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ARTICLE

Natural glycyrrhizic acid: improving stress relaxation rate and glass transition temperature simultaneously in epoxy vitrimers

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Epoxy vitrimers based on transesterification reactions (TERs) is a kind of recyclable thermosets which have been developed prosperously in recent years. However, the good thermal performance and the quick network rearrangements are somehow contradictory and difficult to achieve simultaneously in TERs-based epoxy vitrimers. This contradiction has been resolved in this work through a green and facile yet effective strategy, where natural glycyrrhizic acid (GL) was associated with sebacic acid (SA) as curing agents to prepare epoxy vitrimers based on TERs with different monomer compositions (V1 to V5). Thanks to the unique structure of GL, the glass transition temperatures (T_g) of vitrimers rose from 31 to 89°C, and their stress relaxation time shortened from 390 to 130 s at 180°C with the increase of GL content. Especially, the vitrimer V4 exhibited good thermal stability (decomposition temperature T_{d5} of 263°C), fast stress relaxation (relaxation time of 130 s at 180°C), low malleability temperature (T_{mali} of 116°C) and usable T_g (61°C). Moreover, this vitrimer could be welded, reprocessed, repaired, recycled and chemically degraded at a relative mild temperature (130°C). This work provides a green strategy for vitrimer design, which might guide the preparation of recyclable thermosets with high comprehensive performance in the future.

Introduction

Thermosets, such as epoxy and Bakelite, possess cross-linked networks and have been widely used in our daily life for adhesives, composites, coatings, *et al.*^{1,2} Taking advantages of the cross-linked structures, they exhibit good thermal and dimensional stability, as well as satisfactory mechanical properties. But the permanent cross-linked networks result in hardly recycling at the end of their service life, which place enormous burden on environment. To tackle this problem, recyclable thermosets based on dynamic cross-linked networks have been developed in the past few years.³⁻⁵ Vitrimers, invented by Leibler in 2011,⁶⁻⁸ is one of the most popular dynamic cross-linked networks that can topologically rearrange via thermal-activated associative bond exchange reactions. They not only behave like classical thermosets at low temperatures, but also flow like viscoelastic liquids at high temperatures where they can be reprocessed and recycled like thermoplastics.⁹⁻¹¹ To date, many vitrimers based on different dynamic bond exchange reactions like transesterifications,⁶⁻⁸

transaminations,¹²⁻¹⁴ imine metathesis^{15,16} and boronic ester exchange^{17,18} have been reported consecutively. Among them, transesterification reactions (TERs)-based epoxy vitrimers are the most frequently used ones because of their accessibility and good stability of ester bond.¹⁹ They have rapidly participated in shape memory materials,²⁰ soft actuators^{21,22} and 3D printing thermosets.²³ Nevertheless, the stability of ester bonds also causes the difficulty in the occurrence of TERs, as the exchange of ester bonds often requires high temperatures even in the presence of catalyst.^{24,25} Thus, there is a long way to go before TERs-based epoxy vitrimers can be used as recyclable thermosets. One challenge has to be taken up: achieving the good thermal performance and the quick network rearrangement simultaneously in one system.

The strategies in the past can be divided into two classes. One strategy, defined as extrinsic regulations, is to adjust the category and content of catalysts to improve network rearrangement rate. For example, Leibler and co-workers found that both zinc acetate and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) exhibited a higher efficiency than triphenylphosphine for catalyzing TERs.⁸ And higher catalyst concentration led to faster TERs rate, although the activation energy (E_a) for topology freezing in these epoxy vitrimers was same. However, the large amount of catalysts often influences the vitrimer preparation and cause the poor thermal stability of vitrimers. Another strategy, defined as intrinsic regulations, is to modulate the structures of polymer chains. Note that a paradox often exists in this strategy because a rigid polymer structure means a higher T_g whereas a lower bond exchange rate.²⁶⁻³¹ For example, Zeng *et al.* reported a series of epoxy vitrimers constructed by two curing agents with different

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flexibility. Their results showed that vitrimers with higher T_g led to a reduction of bond exchange rate.²⁷ Besides, other factors in network structures can also promote the bond exchange reactions,³²⁻³⁶ such as the high density of hydroxyl groups,³² ester bonds³³ and cross-linking sites,³⁴ as well as the closer statistic distance between reactive groups.³⁵ For example, Zhang et. al. developed a hyperbranched epoxy-vitrimer with a large amount of free hydroxyl groups, which maintained the high rate of TERs without catalyst.³² Hayashi et al. have designed two epoxy vitrimers by varying cross-linking density with keeping hydroxyl groups constant, a higher cross-linking density, a faster stress relaxation rate.³⁴ While Du Prez et al. reported that the closer statistic distance between reactive groups led to a higher exchange rate in their vitrimers.³⁵ In short, the considerable improvements have been achieved in regulation of exchange reaction rate and T_g of vitrimers in the past ten years, but how to prepare a comprehensive TERs-based epoxy vitrimers with fast stress relaxation and usable T_g still remains a challenge.

In this research, we proposed an effective strategy for the simultaneous improvement in stress relaxation rate and glass transition temperatures (T_g) by tuning network structures in TERs-based epoxy vitrimers. In this strategy, the key point is to find an epoxy curing agent with rigid skeleton, multiple hydroxyl groups and close statistic distance between hydroxyl-carboxyl groups, where the rigid skeleton structure increases T_g , while multiple hydroxyl groups and close statistic distance between hydroxyl-carboxyl groups reduce the detrimental effect by rigid networks. Fortunately, natural glycyrrhizic acid (GL) meets all these requirements. GL is a triterpene saponin and usually exists in licorice roots.^{37,38} It has a unique rigid skeleton, three carboxyl groups and five hydroxyl groups.

Meanwhile, the statistic distances between hydroxyl groups and ester bonds are close enough in networks after curing. In general, this vitrimer system was constructed by using GL and sebacic acid (SA) as complex curing agents to react with diglycidyl ester of aliphatic cyclo (DGEAC), and the cross-linked network was able to rearrange through TERs in the presence of TBD as shown in Fig. 1. DGEAC, a traditional epoxy, offers three epoxy groups for increasing the cross-linking density and provides two extra ester groups for promoting TERs.^{39,40} SA, a castor oil-derived biobased curing agent, supplies soft segments to control the flexibility of polymer chains.^{21,22} For better illustrating our design, a series of vitrimers (V1 to V5) were prepared with an increase of GL contents and their properties were investigated thoroughly. Their performance was comprehensible as we expected. With an increase of GL contents, T_g rose from 31 to 89°C with a significant increase in tensile strength and modulus from V1 to V5, while stress relaxation time by TERs shortened from 390 to 130 s at 180°C from V1 to V4, with a slight augment for V5 (190 s). Note that V4 ($T_g = 61^\circ\text{C}$) maintained a fast stress relaxation rate, as they relaxed to $1/e$ for only 130 s with a full relaxation time of 350 s at 180°C, which was less than those of reported TERs-based epoxy vitrimers.^{6,8,21,26,41-44} Obviously, V4 held the good mechanical properties at room temperature and meanwhile could be quickly welded, reprocessed, repaired, recycled and chemically degraded at a relative mild temperature (130°C). Effectively, GL has improved bond exchange rate and T_g simultaneously, which provides a green strategy for vitrimer design and makes it possible to prepare recyclable thermosets with high performance and comprehensive properties in the future.

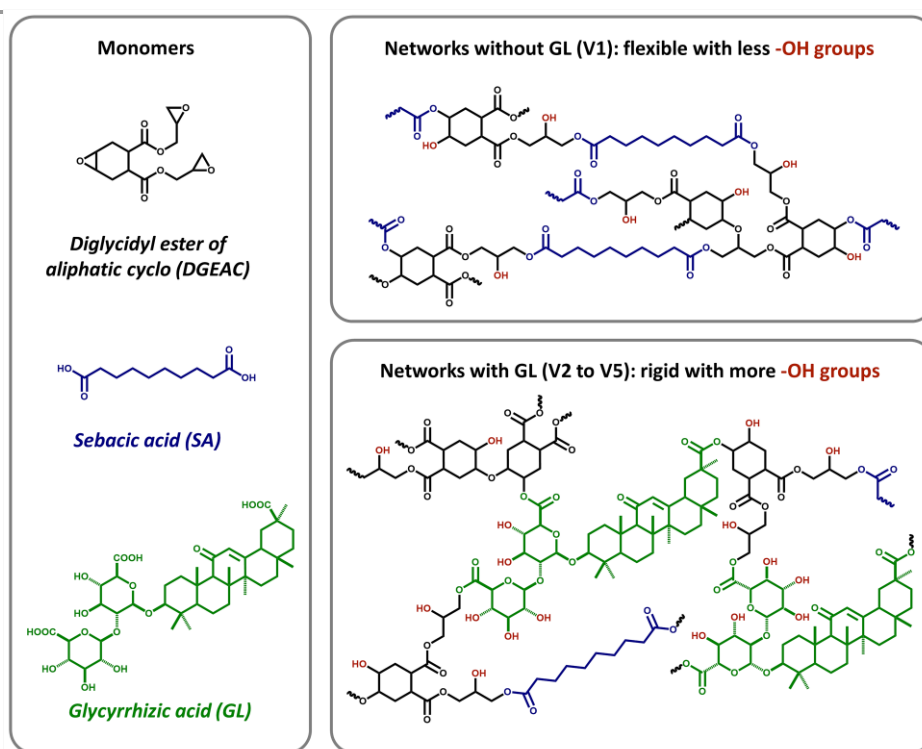


Fig. 1 Chemical structures of monomers (left) and schematic illustration of vitrimer networks without (V1) and with (V2 to V5) glycyrrhizic acid (right).

V4	1.00	0.80	0.20	0.33
V5	1.00	0.70	0.30	0.50

Experimental section

Materials

Diglycidyl ester of aliphatic cyclo (DGEAC, Tianjin Jindong Chemical Factory), glycyrrhizic acid (GL, Energy Chemical, 95%), sebacic acid (SA, Inno Chem, 99%) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, Ark Pharm, 98%) were used directly as purchased without further purifying.

Preparation of DGEAC/SA/GL networks

TBD (5% molar ratio to carboxylic acid) was first added into DGEAC using a beaker at 70°C, and then SA was added into solution. Upon addition of GL, the mixture was poured into a mould with a dimension of 80 mm × 60 mm × 1 mm at 100°C. Lastly, the mould was put into a press vulcanizer and cured at 120°C for 1 h, 150°C for 2 h, and 170°C for 2 h at a pressure of 10 tons.

Characterization

Details of characterization see Supporting Information.

Results and discussion

Preparation, network structure, thermal and mechanical properties of DGEAC/SA/GL vitrimers

Five networks (V1 to V5) were prepared by crosslinking DGEAC with SA and GL (epoxy/carboxyl = 1, molar ratio) in presence of 5 mol % TBD as a catalyst for TERs (Fig. 1). As shown in Table 1, the stoichiometric ratio of carboxyl group from SA was set as 1.00, 0.95, 0.90, 0.85, and 0.70 for V1 to V5 while keeping the total carboxyl groups constant (as 1.00) by increasing the GL content. In this case, extra hydroxyl groups were introduced into vitrimer systems because of the increase of GL content.

Differential scanning calorimeter (DSC) was used to study the curing reaction for working out a rational curing process. Broad exothermic peaks appeared at around 130°C for the DGEAC/SA/GL mixtures M-V1 to M-V5 (Fig. 2a), which were different from the melting point of each monomer (Fig. S1). This observation strongly revealed the occurrence of curing reactions. According to the DSC results, the curing process was set as “120°C/1 h + 150°C/2 h + 170°C/2 h” with 10 tons pressure.

Table 1 Stoichiometric ratios of monomers (TBD 5 mol %)

Vitrimer	Epoxy groups	Carboxyl groups		Extra hydroxyl groups from GL
		SA	GL	
V1	1.00	1.00	0	0
V2	1.00	0.95	0.05	0.08
V3	1.00	0.90	0.10	0.17

Vitrimer samples of DGEAC/SA/GL after curing were shown in Fig. 2b, where the transparency reduced and the color became deeper from V1 to V5 with an increase of GL content. It might be attributed to the oxidation of a trace of diglucuronic unit on GL. Thermogravimetric analyzer (TGA) was used to evaluate their thermal stability under nitrogen atmosphere. The temperature at 5% of weight loss (T_{d5}) for each sample was above 260°C, revealing a good thermal stability of DGEAC/SA/GL networks (Fig. S2). Notably, T_{d5} declined from 283 to 262°C from V1 to V5, corresponding to the decomposition of unstable glycosyl units at high temperature. Therefore, these vitrimers were stable enough when they were processed or reprocessed below 180°C.

To identify the formation of cross-linked networks, monomers and vitrimers were investigated by FTIR spectra. As shown in Fig. S3a, the signals at 1740 and 905/853 cm^{-1} were assigned to ester bonds and epoxy groups from DGEAC, the signals at 2925/2853 and 1710 cm^{-1} to methylene and carboxyl groups from SA, and the signals at 3430, 2925/2853, 1730, and 1655 cm^{-1} to hydroxyl, methylene, carboxyl and ketone groups from GL. After cross-linking, epoxy peaks from DGEAC at 905/853 cm^{-1} disappeared (Fig. 2c), while the large hydroxyl peak at 3430 cm^{-1} and the ketone peak at 1655 cm^{-1} remained, and were enhanced with the increase of GL content (Fig. S3b). All FTIR results implied that both GL and SA had been successfully linked into the cross-linked networks with a complete consumption of epoxy groups. In addition, gel contents and swelling tests showed that all five vitrimers hardly dissolved in dichloromethane (DCM) with the gel content above 90%, and the swelling ratio declined from 74 to 61% from V1 to V5 because of the enhancement in network rigidity (Fig. S4 and Table S1).

For better understanding the glass transition and viscoelastic properties of these vitrimers, dynamic thermomechanical analysis (DMA) was used with a heating rate 5°C/min. The storage modulus of each sample at glass plateau was around 2,000 MPa, and a distinct transition from glass to rubber platform was detected for all samples (Fig. S5). Meanwhile, the peaks of $\tan \delta$ at 31, 41, 46, 61, and 89°C were assigned as the glass transition T_g for V1, V2, V3, V4 and V5, respectively (Fig. 2d). It is known that the high cross-linking density and the stiff polymer chains often result in a high value of T_g .²⁹ As we expected, the network chains became significantly stiffer as more rigid structures on GL were introduced (Fig. 1, right). Hence, the enhancement of T_g was achieved from V1 to V5, especially for V4 ($T_g = 61^\circ\text{C}$) and V5 ($T_g = 89^\circ\text{C}$) which had higher T_g values than most reported epoxy vitrimers.^{6-8,21,41-44} In general, T_g also determines the mechanical properties of polymer materials. The strength and modulus of each vitrimer in tensile tests were summarized in Fig. 2e and Table S2. The tensile strength and modulus

dramatically increased from 0.56 to 11.28 MPa and from 2.37 to 542.26 MPa, respectively, from V1 to V5, because the stiffness of polymer networks were enhanced with addition of GL.

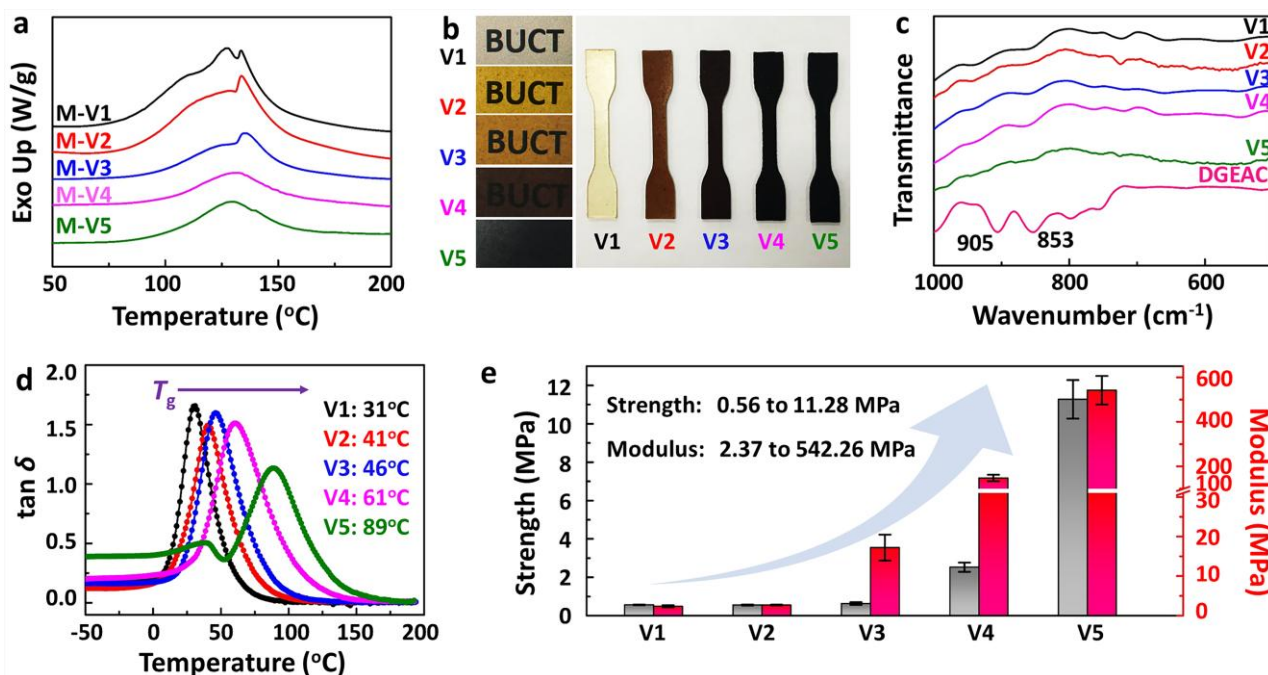


Fig. 2 (a) DSC thermograms of DGEAC/SA/GL mixture (M-V1, M-V2, M-V3, M-V4, M-V5) before curing at a heating rate 5°C/min. (b) Digital photos of DGEAC/SA/GL vitrimers after curing. The background of “BUCT” was used to demonstrate the transparency of each sample. (c) FTIR spectra of DGEAC/SA/GL networks (V1, V2, V3, V4, V5) and DGEAC monomer. (d) Tan δ of DGEAC/SA/GL networks (V1, V2, V3, V4, V5) by using dynamic thermomechanical analysis (DMA) at a heating rate 5°C/min. (e) Mechanical properties of DGEAC/SA/GL networks (V1, V2, V3, V4, V5) using tensile tests. The gray and red column represents tensile strength and tensile modulus of each network, respectively.

Regulation of topological network rearrangements

At present, the reported rigid vitrimer networks (high T_g) based on TERs often suffer from the extremely slow mobility of polymer chains, consequently causing a low rate of topological network rearrangements.^{26-28,45} Fortunately, in our system the introduction of GL resolved this contradiction. Although the addition of rigid GL weakened the flexibility of polymer chains which was unfavorable for TERs, it brought more hydroxyl groups, and closed the statistic distance between reactive groups on account of the neighboring hydroxyl and ester bonds from diglucuronic units, which benefited the TERs. In this way, the topological network rearrangements can be regulated effectively by network structures, thus realizing the high bond exchange rate by optimizing the component proportions.

To verify this assumption, DGEAC/SA/GL networks (V1, V2, V3, V4 and V5) were investigated in detail by using DMA. At elevated temperatures, the DGEAC/SA/GL networks start to rearrange topologically due to the TERs, where hydroxyl groups attacked ester bonds to generate other hydroxyl groups and ester bonds. The evidence of TERs came from thermal stress relaxation experiments. As shown in Fig. 3a and S6, all vitrimers (V1 to V5) exhibited rapid stress relaxation at high temperatures. Taking V4 as an example (Fig. 3a), the relaxation time (τ^*), determined as the time when the material relaxed to $1/e$ of the initial modulus ($G/G_0 = 1/e$), was 6096 s (1.69 h) at 120°C, 1388 s (23 min) at 140°C, 394 s (6.6 min) at 160°C, and 130 s at 180°C. Moreover, the full stress relaxation achieved after 4600 s (1.28 h) at 140°C, 1060 s (18 min) at

160°C, and mere 350 s (5.8 min) at 180°C. Obviously, its relaxation time was much shorter than those of TERs-based epoxy vitrimers which performed like traditional thermosets.^{6,8,21,26,41,44} Similar to V4, the stress of V1, V2, V3 and V5 could also relax to zero at elevated temperatures (Fig. S6), proving their “plasticity” which was different from conventional thermosets. The relaxation of these vitrimers followed a Maxwell model fitted by an Arrhenius-type equation:

$$\ln \tau^* = \frac{E_a}{RT} - \ln A \quad (1)$$

where τ^* is the relaxation time, E_a is the activation energy of bond exchange, T is the experimental temperature, and R is the

universal gas constant. As shown in Fig. 3b, a perfect fitting (Pearson correlation coefficient $r \geq 0.9990$) was obtained, where E_a was 101.0, 92.3, 95.3, 95.0, and 90.2 kJ/mol for V1, V2, V3, V4, and V5, respectively. The value of E_a was in good agreement with those reported by Leibler and other researchers (69~150 kJ/mol), exhibiting viscosity properties of typical transesterification vitrimers.^{6,8,40,46}

Comparing the relaxation times of V1, V2, V3, V4, and V5 at 180, 160, and 140°C (abscissa from 2.20 to 2.45 in Fig. 3b), it was found that the relaxation time was reduced significantly as the GL content increasing from V1 to V4, whereas V5 did not follow this tendency. As mentioned above, there are four factors that can accelerate the exchange reactions: (1) catalyst with high activity and large contents,^{8,47} (2) flexible polymer

chains,²⁶⁻²⁹ (3) high concentration of hydroxyl groups or ester bonds,^{32,33} and (4) closer statistic distance between reactive groups.³⁵ In our system, the above factors (2), (3), and (4)

should be mainly considered without regard to catalyst. On one hand, GL can afford extra five hydroxyl groups, and the distance

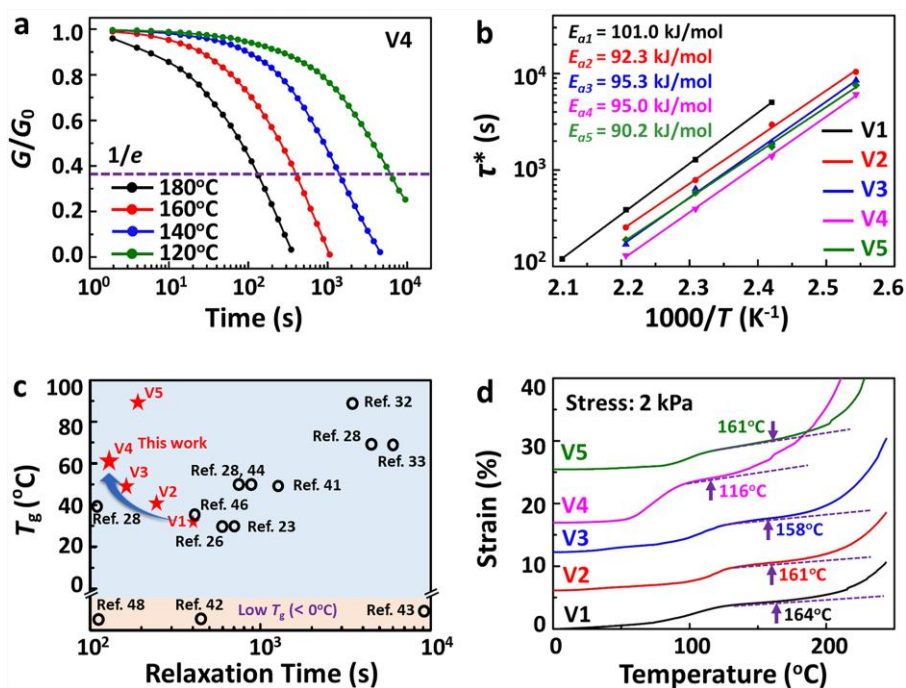


Fig. 3 (a) Stress relaxation of DGEAC/SA/GL network (V4) at different temperatures (180, 160, 140 and 120°C) using DMA tension mode with a strain of 2%. (b) Fitting of experimental values of relaxation times (τ^*) derived from V1, V2, V3, V4 and V5 to an Arrhenius-type equation. (c) Comparison of stress relaxation times (τ^*) at 180°C and T_g of DGEAC/SA/GL networks with other reported epoxy vitrimers based on TERs. Circle represents other reported epoxy vitrimers; red star represents vitrimers (V1 to V5) in this work; blue area represents the performance of most reported epoxy vitrimers (0°C < T_g < 100°C and 10² s < τ^* < 10⁴ s); pink area represents vitrimers with low T_g (< 0°C). (d) Thermaldilation tests for V1, V2, V3, V4 and V5 at a heating rate 5°C/min with a constant stress of 2 kPa.

between hydroxyl groups and ester bonds on glycosyl moiety was close enough for facilitating the TERs (Fig. 1, left). On the other hand, the presence of rigid GL made the polymer chains stiffer which had already been identified in Fig. 2d, thus causing a slow mobility and a high energy contribution from the conformational entropy of polymer chains. In this case, when the stoichiometric ratio of GL was low, the active factor (3) and (4) dominated vitrimer networks (V1 to V4) which accelerated the rate of TERs. Conversely, when the content of GL reached a threshold value, the negative effect caused by factor (2) induced by the rigid structure of GL started to take over the network rearrangements, resulting in a reduced rate of TERs (V5).

An ideal epoxy vitrimer as the candidate of reprocessable and recyclable thermosets should have both the good thermal performance (high T_g) and the fast network rearrangements. For better comparing DGEAC/SA/GL with other epoxy vitrimers based on TERs, the relaxation time at 180°C was demonstrated with considering T_g as shown in Fig. 3c. As can be seen from the blue area, most of TERs-based epoxy vitrimers maintained a relaxation time from 100 to 10,000 s with T_g from 0 to 100°C. The relaxation times of V2 to V5 (red stars) were much shorter than those of most reported vitrimers in this region, except the one ($\tau^* = 66$ s and $T_g = -18^\circ\text{C}$) by Hayashi⁴⁸ and another one ($\tau^* \sim 100$ s and $T_g = 40^\circ\text{C}$) by Tournilhac.²⁸ Especially for V4, it exhibited a short relaxation time $\tau^* = 130$ s with $T_g = 61^\circ\text{C}$. Besides, although some reported TERs-based epoxy vitrimers exhibited higher T_g (88°C, 65°C, 187°C) than V4,^{32,33,45} their

relaxation time was over 10 times longer, which greatly hindered vitrimer welding, reprocessing, and recycling process. For V5, it exhibited a higher T_g (89°C) than V4, but still maintained a relatively short relaxation time (190 s). Notably, both the relaxation time and T_g of V1 were similar with the reported TERs-based epoxy vitrimers using SA as curing agent with 5 mol % TBD,⁴⁶ which confirmed that the fast relaxation and the enhancement of T_g were attributed to GL, not to the only DGEAC/SA networks or catalyst.

Deduced from the stress relaxation using Maxwell equation, the topology freezing temperature (T_v) was determined as 73, 54, 52, 42, and 49°C from V1 to V5 (Table S3). This result corresponded well to the relaxation rate as discussed. Furthermore, the malleable temperature (T_{mall}) of these vitrimers were measured by using DMA thermal dilation test (Fig. 3d). A notable increase in the expansion coefficient appeared at the temperature of 164, 161, 158, 116 and 161°C for V1, V2, V3, V4 and V5, respectively, the tendency of which was consistent with T_v . These observations can be explained by TERs rates. From V1 to V4, the rate of TERs increased while in the rigid network (V5) the rate of TERs decreased because of the movement limitation of polymer chains.

To further analyze our vitrimer materials in depth for guiding welding, repairing, reprocessing and recycling, the above four thermal parameters (T_g , T_v , T_{mall} , T_d) from V1 to V5 were summarized in Fig. 4. Since T_g reveals the thermal resistance of thermosets, the region below T_g can be defined as working window (pink color area in Fig. 4). When vitrimer

networks start to rearrange, topology freezing temperature (T_v) and malleable temperature (T_{mall}) reflect bond exchange properties. Because T_v is deduced from stress relaxation results, in many reports T_v is lower than T_g like V4 and V5 in Fig. 4, where T_{mall} can be another helpful parameter to guide reprocessing. Thus, the region from T_g to T_{mall} is defined as shape memory window (blue color area in Fig. 4), where the temporary shape of vitrimers can be fixed after cooling process. In addition, the thermal region from T_{mall} to T_d is defined as reprocessing window (green color area in Fig. 4). In this region a vitrimer material can be welded, recycled, reprocessed and chemically degraded through network topological rearrangements. When temperature elevated across T_d , vitrimer starts to decompose and this region is defined as useless region (gray color area in Fig. 4). Apparently, the wider the working window and the reprocessing window, the better the vitrimer materials, because they should not only function like thermosets at room temperature or even higher temperature, but also need start network exchange rapidly at a temperature just little higher than T_g . This aim has been approached by using GL in this work. That is to say, the thermal performance and network rearrangement properties were improved simultaneously in our vitrimers.

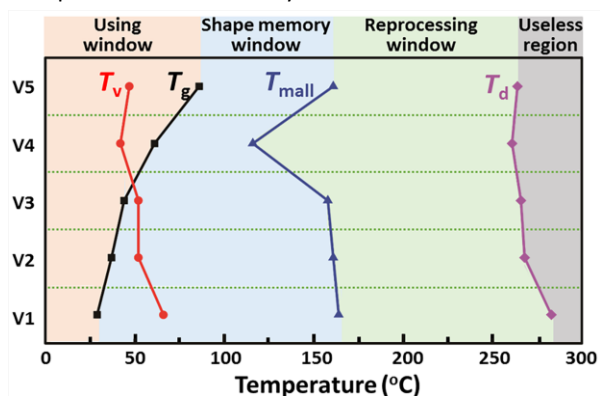


Fig. 4 Thermal behaviors of vitrimers from V1 to V5. Four characteristic temperatures were glass transition temperature (T_g), topology freezing transition temperature (vitrification temperature, T_v), malleability temperature (T_{mall}), and decomposed temperature (T_d). T_{d5} was used as T_d from TGA results.

Welding, reprocessing, repairing, recycling and chemical degrading of DGEAC/SA/GL materials

Due to the fast exchange reactions, the welding, reprocessing (shape changing), repairing, recycling and chemical degrading of DGEAC/SA/GL vitrimer V4 was performed at a mild temperature (130°C). Note that this temperature was lower than those of most reported TERs-based epoxy vitrimers (Table S4), which revealed the good dynamic properties of V4. Its welding property was shown in Fig. 5a, where two films were easily welded to an integral structure “L” at 130°C for 1 h with the help of ethylene glycol (EG). This new structure can bear 20 g weight, over 70 times heavier than itself. Fig. 5b demonstrated the reprocessing of V4. A flat film was fixed to a spiral shape of “W”, and after heating at 130°C for 1 h, the new shape “W” was obtained by TERs. This new permanent shape cannot recover to its original flat shape when cooling

down to room temperature because of the “plasticity deformation”,^{12,49} which reflected the “thermoplastic” properties of DGEAC/SA/GL. To study the repairing properties of V4, a film was scratched to have a crack on the surface initially, followed by the heating with the help of EG at 130°C. As observed under optical microscope, the width of crack reduced from 190 to 90 μm within 30 min, and nearly disappeared after 120 min, indicating its good reparability (Fig. 5c). In addition, the fragments of V4 had been reconfigured to an integral film at 130°C for 1 h under a pressure of 10 tons, which could be further used to prepare dumbbell-shaped samples as shown in Fig. 5d. Tensile tests showed that the strength and modulus of original V4 was 2.52 MPa and 147.67 MPa, respectively, while 1.48 MPa and 83.81 MPa after recycle (Table S2). The recycle efficiency of strength and modulus were near 60%. Note that the loss in strength and modulus of recycled V4 could be reduced well by extending the recycling time to 5 h at the same temperature (130°C), where the materials exhibited a high recycle efficiency around 90% (Table S2). Besides, the chemical degradability of V4 was studied by using EG (Fig. 5e). Because of the fast exchange reactions between networks and EG, the rectangular sample was totally degraded after 5 h at 130°C. In brief, V4 exhibited comprehensive dynamic properties and was suitable to be utilized in actual situations.

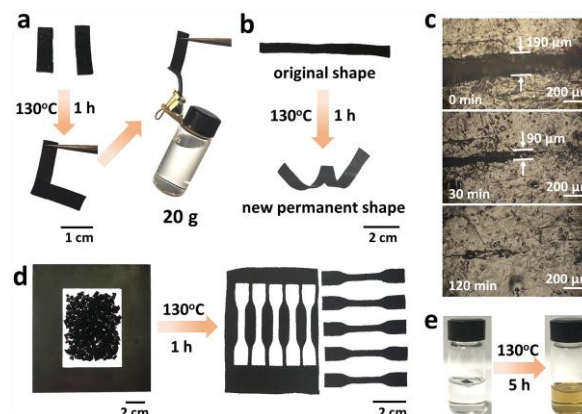


Fig. 5 Welding (a), reprocessing (b), repairing (c), recycling (d) and chemical degrading (e) of the DGEAC/SA/GL vitrimer V4.

For better illustrating the high-efficiency reprocessing and shape memory of DGEAC/SA/GL vitrimer V4, Fig. 6, Movie S1 and S2 were demonstrated directly. Initially, the right-handed twisted ribbon of V4 was deformed into a left-handed twisted ribbon by heating above T_g and then fixing with a tweezer (process I). Subsequently, a blower was used to heat this new shape (left-handed rotation) for 2 min (temperature above T_{mall}), resulting in the stress relaxation of materials. After revoking the tweezer, the permanent left-handed twisted ribbon was obtained (process II). Note that this processing time (the whole process II in Movie S2) was very short (2 min), because of the fast TERs rate of V4. Meanwhile, this permanent left-handed twisted ribbon could also be deformed into another temporary form “J” (process III) and recovered using heating-cooling process (process IV), because of the

“elasticity deformation” of vitrimers.^{12,49} This cycle not only exhibited the shape memory properties of V4, but also confirmed the successful reprocessing of V4 in process II. In summary, the fast permanent deformation (2 min) and shape memory properties allow the convenient design of 3D structures from our vitrimers, and also provided potential to use these recyclable smart materials in real scenario.

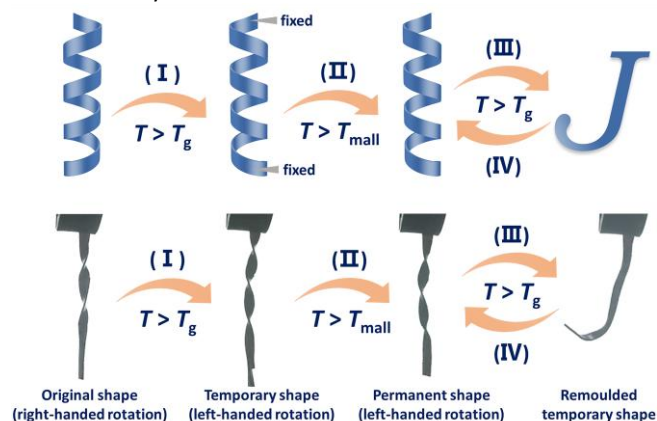


Fig. 6 Schematic illustration (top) and photographs (bottom) of reprocessing and shape memory of V4. (I) Deformation from original shape (right-handed rotation) to temporary shape (left-handed rotation) at temperatures above T_g for 5 s. A tweezer was used to fix the new shape. (II) The new permanent shape (left-handed rotation) was obtained by heating above T_{mall} for 2 min and then revoking the tweezer. (III) The new permanent shape (left-handed rotation) was remoulded into another temporary shape at temperatures above T_g for 5 s and kept after cooling to room temperature. (IV) The permanent shape (left-handed rotation) was recovered after heating above T_g for 10 s.

Conclusions

A green, facile and effective strategy was reported in this work for resolving the contradiction between the high rate of networks topological rearrangements (fast stress relaxation) and the usage glass transition temperature (T_g) in epoxy vitrimers based on transesterification reactions (TERs). By using natural glycyrrhizic acid (GL) and sebacic acid (SA) as complexed curing agents to react with diglycidyl ester of aliphatic cyclo (DGEAC), a series of TERs-based epoxy vitrimers (from V1 to V5) had been prepared. Because of the unique rigid skeleton, multiple carboxyl groups and close hydroxyl groups of GL, their T_g values rose from 31 to 89°C from V1 to V5 while T_{mall} declined from 164 to 116°C from V1 to V4 with an augmentation to 161°C for V5. Especially for V4, it is a comprehensive TERs-based epoxy vitrimer with good thermal stability (T_{dis} 263°C), usable T_g (61°C), low T_{mall} (116°C), and fast stress relaxation (130 s at 180°C). Furthermore, it could be welded, reprocessed, repaired, recycled and chemically degraded at a relative mild temperature (130°C). This system achieved the enhanced stress relaxation rate and T_g simultaneously in TERs-based epoxy vitrimers by using natural GL as curing agents. It provides a green strategy for vitrimer design and makes it possible to prepare recyclable thermosets with high performance and comprehensive properties both at the level of laboratory and industry.

Conflicts of interest

There are no conflicts to declare.

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