Ji, *Nat. Mater.*, 2013, **13**, 36–41.
- 40 Y. Yang, Z. Pei, X. Zhang, L. Tao, Y. Wei and Y. Ji, *Chem. Sci.*, 2014, **5**, 3486.
- 41 K. Yu, P. Taynton, W. Zhang, M. L. Dunn and H. J. Qi, *RSC Adv.*, 2014, **4**, 10108.
- 42 F. I. Altona, J. Antonacci, G. F. Arenas, V. Petta rin, C. E. Hoppe and R. J. J. Williams, *Mater. Res. Express*, 2016, **3**, 45003.
- 43 J. P. Brutman, P. A. Delgado and M. A. Hillmyer, *ACS Macro Lett.*, 2014, **3**, 607–610.
- 44 M. Sauer, D. Porro, D. Mattanovich and P. Branduardi, *Trends Biotechnol.*, 2008, **26**, 100–108.
- 45 S. Ma and D. C. Webster, *Macromolecules*, 2015, **48**, 7127–7137.
- 46 J.-P. Pascault, H. Sautereau, J. Verdu and R. J. J. Williams, *Thermosetting Polymers*, Marcel Dekker, New York, 1st edn., 2002.
- 47 J.-P. Pascault and R. J. J. Williams, in *Epoxy Polymers*, eds. J.-P. Pascault and R. J. J. Williams, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2010, pp. 1–12.
- 48 W. Denissen, G. Rivero, R. Nicolaÿ, L. Leibler, J. M. Winne and F. E. Du Prez, *Adv. Funct. Mater.*, 2015, **25**, 2451–2457.



The shape of the epoxy-acid based vitrimers can be changed either temporarily or permanently by selecting the appropriate thermal treatment.