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An Interfacial Dynamic Crosslinking Approach toward Catalyst-free and Mechanically Robust Elastomeric Vitrimer with a Segregated Structure

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 Electronic supplementary information

Abstract Elastomeric vitrimers with covalent adaptable networks are promising candidates to overcome the intrinsic drawbacks of conventional covalently-crosslinked elastomers; however, most elastomeric vitrimers show poor mechanical properties and require the addition of exogenous catalysts. Herein, we fabricate a catalyst-free and mechanically robust elastomeric vitrimer by constructing a segregated structure of sodium alginate (SA) in the continuous matrix of epoxidized natural rubber (ENR), and further crosslinking the composite by exchangeable hydroxyl ester bonds at the ENR-SA interfaces. The manufacturing process of the elastomeric vitrimer is facile and environmentally friendly without hazardous solvents or exogenous catalysts, as the abundant hydroxyl groups of the segregated SA phase can act as catalyst to activate the crosslinking reaction and promote the dynamic transesterification reaction. Interestingly, the segregated SA structure bears most of the load owing to its high modulus and small deformability, and thus ruptures preferentially upon deformation, leading to efficient energy dissipation. Moreover, the periodic stiffness fluctuation between rigid segregated SA phase and soft ENR matrix is beneficial to the crack-resisting. As a result, the elastomeric vitrimer manifests exceptional combination of catalyst-free, defect-tolerance, high tensile strength and toughness. In addition, the elastomeric vitrimer also exhibits multi-shape memory behavior which may further broaden its applications.

Keywords Tough; Defect-tolerant; Elastomeric vitrimer; Interfacial dynamic crosslinks; Segregated structure

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INTRODUCTION

Rubbers, as a class of soft materials that can deform largely and reversibly, are widely applied in almost every aspect of modern society such as automotive engineering, biomedical materials and aerospace applications.^[1–5] Universally, the covalent crosslinking of rubbers is prerequisite for acquiring good mechanical properties such as high elasticity, toughness and chemical resistance to satisfy the requirements of actual working conditions. However, the irreversible covalent crosslinks impose a huge dilemma for the recycling of rubbery objects, which is a common and insurmountable obstacle for all thermosetting polymers. Vitrimers, a novel type of covalently cross-linked polymer network capable of shuffling chemical bonds to rearrange its network topology, have been demonstrated as a straightforward approach to resolving the inherent conflict between chemical cross-linking and recycling of thermosetting materials.^[6,7] Differ-

ent from traditional self-healing materials, vitrimers can preserve network connectivity and integrity during topology rearrangements ascribed to the unique associative exchange mechanisms.^[8] Therefore, vitrimers are chemically crosslinked yet highly processable. Until now, a variety of chemistries, such as the transesterification reaction,^[9,10] boronic ester exchange,^[11,12] transalkylation,^[13,14] dioxaborolane metathesis,^[15,16] imine exchange,^[17,18] and metatheses of olefins^[19] have been included in the realm of vitrimers. Among these chemistries, the most pioneering and representative one is epoxy-based dynamic transesterification reaction (TER) owing to its broad availability of monomers and ease of synthesis.

By far, TER-based vitrimer chemistry has been widely explored and applied in fabricating various recyclable elastomers. For example, Chen and co-workers report a type of recyclable epoxidized natural rubber (ENR) utilizing oxidized cellulose nanocrystals (TOCNs) with a large number of carboxyl groups as curing agents to dynamically crosslink ENR by forming exchangeable β -hydroxyl ester bonds.^[20] Xu and co-workers introduce TER into polydimethylsiloxane (PDMS), resulting in a PDMS elastomer with excellent solvent resist-

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ance and recyclability.^[21] Guo and co-workers fabricate a TER-based elastomer by crosslinking epoxy-functionalized EPDM (e-EPDM) with dicarboxylic acids.^[22] Despite these significant advances, several enormous challenges remain to be addressed in the current TER-based elastomeric vitrimers. First and foremost, exogenous catalysts are required in the TER-based vitrimers for catalyzing the curing and bond-exchanging reactions as in most other vitrimer systems. Ineluctably, the inclusion of catalyst causes grievous negative effects, including the toxicity of catalyst, the undermining of recyclability caused by the leaching of catalyst and the accelerated thermal degradation in the presence of catalyst.^[23–25] Second, most of the current synthetic elastomeric vitrimers suffer from insufficient mechanical properties, and thus require the incorporation of fillers.^[26–28] However, the inclusion of fillers could hinder the network topology rearrangements and ultimately attenuate the processability of vitrimers. Although this issue can be alleviated by designing exchangeable interfacial linkages between fillers and matrices,^[29–31] additional modifying processes of fillers are required, which not only include hazardous chemical solvents, but also complicate the manufacturing process. Last but not the least, the current filler-reinforced elastomeric vitrimers completely ignore the significance of microstructural design. Thus, it is extremely difficult to fabricate elastomeric vitrimers integrating high strength, great toughness and even defect resistance simultaneously, despite the fact that such vitrimers are highly desirable to ensure long-term durability and service reliability under the complex practical environments. To resolve the above-mentioned issues, a pioneering strategy is highly demanded.

In the present work, we report a class of catalyst-free, defect-tolerant, strong and tough elastomeric vitrimer (DTST-EV) prepared by an extremely simple and eco-friendly method based on latex assembly. The DTST-EV is featured by a unique microscopic 3D segregated structure of sodium alginate (SA) in epoxidized natural rubber (ENR) matrix formed by the evaporation-induced phase segregation. Specially, the segregated SA phase can not only serve as reacting moiety for the esterification reactions (ERs) between its carboxyl groups and the epoxy groups of ENR to form exchangeable hydroxyl ester bonds at the ENR-SA interphase, but also act as internal catalyst to activate both the ERs and the TERs at elevated temperatures with the presence of abundant free hydroxyl groups on the backbone of SA molecules. In addition, the segregated SA phase, owing to its rigid and interconnected characteristic, can bear most of the applied load and act as sacrificial bonds to effectively dissipate energy upon deformation; moreover, the distinct stiffness variation between the rigid segregated phase and the soft matrix enables the resistance to crack propagation. The cooperative effects of sacrificial property and stiffness variation induced by the segregated structure can simultaneously increase the fracture toughness, tensile strength and the crack propagation resistance of the elastomer. Moreover, the DTST-EV exhibits multishape memory behavior toward temperature, which further broadens its potential application. Since ENR and SA are bio-derived materials, and the manufacturing process of the elastomeric vitrimer is exceedingly environmentally friendly, we envisage that the present work will open up new avenues

for future design of sustainable polymer materials.

EXPERIMENTAL

Materials

Natural rubber (NR) latex (60 wt% solid content) and epoxidized natural rubber (ENR) latex (30 wt% solid content, 50% epoxidization degree) were obtained from Chinese Academy of Tropical Sciences. Sodium alginate (SA) (500–1000 mPa·s) was received from Shanghai Titan Scientific Co., Ltd. Rhodamine 6G was obtained from Adamas Reagent Co., Ltd. 1,2-Dimethylimidazole (DMI, 99%) and zinc acetate ($\text{Zn}(\text{Ac})_2$, 98%) were supplied by Sigma-Aldrich.

Preparation of DTST-EV with Microscopic 3D Segregated Structure

The DTST-EV_x with segregated structure were prepared by a facile and eco-friendly latex assembly method. Briefly, sodium alginate (SA), dissolved in distilled water, was mixed with ENR latex under vigorous stirring for 12 h to get compounded latex with various SA concentrations. Dry compounds with SA content ranging from 0 phr to 20 phr (parts per hundred of rubber) were obtained by film casting the blends and dried naturally to constant weight. DTST-EV hybrid films were obtained by curing the dried compounds at 180 °C by hot-pressing for the optimum curing time obtained from a vulcameter. The recycle of the samples was achieved by cutting the as-moulded samples into pierces, and then remolding at 180 °C. The remolding time was obtained from the stress relaxation experiment.

Preparation of ENR/SA with Dispersed SA Structure

ENR/SA_x samples with dispersed SA distribution in ENR matrix were prepared to illustrate the significance of the segregated structure. Specifically, SA was compounded with ENR in the same way with DTST-EV_x. After totally dried, the compounds were firstly subjected to two-roll mixing before hot-pressing. The powerful shearing force of two-roll mixing can destroy the interconnected SA segregated phase formed by the volatilization induced co-assembly during drying. Therefore, NR/SA_x samples with a dispersed distribution of SA in ENR matrix were obtained.

Characterization

Fourier transform infrared spectroscopy (FTIR) spectra were obtained on Thermo Scientific Nicolet iS50 FTIR. Scanning electron microscopy (SEM) tests were performed on JEOL JSM-5900LV, and all images were taken from the cross section of the material. TEM images were obtained by using a transmission electron microscope (TEM, FEI TecnaiG2F20S-TWIN). The 3D interconnected SA segregated phase in ENR matrix was examined by a laser scanning confocal microscope (Zeiss LSM 710, Carl Zeiss, AG, Germany). SA was labeled by immersing the DTST-EV thin films in the solution of rhodamine 6G overnight in the dark and repeatedly washed with distilled water to remove the residual dye molecules on the surface. A 350 nm laser was applied to excite the rhodamine 6G probes. Natural rubber (NR) was used to replace ENR to avoid the influence of labeling SA. The morphology evolution of the 3D interconnected SA phase in DTST-EV was recorded by stretching the thin film of DTST-EV₁₀ to a certain strain and fixing it on slide glass *via* adhesive tape. For dynamic mechanical analysis (DMA), a tensile mode

with a frequency of 1 Hz and a strain of 0.5% was used. The rectangle samples were heated from $-80\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$ at a heating rate of $3\text{ }^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere. Stress relaxation experiments were performed with a 5% constant applied on the DMA machine. The characteristic relaxation time τ^* was determined as the time required to relax to 37% of the initial relaxation stress. Characteristic relaxation time τ^* follows an Arrhenius law $\tau(T) = \tau_0 \exp(E_a/RT)$, where E_a refers to the activation energy for the TER, τ_0 represents the characteristic relaxation time at infinite T , R is the universal gas constant and T is experimental temperature. The multi-shape memory behavior was tested by the procedure as follows. Step 1: the sample of ENR/SA₁₅ was kept at $90\text{ }^{\circ}\text{C}$ isothermally for 5 min; step 2: the sample was stretched to a set stress of 0.22 MPa in 1 min followed by cooling to $0\text{ }^{\circ}\text{C}$ and held under this stress for 10 min; step 3: the sample was unloaded in 1 min and kept isothermally for 10 min to fix the temporary shape; step 4: the sample was heated to $90\text{ }^{\circ}\text{C}$ in a step-wise manner with a step interval of $15\text{ }^{\circ}\text{C}$. During each step interval, the sample was isothermally held for 15 min to allow shape recovery. Mechanical properties were measured on an Instron 5966 testing machine and the deformation rate was 100 mm/min. Fracture toughness was measured by classical single edge notch test with a deformation rate of 6 mm/min and the fracture toughness (G_c) was calculated by the Greensmith method.

RESULTS AND DISCUSSION

Fabrication and Characterization of DTST-EV with Segregated Structure

Sodium alginate (SA) derived from marine algae is a nontoxic and renewable natural polysaccharide. The abundant carboxyl groups on the molecular chain of SA make it an ideal multi-functional curing agent for epoxidized natural rubber (ENR) which is a unique derivative of natural rubber harvested from Hevea trees. Fig. 1(a) schematically illustrates the facile and environmentally friendly latex assembly process to fabricate vitrimers based on ENR and SA, and the formation of the segregated structure. Specifically, SA aqueous solution is mixed with ENR latex followed by stirring at room temperature to form a stable and homogeneous blend. Thereafter, the mixture is film casted and dried naturally, enabling the latex particles to co-assemble with the SA molecules. The gradual evaporation of water compels ENR particles to aggregate and deform, squeezing the SA molecules into the interstitial spaces of the ENR rubber particles. After being totally dried, the hybrid compound is subjected to compression molding at $180\text{ }^{\circ}\text{C}$ for the optimum curing time determined by a vulcameter (Fig. S1 in the electronic supplementary information, ESI). During this process, the rubber chains inter-diffuse between rubber particles and ultimately merge into a continuous matrix, meanwhile the SA molecules are further extruded to form the 3D interconnected and segregated structure. Ultimately, the hybrid material manifests a unique microstructure comprising a segregated rigid phase of SA and a continuous soft phase of ENR, as confirmed by SEM and TEM micrographs in Figs. 1(b) and 1(c). This microstructure is solidified with the formation of hydroxyl ester bonds at the ENR-SA interphases through the esterification reaction between the carboxyl groups on the backbone of SA and the epoxy groups on the ENR chains (Fig. 1d, Scheme S1 in

ESI). Significantly, no exogenous catalysts are required as the abundant free hydroxyl groups on the backbone of SA molecules can induce the ring-opening of epoxy groups for the subsequent curing process and activate the TER for the network topology rearrangement.^[32] To study the influence of catalyst on the curing process, different contents of catalysts are added into the current system and the curing process was monitored and compared with that of catalyst-free sample. Strikingly, the addition of catalyst does not accelerate the curing process as the curing curves of all samples almost coincide perfectly (Fig. 1e). This result suggests that the large amount of free hydroxyl groups of SA is effective to induce the curing reaction.

To confirm the formation of hydroxyl ester bonds by esterification reactions between SA and ENR, FTIR spectra are recorded to monitor the evolutions of the absorption bands of the epoxy and ester groups during the curing process. Clearly, the absorption band of the epoxy group at 877 cm^{-1} is gradually weakened, while the band intensity of ester groups at 1718 cm^{-1} increases constantly as the curing progresses (Fig. 1f). Moreover, these changes become more prominent with the increase of SA content (Fig. S2 in ESI). These results collectively demonstrate the formation of interfacial β -ester linkages between SA and the ENR matrix;^[33,34] such linkages are capable of undergoing thermal activated transesterification reaction. Despite the dynamic nature, the ester linkages can be regarded as covalent crosslinks because the exchange reaction is associative, *i.e.*, the fracture of bonds happens only when new bonds are formed. To verify the formation of covalently crosslinked molecular architecture of DTST-EV, the swelling behavior is investigated. As expected, the DTST-EV sample only slightly swells rather than dissolves after soaking in THF for 24 h (Fig. S3 in ESI), and the gel contents of all vitrimers are higher than 98% (Table S1 in ESI).

A series of elastomeric vitrimers with such a segregated structure were fabricated by adjusting the SA loading systematically. The obtained elastomeric vitrimers are named as DTST-EV_x, where x represents x parts of SA relative to per hundred parts of rubber. To illustrate the importance of the microstructural design, the samples with randomly dispersed SA particles in the ENR matrix were prepared as a control through an extra two-roll mixing process before hot-pressing (see details in Experimental Section). The resultant samples are denoted as ENR/SA_x. The microstructure of ENR/SA exhibits a distinctly different phase distribution from that of DTST-EV (Fig. S4 in ESI). The powerful shear force during two-roll mixing completely destroys the interconnection of the segregated SA phase, leading to random dispersion of elongated SA particles in the ENR matrix.

Network Topology Rearrangements of DTST-EV

To confirm the network topology rearrangements of DTST-EV based on the transesterification reaction (Fig. 2a), the cyclic strain/recovery experiment at different temperatures of the DTST-EV₁₀ was carried out. The DTST-EV₁₀ sample deforms along the force direction immediately at $30\text{ }^{\circ}\text{C}$ with external force applied and the deformation can completely recover after unloading the force, showing a good elastic-recovery behavior similar to that of a covalently cross-linked elastomer (Fig. 2b). In contrast, a different viscoelastic response is exhibited with the temperature increased to $180\text{ }^{\circ}\text{C}$. At the elevated temperature,

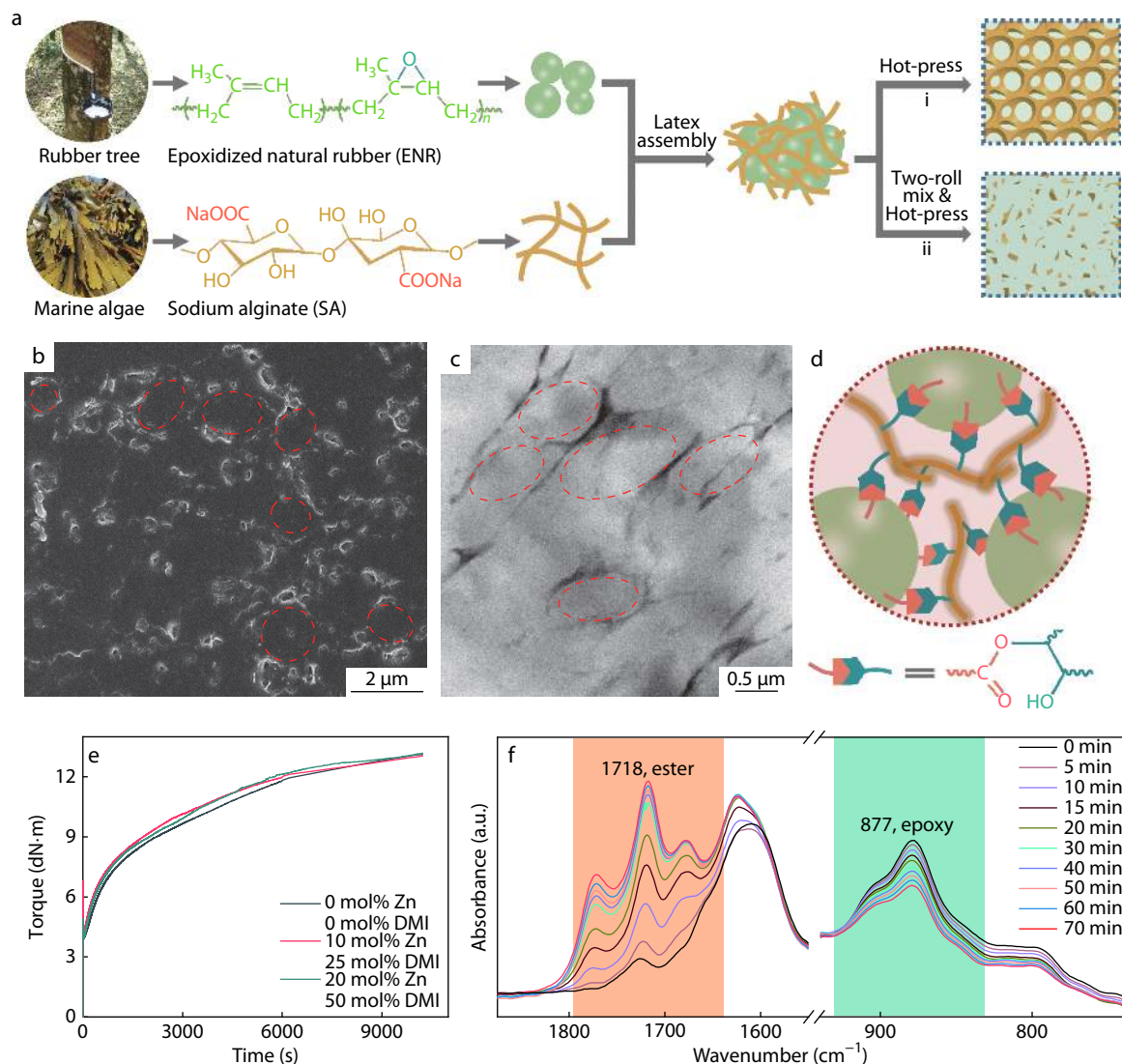


Fig. 1 Fabrication and morphology of DTST-EV. (a) Illustration for the fabrication of DTST-EV with microscopic 3D segregated structure and ENR/SA hybrid materials with dispersed SA phase using a simple and environmentally friendly latex assembly method. (b) SEM and (c) TEM images for the microstructures of DTST-EV₁₀, respectively. (d) Illustration for the exchangeable hydroxyl ester bonds at the interfaces of rubber particles and SA. (e) The effect of catalyst content on the curing process of DTST-EV₁₅, the quantities of DMI and Zn(Ac)₂ are relative to the carboxyl group of SA. (f) The evolutions of the absorption band of the carboxyl and epoxy groups for DTST-EV₁₀ during curing at 180 °C.

an initial thermal expansion and elastic response were observed followed by a viscous response, after which the sample could not regain its initial length when the external force was released. Such significant differences can be interpreted on the basis of the topology freezing transition, which is a typical characteristic of vitrimers. At low temperature, the network topology is frozen as the transesterification reaction is dormant, whereas elevated temperature activates the interfacial transesterification reaction, allowing rearranging the network topology to adapt to external force despite the absence of external catalyst. Stress relaxation tests were conducted to further disclose the evidence of the thermal-activated transesterification reaction induced network topology rearrangement. Clearly, all DTST-EV samples can completely relax the applied external stress, indicating that the covalently cross-linked network can flow at elevated temperature (Fig. 2c). A closer observation reveals increasing the SA

loading slows down the relaxation rate, because higher SA loadings leads to higher cross-linking density, thereby requiring more exchanges for the topology rearrangement. Moreover, the SA phase, behaving like rigid fillers, may restrict the mobility of the rubber chains and hinder the exchange reaction, which is likely to retard the relaxation process. The temperature-dependence of stress relaxation for DTST-EV is shown in Fig. 2(d). The relaxation rate of the DTST-EV sample substantially increases with increasing temperature, as the transesterification reaction can be accelerated at higher temperatures. The characteristic relaxation time τ^* , determined as the time span that the relaxation stress reaches 37% of its initial value, follows the Arrhenius law (Fig. 2e), according to which the activation energy (E_a) is calculated to be 156.33 kJ/mol. This activation energy is higher than the value (~80 kJ/mol) reported by Leibler *et al.*^[7,25] This result is ascribed to the high molecular weight of

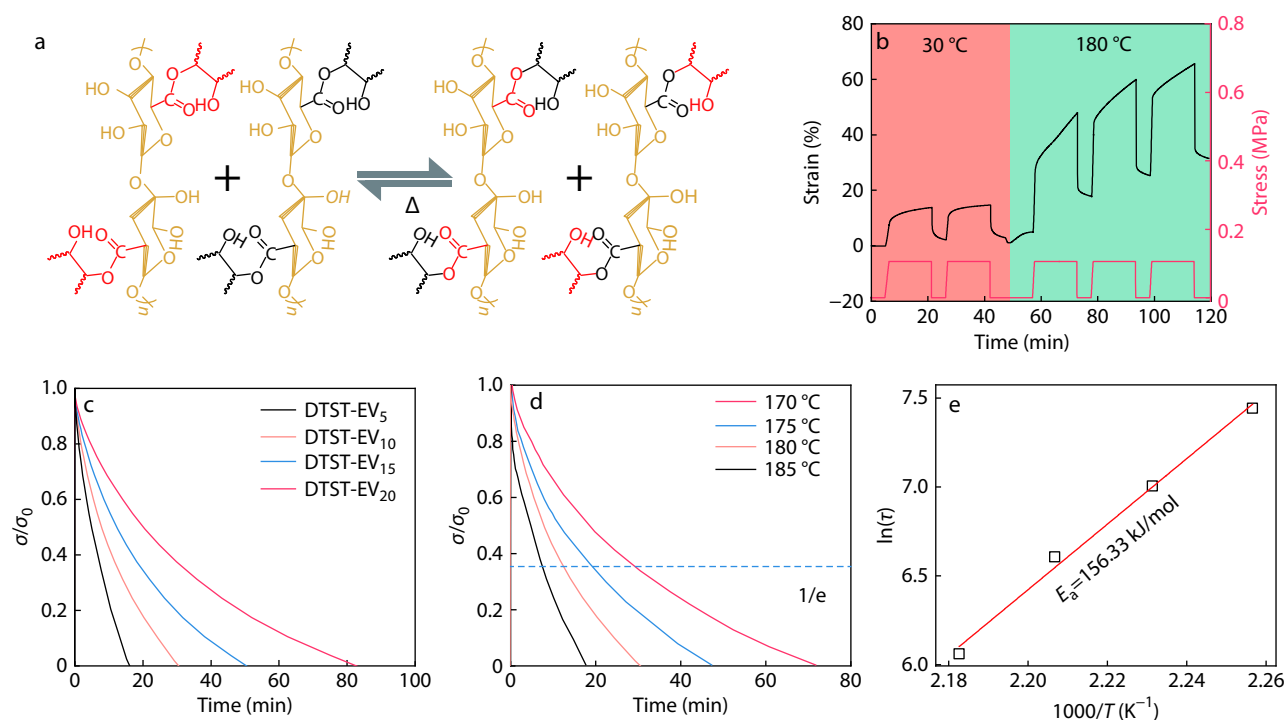


Fig. 2 Network topology rearrangements of DTST-EV samples. (a) Illustration of the thermal activated transesterification reaction without catalyst. (b) Cyclic strain-recovery tests of DTST-EV₁₀ at 30 and 180 °C. (c) Normalized relaxation stress (σ/σ_0) as a function of time for DTST-EV with different SA loading. (d) Normalized stress relaxation curves for DTST-EV₁₀ at different temperatures (170, 175, 180, 185 °C, respectively). (e) Fitting of the measured relaxation times for DTST-EV₁₀ according to the Arrhenius equation.

SA and the structure of its molecular backbone, in which the glycoside structures cause obvious steric hindrance that raises the barrier of transesterification. Besides, the absence of external catalyst may also be a potential cause of the high activation energy accordingly.^[22,33,35–37]

Energy Dissipation and Crack Resistance of DTST-EV

To distinguish the influence of microstructural morphology on energy dissipation, cyclic tensile tests were carried out. Both ENR/SA₁₀ and DTST-EV₁₀ manifest obvious hysteresis in the first loading-unloading cycle, revealing a large amount of energy is dissipated in both samples during stretching (Figs. 3a and 3b). Significantly, the hysteresis of DTST-EV₁₀ is much more prominent than that of ENR/SA₁₀, indicating that the 3D interconnected segregated structure performs better in energy dissipation. To quantitatively compare the energy dissipating ability between different microstructures, the energy dissipation efficiency is quantified as the value of the integrated area of the hysteresis loop divided by that under the loading curve. Apparently, the energy dissipation efficiency of DTST-EV₁₀ ($\approx 70\%$) is much higher than that of ENR/SA₁₀ (53%); moreover, such high efficiency nearly keeps constant regardless of the extent of deformation up to a strain of 3. Such a phenomenon represents a typical feature of tough materials.^[38–40] The underlying cause of such remarkable energy dissipation is attributed to the interconnected and segregated SA phase in DTST-EV, which bears most of the applied load and ruptures preferentially upon deformation owing to its much smaller fracture strain than rubber matrix, dissipating large amounts of energy. To visualize the energy dissipating process aroused by microstructural change during stretching, the SA molecules were labeled by

Rhodamine 6G, and laser scanning confocal microscopy (LSCM) was employed to monitor the morphology change of the segregated SA phase upon deformation (Fig. 3d). Initially, an interconnected and segregated SA structure within the rubber matrix is conspicuously observed before stretching, which is highly consistent with the results of SEM and TEM. When applying a strain of 0.5, destruction of the interconnected segregated structure takes place at different regions concurrently, indicating the local destruction of the segregated SA phase. When further increasing the strain, the areas of the disconnected region extend gradually along the tensile direction. Ultimately, the SA phase manifests a dispersed structure at $\varepsilon=3$, which is similar to the microstructure of undeformed ENR/SA₁₀. Overall, the 3D interconnected and segregated SA phase fractures repeatedly at various localized positions during deformation. Such an interesting fracture behavior enables it to dissipate energy in a wide range of strain.

Usually, it is difficult to propagate a steady crack through the sample from a pre-existing crack for a tough material.^[41–43] In this case, the remarkable energy dissipating ability of the rigid 3D segregated structure in DTST-EV enables dramatic stress redistribution at the crack tip, thus enhancing the resistance to crack propagation. To demonstrate the crack resistance of DTST-EV, edge notch with systematically changed width (L) is prefabricated on dumbbell-shaped samples with the central width L_0 . Tensile tests were performed to obtain the stress-strain response for both unnotched and notched DTST-EV₁₀ samples (Figs. 4a and 4b). Clearly, the DTST-EV₁₀ samples exhibit much better defect-tolerance than ENR/SA₁₀ samples, of which the tensile strength and fracture

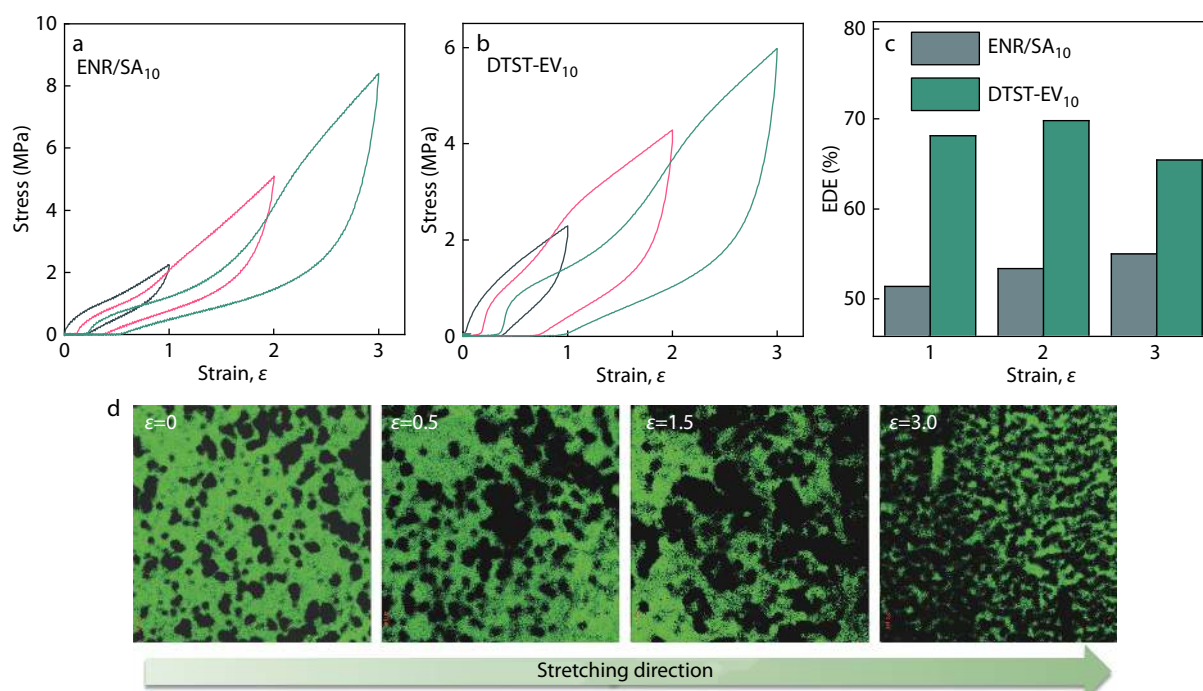


Fig. 3 Sacrificial properties and defect-tolerance of DTST-EV. Representative cyclic stress-strain curves of (a) ENR/SA₁₀ with dispersed SA and (b) DTST-EV₁₀ with 3D interconnected and segregated SA phase. (c) Energy dissipation efficiency of ENR/SA₁₀ with dispersed SA and DTST-EV₁₀ with 3D interconnected and segregated SA phase. (d) LSCM images showing the evolution of the 3D interconnected SA phase in DTST-EV₁₀ during stretching.

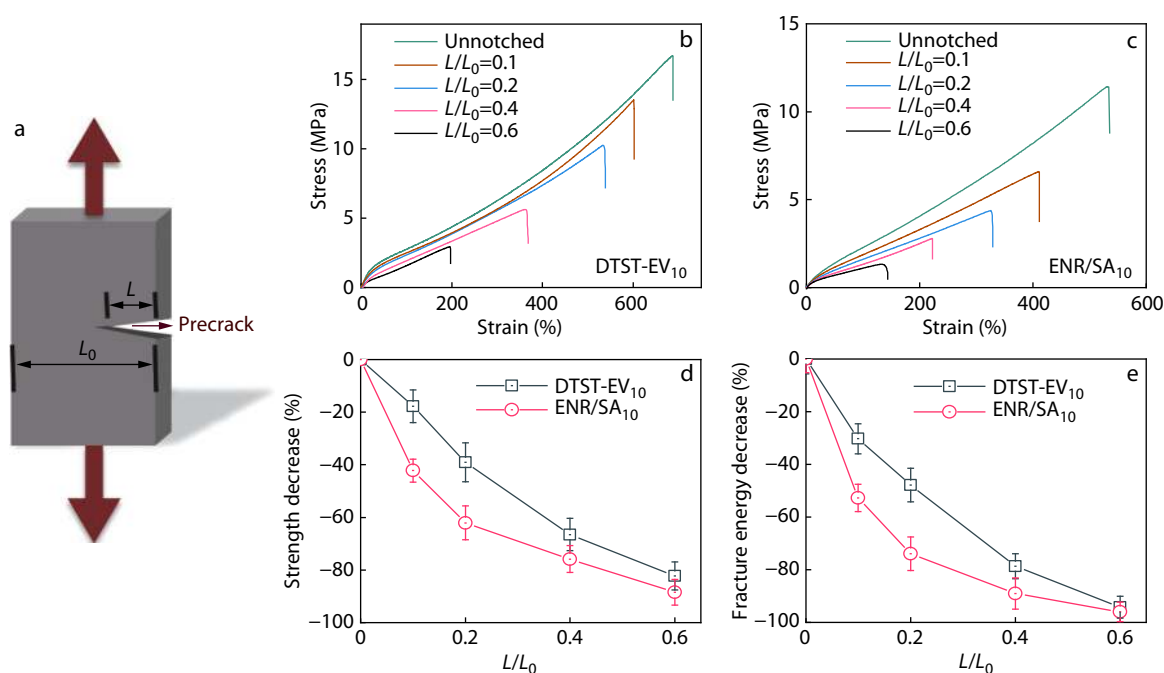


Fig. 4 The defect-tolerance of DTST-EV. (a) The diagrammatic sketch of the notched tensile test. (b) Stress-strain curves for the uncracked and precracked DTST-EV₁₀. (c) Stress-strain curves for the uncracked and precracked ENR/SA₁₀. (d) The strength decrease ratio and (e) fracture energy decrease ratio of the notched DTST-EV₁₀ samples in comparison with the ENR/SA₁₀ samples.

strain decrease drastically even with the appearance of a small notch (Fig. 4c). We further plot the strength decrease ratio and the fracture energy decrease ratio as a function of L/L_0 , as shown in Figs. 4(d) and 4(e), respectively. The strength

and fracture energy decrease rates of DTST-EV₁₀ are much lower than those of ENR/SA₁₀, especially when $L/L_0 < 0.4$. For example, when the width of the precrack is 10% the width of sample ($L/L_0 = 0.1$), ENR/SA₁₀ sample loses approximately 30%

of its strength and 50% of its fracture energy, which was calculated by integrating the stress-strain curves. By striking contrast, DTST-EV₁₀ sample only loses 17% of its strength and 37% of its fracture energy in the presence of a precrack with the same length. Such significant difference in defect-tolerance is ascribed to the better energy dissipating ability of DTST-EV than ENR/SA. The internal fracture of the 3D segregated SA phase in DTST-EV can release the stress concentration at the crack tip, thereby dramatically enhancing crack propagation resistance. Moreover, the inclusion of the interconnected rigid phase induces significant stiffness fluctuation in the soft rubber matrix, which is an exquisite and characteristic strategy for living organisms to build defect-tolerant structures.^[44–47] Such stiffness fluctuation has also been shown theoretically and demonstrated experimentally to hinder crack propagation and increase toughness of many synthetic materials as well.^[48,49]

Dynamic Mechanical Properties and Shape Memory of DTST-EV

To evaluate the effect of interfacial hydroxyl ester linkages on the overall network mobility of DTST-EV system, dynamic mechanical analysis (DMA) was carried out and the results are displayed in Fig. 5. The storage modulus (E') in the tested temperature region is consistently enhanced while the value of $\tan\delta$ decreases with increasing SA loading (Figs. 5a and 5b). This is quite reasonable when considering the mobility of the rubber chains that are attached onto the SA surface is seriously restricted. Such restriction reduces the amount of rubber chains that participate in the bulk relaxation and increases the modulus. Significantly, a constant plateau appears after the obvious drop in E' around glass transition, implying that the network can keep its structural integrity at evaluated temperatures. Meanwhile, it has been reported that the TER-induced stress relaxation enables the shape memory of the materials.^[50–52] To

prove the shape memory behavior of DTST-EV, a rectangular sample of DTST-EV₂₀ was deformed at 90 °C and fixed at 0 °C with a temporary strain of about 75%. Thereafter, the sample was heated from 0 °C to 90 °C in a step-wise manner with a step interval of 15 °C and allowed to recover for 15 min in each step (Fig. 5c and experimental section for details). Apparently, the sample (Fig. 5d) shows the multi-shape memory behavior. As such, the sample can be sequentially folded into different temporary shapes at different temperatures, after which the sample can recover its shape step by step upon heating to the corresponding fixing temperature (Fig. 5e, Fig. S5 in ESI).

Mechanical Properties of DTST-EV

The typical stress-strain curves of DTST-EV and ENR/SA are displayed in Figs. 6(a) and 6(b), respectively. The incorporated SA serves as both crosslinker and reinforcer, thus the tensile modulus and strength of both samples are dramatically increased with increasing SA loading. Such prominently improved mechanical properties benefit from the interfacial hydroxyl ester linkages between the carboxyl groups on the surfaces of SA and the epoxy groups on ENR chains. These crosslinks enable strong interfacial adhesion, which facilitates efficient interfacial stress transfer. Significantly, the mechanical properties of DTST-EV are better than those of the ENR/SA counterparts (Fig. 6c), indicating the microstructure also plays a vital role in the reinforcing effect. For example, when the SA loading is 20 phr, the DTST-EV₂₀ shows an extraordinary tensile strength of 26.5 MPa and an elongation at break of 432%, while the ENR/SA₂₀ shows a much lower tensile strength (22.4 MPa) and fracture strain (360%). Such a distinct difference in mechanical properties can be interpreted in terms of the aforementioned better load-bearing and sacrificial ability of the segregated SA phase in DTST-EV than that of the dispersed SA structure in ENR/SA. Although the fracture strain of all samples decreases with increasing SA loading, the fracture toughness (G_c), which is obtained from the

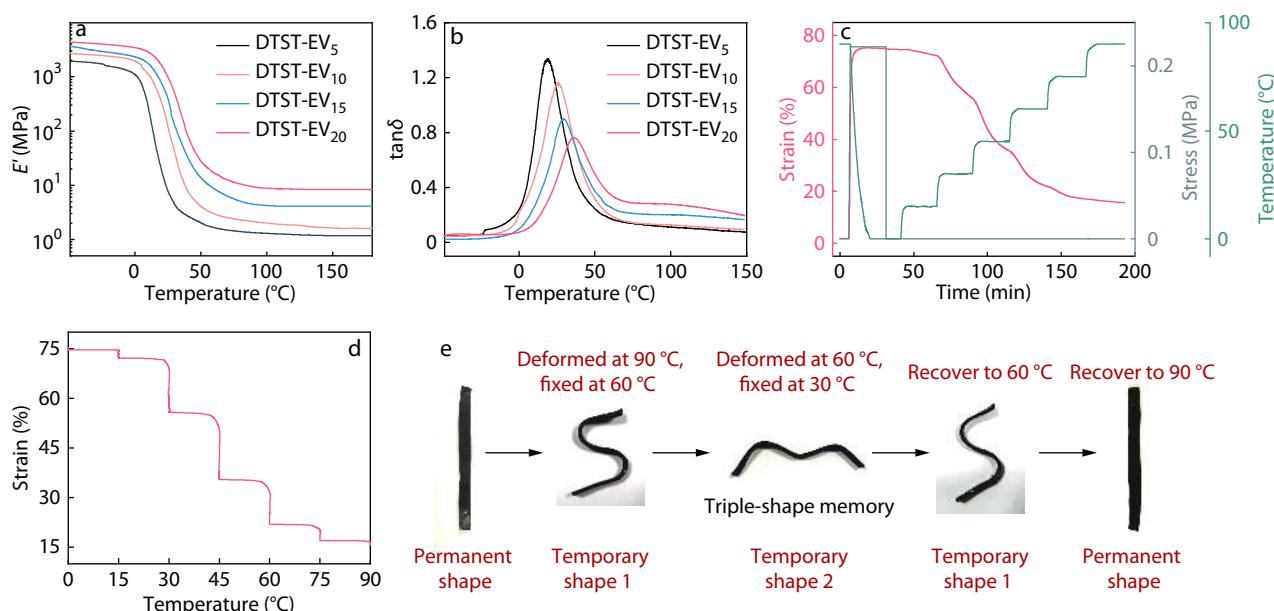


Fig. 5 The multiple shape memory behavior of DTST-EV. (a) Storage modulus and (b) temperature-dependent $\tan\delta$ curves of DTST-EV samples. (c) Multi-stage shape recovery process of DTST-EV₁₅. (d) The strain versus temperature map of multiple shape memory of DTST-EV₁₅. (e) Images demonstrating the triple-shape memory behavior of DTST-EV₁₅.

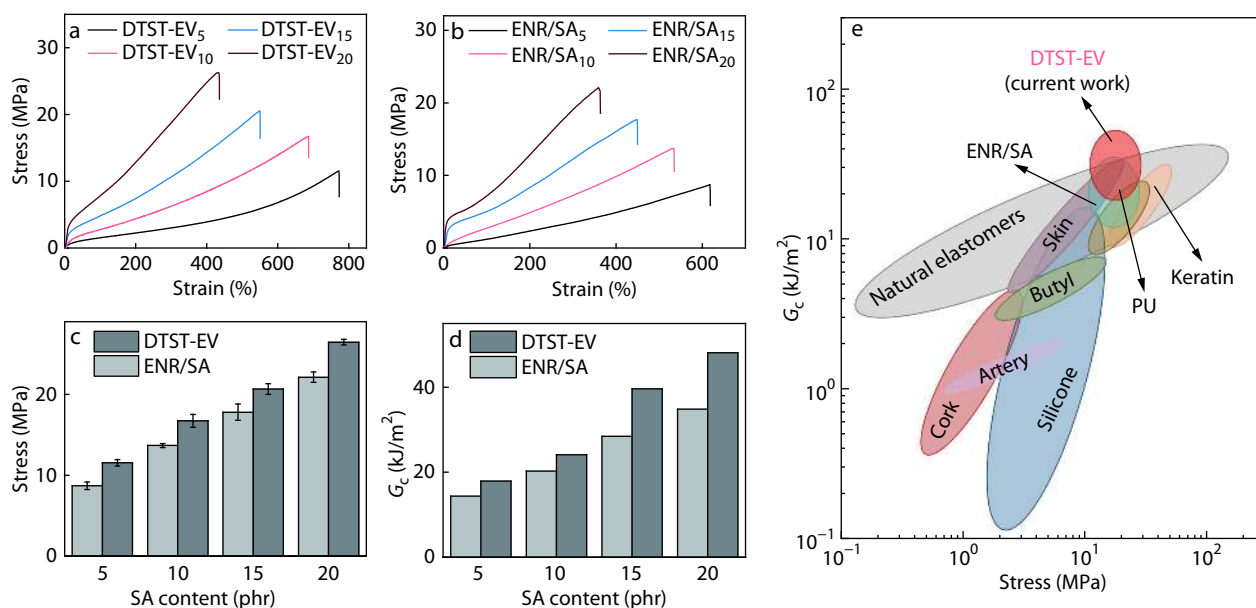


Fig. 6 Mechanical properties and recycling of DTST-EV. (a) Stress-strain curves of DTST-EV with various SA contents. (b) Stress-strain curves of ENR/SA₁₀ with various SA contents. The comparison of the (c) ultimate strength and (d) fracture toughness between DTST-EV with interconnected SA phase and ENR/SA with dispersed SA, respectively. (e) Ashby diagram showing the fracture toughness for DTST-EV with other natural and synthetic elastomers as a function of their strength.

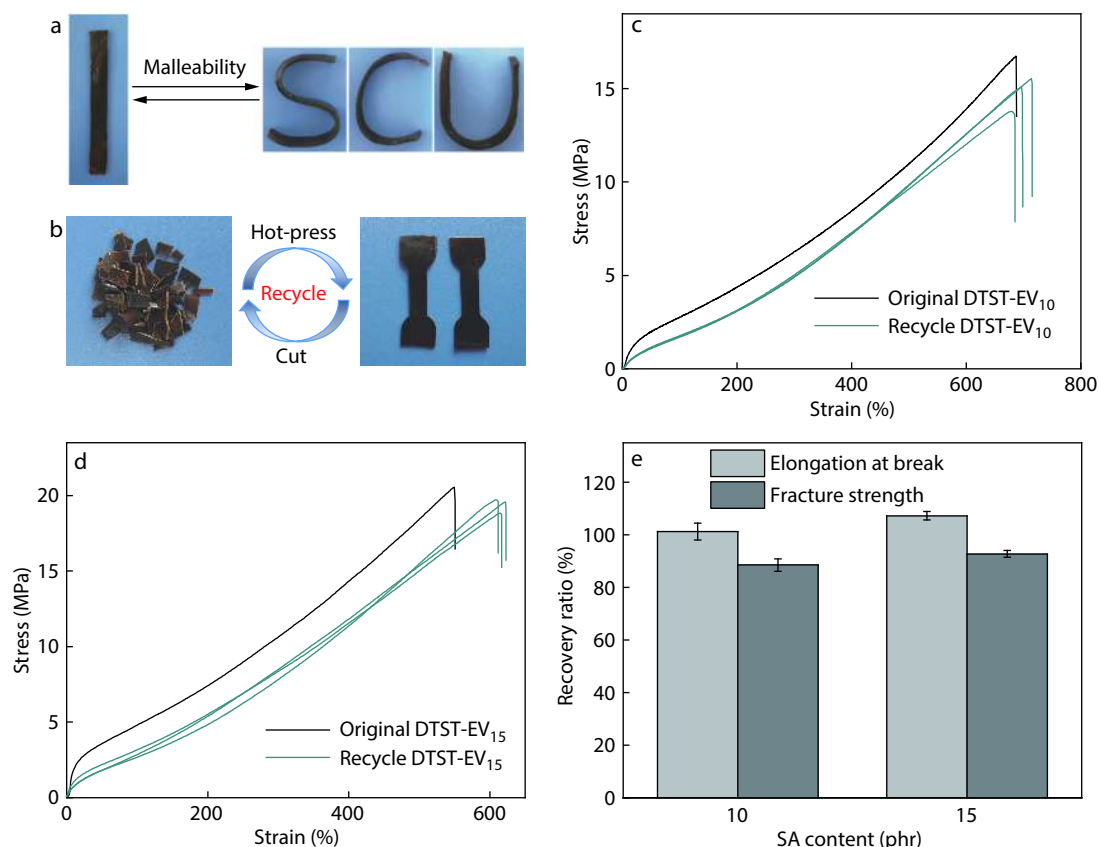


Fig. 7 The recycling of DTST-EV samples. (a) Image presentation of malleability for DTST-EV samples. Various complex shapes can be obtained by bending or twisting a flat DTST-EV₂₀ film at 180 °C without the need of molds. (b) Image presentation of the recyclability for DTST-EV samples. The cured DTST-EV₁₅ is cut into pieces and remolded into new coherent samples. Stress-strain curves of the original and the recycled samples of (c) DTST-EV₁₀ and (d) DTST-EV₁₅. (e) Recovery ratio of tensile strength and elongation at break of the DTST-EV samples after recycling.

Greensmith method,^[53] exhibits substantial increase. Notably, DTST-EV also shows much higher fracture toughness than ENR/SA, benefitting from its superior energy dissipation and crack tolerance. In particular, DTST-EV₂₀ has a fracture toughness of 48 kJ/m², which is higher than that of most natural and synthetic elastomers (Fig. 6e).^[54–57]

Recycling of DTST-EV

Since the crosslinking network based on the TERs can reconfigure at elevated temperature, DTST-EV exhibits excellent malleability and recyclability (Fig. 7a). Therefore, the DTST-EV samples are cut into pieces and then remolded into new samples at 180 °C, as shown in Fig. 7(b). The stress-strain curves of the original and recycled DTST-EV₁₀ and DTST-EV₁₅ samples are displayed in Figs. 7(c) and 7(d), respectively. Surprisingly, all samples can recover most of the mechanical properties after recycling. For example, DTST-EV₁₅ can recover 93% of its initial tensile strength and 100% of its initial strain at break (Fig. 7e). The slightly decreased tensile strength and modulus after recycling can be interpreted in term of the fact that the high activation energy of transesterification reactions makes the network topology restructuring incomplete in the process of remolding.

CONCLUSIONS

In conclusion, a segregated structure of SA is constructed in ENR matrix through latex assembly, resulting in a catalyst-free and mechanically robust TER-based elastomeric vitrimer by the esterification reaction between the carboxyl of SA and epoxy groups of ENR. The esterification reaction proceeds without addition of an external catalyst as the abundant free hydroxyl groups in SA can initiate the curing process and activate the dynamic TER. Interestingly, the unique microstructural design enables the load-bearing and sacrificial capability of the segregated rigid SA phase, the extensibility and stress redistribution of the soft rubber matrix, thereby endowing the resultant vitrimers with great comprehensive mechanical properties including high strength, toughness and exceptional defect-tolerance. Moreover, the elastomeric vitrimer also shows outstanding multiple shape memory. Our study provides a promising access towards sustainable materials with excellent integrated mechanical properties and multifunctionalities.

Electronic Supplementary Information

Electronic supplementary information (ESI), which includes vulcanization curves, FTIR spectra and the swelling behavior of DTST-EV, the microstructure of ENR/SA, image presentation of the triple-shape memory process of DTST-EV, is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-020-2479-6>.

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