Supporting Information

Multireusable Thermoset with Anomalous Flame-Triggered Shape Memory Effect

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Figure S1. Synthetic routes of the multifunctional curing agent and the epoxy thermoset.
Figure S2. Photograph (left) and SEM image (right) of the as-prepared DOPO-MA curing agent.

The solid DOPO-MA curing agent can be easily stored and transported. The SEM image shows that most DOPO-MA particles are smaller than 25 μm, suggesting good miscibility with epoxy monomers.
Figure S3. FTIR spectra of the DOPO, MA and DOPO-MA samples.

As compared to the DOPO, the disappearance of the absorption of P-H group in the profile of the DOPO-MA demonstrates the reaction between P-H and C=C bonds in MA. Moreover, some non-overlapping characteristic peaks assigned to DOPO can be found, such as P-C and P-O-C, which further confirms the successful preparation of DOPO-MA curing agent.
Figure S4. DSC curves of the DOPO-MA curing agent.

No any endothermic or exothermic peaks can be observed from 30 to 250 °C on the DSC curves, which suggests the stability in use below 250 °C.
Figure S5. Digital photos of uncured the DOPO-MA/DGEBA mixture (left) and after 10 min curing at 140 °C (right).

Upon complete mixing of all compositions, the mixture rapidly turned into transparent yellow from opaque white at the curing temperature of 140 °C, indicating the high reactivity between the curing agent and the epoxy monomer.
Figure S6. A schematic of compression programming-recovery cycle of the cured epoxy thermoset.
Figure S7. Compression programming profile of the epoxy thermoset.

The programming was conducted at 150 °C with 0.5 mm/min loading rate. According to the initial height of the sample \( (h_0) \) and the compression strain, we can calculate the amount of compression, as well as the height of the sample after compression programming \( (h_1) \).
**Figure S8.** Photographs of flame-triggered epoxy thermoset before (left) and after (right) removing the char residue and pyrolyzed zone by polishing.
Figure S9. SEM images of the recyclable epoxy powders after milled at 400 rpm for 8 h at different magnifications.
Figure S10. Photographs of the steel mold and pushing bar (left) for preparing recycled specimen (right).
Figure S11. The second DSC heat flow curve of the recycled epoxy thermoset after compression at 175 °C for 2h.
Figure S12. SEM images of the fracture surface of the original epoxy thermoset (left) and the recycled epoxy thermoset (right) after compression at 175 °C for 2h at low magnification.
Figure S13. TG and DTG curves of the as-prepared shape memory epoxy thermoset. The heating rate was 10 °C/min.
Figure S14. SEM images of the fracture surfaces of PEVA (top), PEVA-1 (middle) and PEVA-2 (bottom) at low magnification.

The fracture surface of the PEVA composites became rougher as the loading of the epoxy powder increased, demonstrating the change of rupture behavior and the interaction between the epoxy fillers and the PEVA matrix.
**Figure S15.** Photographs showing the dripping behavior of pure PEVA (left) and restrained dripping of PEVA-2 sample (right) during combustion.

The pure PEVA sample showed obvious dripping behavior due to its low melting point.
**Figure S16.** A thermomechanical cycle of the pristine shape memory thermoset by tension programming.

The thermomechanical cycle includes stretching at 150°C, holding the load constant while cooling down, unloading towards the end of cooling, and free shape recovery by heating to 150°C.
Figure S17. A thermomechanical cycle of the recycled shape memory thermoset by tension programming.

The thermosmechanial cycle includes stretching at 150°C, holding the load constant while cooling down, unloading towards the end of cooling, and free shape recovery by heating to 150°C. The thermoset network was recycled at 175 °C for 2h under 14 MPa pressure.
Possibility of chemical recycling

Chemical recycling of thermosets and reuse of the decomposed products can give a possible solution to these situations that physical recycling is limited, such as recycling of glass or carbon fiber reinforced composites. In this part, the DOPO-MA cured epoxy thermoset was reacted with ethylene glycol to achieve the transesterification process catalyzed by the intrinsic Zn$^{2+}$ catalyst, hence no extra catalyst was required (Figure S18). It is obvious that the color of the mixture became darker as the reaction time increases. The hydroxyl groups of the ethylene glycol can exchange with the ester bonds of the DOPO-MA cured epoxy thermoset at the presence of Zn$^{2+}$ catalyst, thus leading to the dissolution and decomposition of the epoxy thermoset.

![Figure S18](image)

**Figure S18.** Potential chemical recyclability of the as-prepared epoxy thermoset by dissolving in ethylene glycol at 180 °C for 8 min, 100 min and 28 h, respectively.
Table S1. Effects of recycling temperature and time on the recycle efficiencies of the epoxy thermoset.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Tensile strength (MPa)</th>
<th>Recycling efficiency (%)</th>
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<td>Original</td>
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<tr>
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