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Multireusable Thermoset with Anomalous Flame-Triggered Shape Memory Effect

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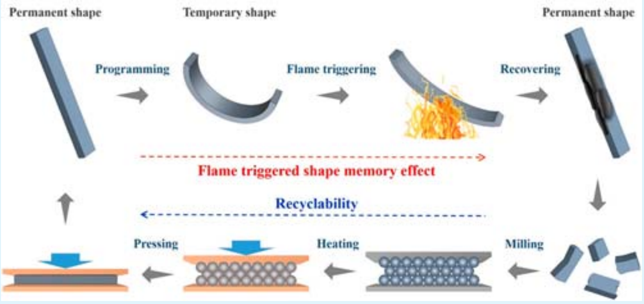
Supporting Information



ABSTRACT: While thermosets with high mechanical properties and shape memory capabilities have been developed in recent years, two main bottlenecks persist in their intrinsic nonreusability and flammability, especially for those shape memory thermosets used in recycling-required field with high glass transition temperatures (T_g) and thus risky high temperatures to trigger shape recovery. Here, we report a new shape memory epoxy thermoset integrated with excellent fire retardancy, recyclability, high mechanical performance, and 100% shape recovery ratio. The shape memory effect of this new thermoset was directly triggered by high-temperature flame for the first time. Furthermore, the survival thermoset can be recycled by a simple solid-state recycling method and reused as reinforcing fillers for polyester. The highest recycling efficiency reached 85.4%, and the reinforced composite presented about four times higher storage modulus compared to that of neat sample. This work may open a door for application of thermoset shape memory polymers in many lightweight engineering structures and devices where fire hazard is a concern. The newly proposed concept of flame-triggered shape memory effect may also find applications in fire-protecting system.

KEYWORDS: *flame triggering, shape memory thermoset, reusability, flame retardancy, fire damper*

1. INTRODUCTION

Compared to shape memory alloys (SMAs), shape memory polymers (SMPs) are attracting more and more attention from scientists and engineers because of several advantages, including light weight, huge recovery strain, low cost, ease of processing, and good insulation. On the basis of different mechanisms, shape recovery behaviors can be triggered by various stimuli, including heat,[1,2] light,[3,4] electricity,[5,6] magnetic field,[7,8] pH,[9] and solvent.[10]. Essentially, the triggering approaches by electrical and magnetic fields just convert other type of energy into heat, in other words, indirect heating. Among these, the widely studied and promising approach is the thermally induced shape recovery. However, the intrinsic flammability of most polymers is always a critical factor that limits their extensive applications in fields with high fire risk, such as electronics, aerospace, transportation, and construction industries. As for SMPs in service, they need external heat to trigger the shape recovery process, which always means risk of thermal runaway and fire hazard. For example, the electrically actuated SMPs may be ignited and burned when the electric voltage or current is too high. Especially for those epoxy thermoset SMPs with high T_g value, the potential fire risk significantly increases because of the nature of high flammability[11,12] and fairly high triggering temperature. Coupled with low thermal conductivity of polymers, a higher heating temperature is always inevitable if we want to speed up the shape recovery process. Therefore, it is especially necessary to improve the fire safety, while maintaining excellent shape memory performance. As far as we known, there are very few studies on solving this challenge in the open literatures.

Along this line, we find that fire, as the earliest heat source controlled by mankind, probably can be used to trigger the shape recovery if the polymer is fire retardant. The temperature of common flame is about 600−1000 °C,[13] which is more than enough to rapidly heat and trigger the shape memory polymer even though the thermal conductivity of which is quite low. However, based on the current flame retardant technologies, it is difficult to achieve a completely fire-proof polymer. Even those nonflammable polymers, such as polyvinyl chloride,[14] will also degrade when exposed to flame. It is noted that triggering shape memory by flame is a kind of destructive process to polymers, which does not fit for two-way and multishape SMPs. However, for one-way SMPs, they are designed to actuate only one time in a thermomechanical cycle, suggesting the potential to be triggered by flame.

Fire retardant SMPs may have many applications. Fire hazard has been a major concern for widespread applications of polymer composites in lightweight structures, such as aircraft, train, ship, car, pressure vessel, pipeline, and electronics.

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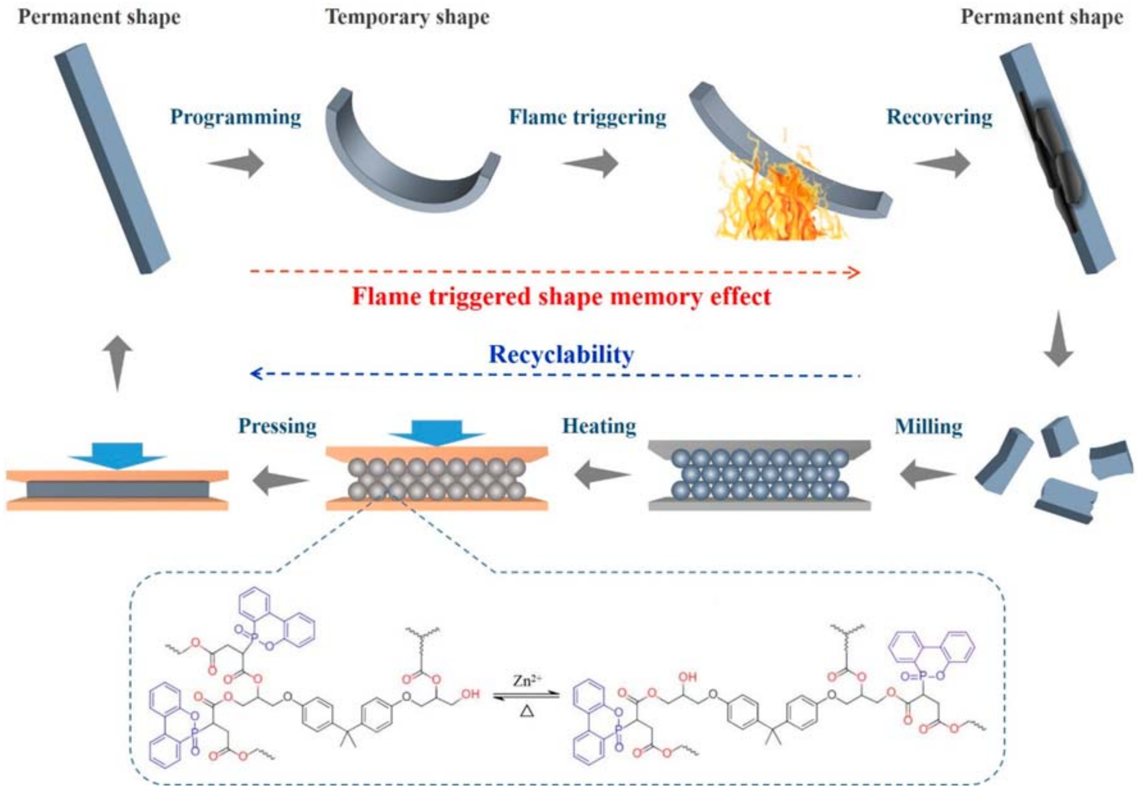

Figure 1. Flame-triggered shape memory concept. Schematic illustration of the flame-triggered shape memory effect and ball milling-hot pressing recycling process of as-prepared epoxy thermoset. The inset is the transesterification process of the cured epoxy thermoset.

Developing high-performance SMPs integrated with multifunctionality is highly desired. In addition to large structures, one potential application of flame-triggered actuation is to replace heat detectors in fire alarm system. When a building or a structure (aircraft, train, ship, car, etc.) is on fire, the SMP fire detector triggered by flame or high temperature can rapidly activate the alarm system, start an automatic water sprinkler system, and block oxygen supply channels, achieving a completely automatic alarm−firefighting process. Actually, different types of devices based on SMAs have been developed in fire extinguishing systems,[15,16] including fire damper, fire alarm, fireman uniform, and automatic sprinkling system. Therefore, we believe that fire triggered SMPs potentially have a wide range of applications.

Considering the large amount of polymers consumed and destructive process caused by flame triggering, it will be of great economic and environmental significance to develop a new thermoset that has great shape memory performance and excellent fire retardancy and, meanwhile, that can be recycled and reused. A large number of publications have reported recycling of thermosets through various mechanisms.[17−20] Among them, vitrimer is popular for fabricating SMPs with high recycling efficiency, which is benefited from the covalent adaptable network or reversible bonds.[21−23] In our previous work,[24] we have reported a high-performance UV-curing epoxy based thermoset with good shape memory properties and fair recycling efficiency. However, all of these reported polymers are highly flammable and cannot be triggered by flame. Therefore, developing a recyclable thermoset polymer integrated with high strength and stiffness, excellent shape memory, and fire retardancy remains a challenge, which motivated us to explore a feasible way of developing high performance flame-triggered and recyclable thermoset shape memory polymers.

Thermoset epoxy, because of its high mechanical strength and stiffness, ease of endowing shape memory capability, and thermal and chemical stability, was selected as the launching pad to achieve our aims in this work. A multifunctional curing agent was first used to prepare the recyclable epoxy thermoset with excellent flame retardancy (Figure S1). On the basis of this newly designed thermoset, we have demonstrated the flame-triggered shape recovery process for the first time, as shown in Figure 1. After it was triggered by flame, the thermoset sample completely returned to its original shape with a little char residue left on the surface. The reversible transesterification of the formed ester groups in the thermoset network warranted the self-healing capability and recyclability. Furthermore, we have presented a prototype of fire damper made by this exceptional thermoset to demonstrate its potential use in structures with high fire risk. It is anticipated that the flame-triggered shape memory concept proposed in this work may open a door to a brand new research field for SMPs.

2. RESULTS AND DISCUSSION

2.1. Shape Memory Properties. For shape memory thermoset, T_g value controls the shape recovery. The T_g value of DOPO-MA cured epoxy thermoset was characterized by DSC and DMA, respectively, as shown in Figure 2. The T_g value tested by DSC is 111.3 °C, which is within the normal ranges of commercial epoxy resins. It is noteworthy that the cured epoxy thermoset displays a transparent yellow appearance (inset of Figure 2a), demonstrating its potential application in the transparency-required fields. In Figure 2b,

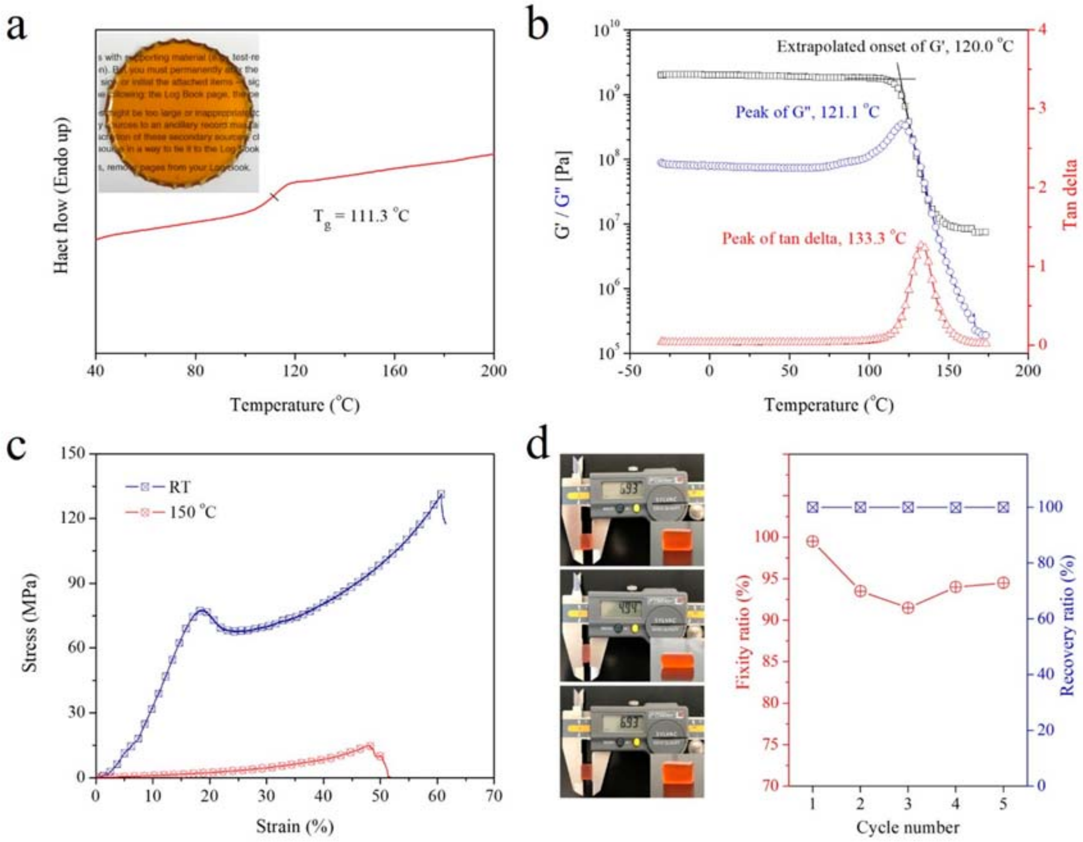

Figure 2. Shape memory properties of the as-prepared epoxy thermosets. (a) Second DSC heat flow curve of the epoxy thermoset with high transparency (inset image). (b) DMA results. (c) Compressive behavior of the epoxy thermosets at room temperature (RT) and 150 °C. (d) Photos of epoxy specimen showing the first compression programming-recovery cycle (left) and shape memory parameters for each of the five thermomechanical cycles (right).

the T_g values determined by the onset of storage modulus, peak of loss modulus and peak of tan delta were depicted. The widely accepted T_g value determined by the peak of tan delta is 133.3 °C. Because a large DOPO unit was introduced as a pendant group in the thermoset network, the steric effect resulted in a higher T_g compared to that of a similar anhydride curing agent used in our previous study,[25] which is in favor of high trigger temperature required fields. The storage modulus of the epoxy thermoset is 1975 MPa at room temperature, indicating high stiffness. Even at 100 °C, the storage modulus is still higher than 1800 MPa, which demonstrates good thermal stability of the epoxy thermoset. The storage modulus remains 9.5 MPa at the temperature of 150 °C (upper temperature limit of the tan delta peak), demonstrating no obvious influence of the large DOPO pendent structure on the main network of the epoxy thermoset. This over two orders drop in storage modulus of the epoxy thermoset from room temperature to 150 °C indicates excellent shape memory performance according to previous reports.[26]

The compressive strength was also determined to provide fundamental information on the mechanical behavior of the epoxy thermoset. As shown in Figure 2c, the epoxy thermoset exhibited a typical yielding-fracture behavior at room temperature (glassy state). When the strain reached 19%, yielding occurred and the yield strength is 77.7 MPa, followed by strain softening, plastic flow, strain hardening, and ultimate failure. The compressive strength is 131.5 MPa and the failure strain is about 60%. The compression test of the epoxy thermoset was also conducted at 150 °C (rubbery state) to provide a reference for subsequent compressive programming study. Obviously, the compressive behavior at high temperature is quite different from that at room temperature. No yielding happened, and the compressive stress increased steadily to 14.7 MPa before fracture. The corresponding failure strain is 48%, demonstrating a commendable compressibility of the epoxy thermoset at rubbery state. Because of the good deformability and ease of precision control in compression mode, the compressive deformation was selected to evaluate the shape memory properties of the epoxy thermoset. The photos in Figure 2d clearly show a compression programming-recovery cycle. The compression programming profile was illustrated in Figure S7. During programming in the first thermomechanical cycle, the sample was compressed from 6.93 to 4.93 mm at 150 °C. The sample was then cooled down to room temperature while holding the strain constant. After load removal, there was a 0.01 mm spring back, leading to a shape fixity ratio of about 99.79%. When heating the sample to 150 °C by traditional heating in a heating chamber, the programmed sample recovered to 6.93 mm, leading to a shape recovery ratio of 100%. A total of five thermomechanical cycles were conducted, and the shape fixity ratios and shape recovery ratios are also shown in Figure 2d. The recovery ratios of all five cycles reached to 100%, and all the fixity ratios were higher than 90%. These results suggest that the cured epoxy thermoset is among the best group of SMPs. Furthermore, the robust compressive ability and high stiffness, together with the high T_g value

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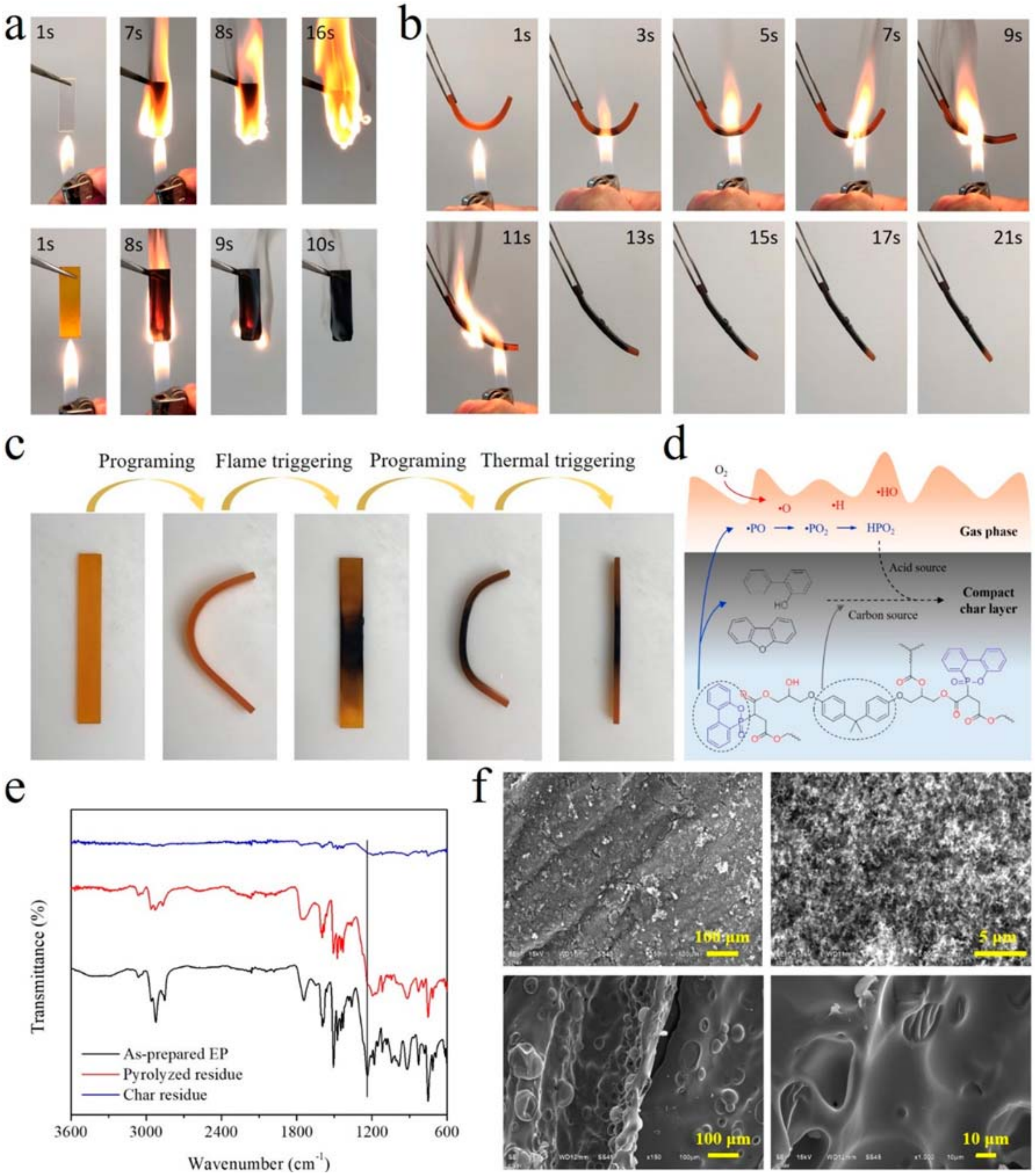

Figure 3. Flame-triggered shape memory performances. (a) Performance of control epoxy sample (top) and as-prepared DOPO-MA cured epoxy thermoset (bottom) under flame. (b) Photos of flame-triggered shape memory behavior of the as-prepared epoxy thermoset. (c) First thermomechanical cycle (first three photos) and second thermomechanical cycle (last two photos) of the epoxy thermoset. (d) Schematic illustration of the proposed flame retardant mechanism of the as-prepared epoxy thermoset. (e) FTIR spectra of the char residue at different depths of the thermoset after ignition by a lighter (EP = epoxy thermoset). (f) SEM images of external surface (top) and inner surface (bottom) of the char residue of the epoxy thermoset at different magnifications.

predict potential applications of the cured epoxy thermoset in load-carrying structures.

The thermomechanical cycle of both the pristine and recycled thermoset epoxy samples was also conducted by classical hot tensile programming. The results suggest that both of them have excellent shape memory performance, as evidenced by the full recovery to the original shape in Figures S16 and S17, respectively.

2.2. Flame-Triggered Shape Recovery. In addition to be triggered by traditional oven heating, the epoxy thermoset can also be triggered by open flame. To achieve flame-triggered shape recovery performance, the epoxy thermoset should have an excellent flame retardancy to endure the flame ignition. Figure 3a shows the ignition and combustion process of a type of epoxy resin cured with commercial diethylenetriamine curing agent. We can see that the commercial thermoset continued burning after removing the external ignition flame (the lighter) in seven seconds. As a contrast, the DOPO-MA-cured epoxy thermoset extinguished two seconds after the lighter was removed, indicating a considerable fire retardancy. Figure 3b displays the flame-triggered shape memory behavior of the flame retardant epoxy thermoset. The sample was

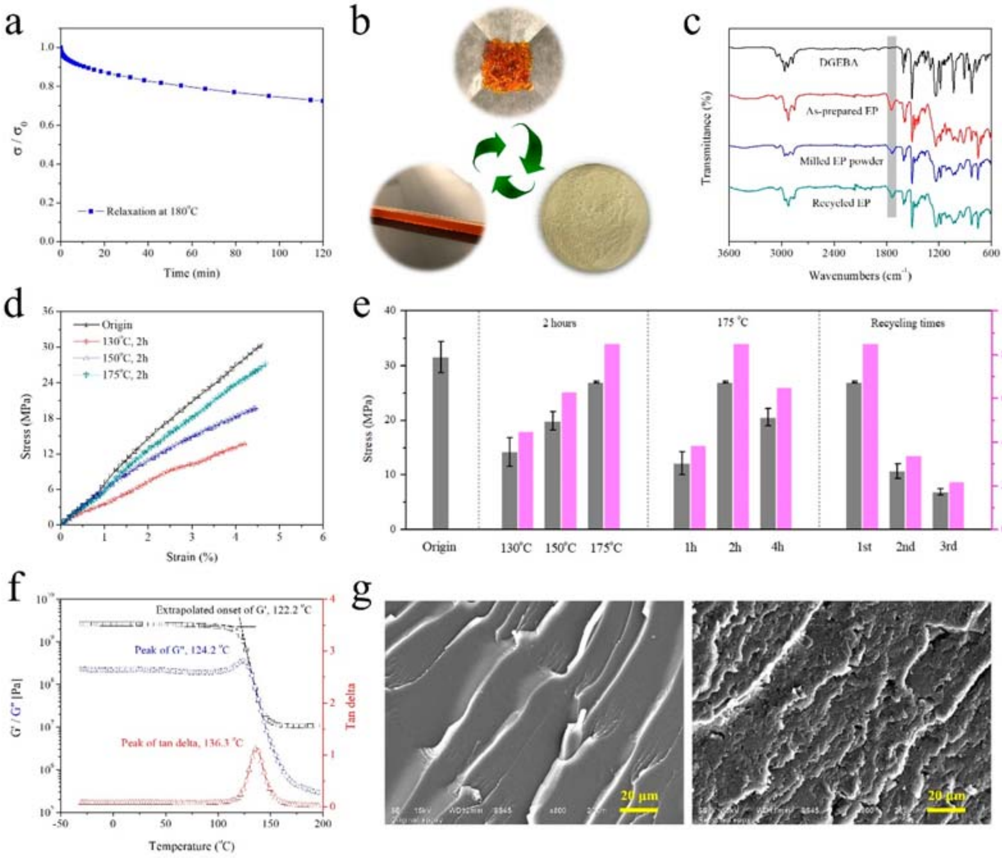

Figure 4. Recyclability of the epoxy thermosets. (a) Stress-relaxation curve during the transesterification process of the epoxy thermoset at 180 °C. (b) Recycling of the as-prepared epoxy thermoset through ball milling of small pieces and hot pressing of the milled powders. (c) FTIR spectra of the different samples. (d) Representative tensile stress−tensile strain curves of the original and recycled epoxy thermoset under varying recycling conditions. (e) Tensile strengths and recycling efficiencies of the recycled epoxy thermoset under varying recycling temperatures and recycling times (gray, strength; pink, recycling efficiency). (f) DMA results of the epoxy thermoset recycled at 175 °C for 2 h. (g) SEM images of the fracture surface of the pristine epoxy thermoset (left) and the recycled epoxy thermoset (right) after compression at 175 °C for 2 h.

programmed into a bent shape first, as shown in Figure 3c. When exposed to the flame, in a few seconds, the sample began to unfold and become straight gradually. After the lighter was removed, the fire on the sample quenched immediately and the sample recovered to straight rod completely. There was only a thin char layer left on the surface of the sample. After the flame-triggered shape recovery process was completed, the recovered sample was programmed one more time and was able to recover to the permanent shape again by conventional thermal heating (Figure 3c). This suggests that the ignition and burning in a short time period did not heavily influence the basic structure and shape memory properties of the epoxy thermoset, which offers the possibility of repeated utilization in real world. In contrast, the conventional epoxy resin was burned out completely in a very short period of time, suggesting the impossibility of flame-triggered shape memory behavior.

To understand the fire retardancy, we have conducted the FTIR and morphology characterization of the char residue of the burned epoxy thermoset. As shown in Figure 3e, compared to the original epoxy, an obviously decreased absorption band at 1233 cm^{-1} (P═O) was observed in the profile of the pyrolyzed residue, suggesting an early decomposition of DOPO structures. Additionally, a rigid and intact inner char layer was observed in the SEM images of the char residue (Figure 3f), indicating the effectiveness in inhibiting the diffusion of combustible gaseous products. Therefore, on the basis of the above results and previous publications,[27,28] a possible route of flame retardant mechanism of the epoxy thermoset was proposed in Figure 3d. When the thermoset was heated by external flame, the DOPO group first degraded into *o*-phenylphenol or benzofurans and PO radical. The PO radical can interact with O, H, and OH radicals in the gas phase of the fire, which can retard further degradation and combustion of the epoxy thermoset. Meanwhile, catalyzed by the acid source (HPO_2 and its derivatives), the pyrolysis products of the biphenyl group and the bisphenol A unit of the DGEBA induce the formation of a compact char layer on the surface of the thermoset sample. The barrier action of the compact char layer restrains the heat transfer and migration of the flammable pyrolysis gases, thereby protecting the inner epoxy from further burning out.

2.3. Recyclability. When the thermoset polymer was attacked by external force or fire in service, it leads to fracture or flame-triggered shape recovery. The surviving epoxy thermoset pieces (the unburned part) from ignition were displayed in Figure S8 after removal of the char residue and pyrolyzed zone by polishing. The resulting epoxy thermoset pieces could be recycled because of its intrinsic transesterification ability, as shown in Figure 4a. The appropriate stress relaxation behavior can guarantee the shape memory performance and recyclability at the same time. In general, no

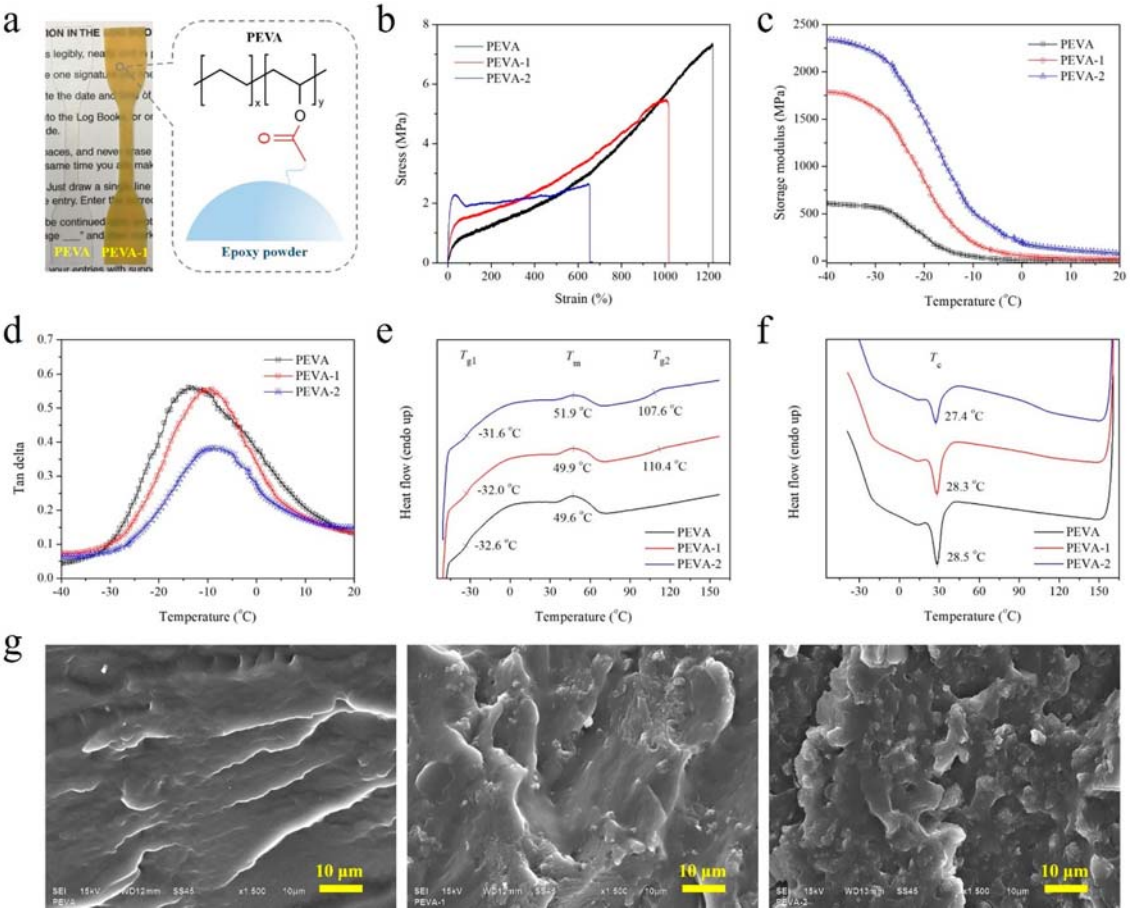

Figure 5. Recycling of the epoxy thermosets as fillers for polymer composites. (a) Digital photos of the PEVA samples and scheme of transesterification at PEVA−epoxy powder interface, (b) Typical tensile stress-tensile strain curves, (c) storage modulus, and (d) tan delta values of the PEVA and its composites. (e) Second DSC heat flow curves and (f) the first cooling curves of the PEVA and its composites marked with characteristic temperature values. (g) SEM images of the fracture surfaces of PEVA (left), PEVA-1 (middle), and PEVA-2 (right).

any stress relaxation means no recyclability. As shown in Figure 4b, the ball milling was performed to facilitate the recycling process.[29] After ball milling, the epoxy thermoset powders with small particle size (Figure S9) can be easily molded into required shapes by compression because the modulus of the epoxy thermoset at the recycling temperature is quite low (Figure 2b). For the calculation of the recycling efficiency by tensile strength, rectangular samples were prepared in this study by a specially designed steel mold, as shown in Figure S10.

The thermoset powders were carefully placed into the groove and hot pressed through a perfectly fitted pushing bar. According to our previous works,[24,25] the recycling temperature, time, pressure, as well as the size of the thermoset powders all have an influence on the final properties of the recycled samples. In this study, with fixed recycling pressure at 14 MPa and ball milling time for 8 h, we only investigated the effect of recycling temperature and time on the performances of the recycled thermosets. As shown in Figure 4d and Table S1, the tensile strength of the original epoxy thermoset is about 31.6 MPa at room temperature, which is comparable to the common commercial epoxy resins. Both the low elongation at break (∼4.5%) and relatively smooth fracture surface (Figure 4g) demonstrate a typical brittle rupture behavior of the epoxy thermoset. It is clearly seen that the tensile strength and ultimate strain of the recycled samples gradually increased as the recycling temperature increased from 130 to 175 °C at the same recycling time of 2 h. This is attributed to the improved reaction rate of transesterification at the higher reaction temperature. In Figure 4e, the recycling efficiency obviously increased from 38.6% for 1 h recycling time to 85.4% for 2 h recycling time at 175 °C, indicating the importance of recycling time. As for recycling at 175 °C for 4 h, a drop of efficiency can be observed. We propose it is caused by the overlarge recycling pressure related to the recycling temperature of 175 °C. The recycling pressure used in this study is 14 MPa, which is slightly lower than the compressive strength of the epoxy thermoset at 150 °C. Because the compressive strength of the epoxy thermoset decreases as temperature rises, it is likely that the recycling pressure is higher than the compressive strength of epoxy thermoset at 175 °C, which can lead to formation of cracks and further broken of the epoxy powders. There should be a balance between the healing and breaking processes during the recycling of the samples. Once a certain balance point is past, the breaking rate is higher than the healing rate, which results in the reduction of the recycling efficiency.

FTIR spectra were used to characterize the evolution of molecular structures of the epoxy thermosets during the recycling process. Figure 4c displays the FTIR spectra of the DGEBA, as-prepared epoxy thermoset, milled epoxy powder, and recycled epoxy thermoset at 175 °C for 2 h. Compared to

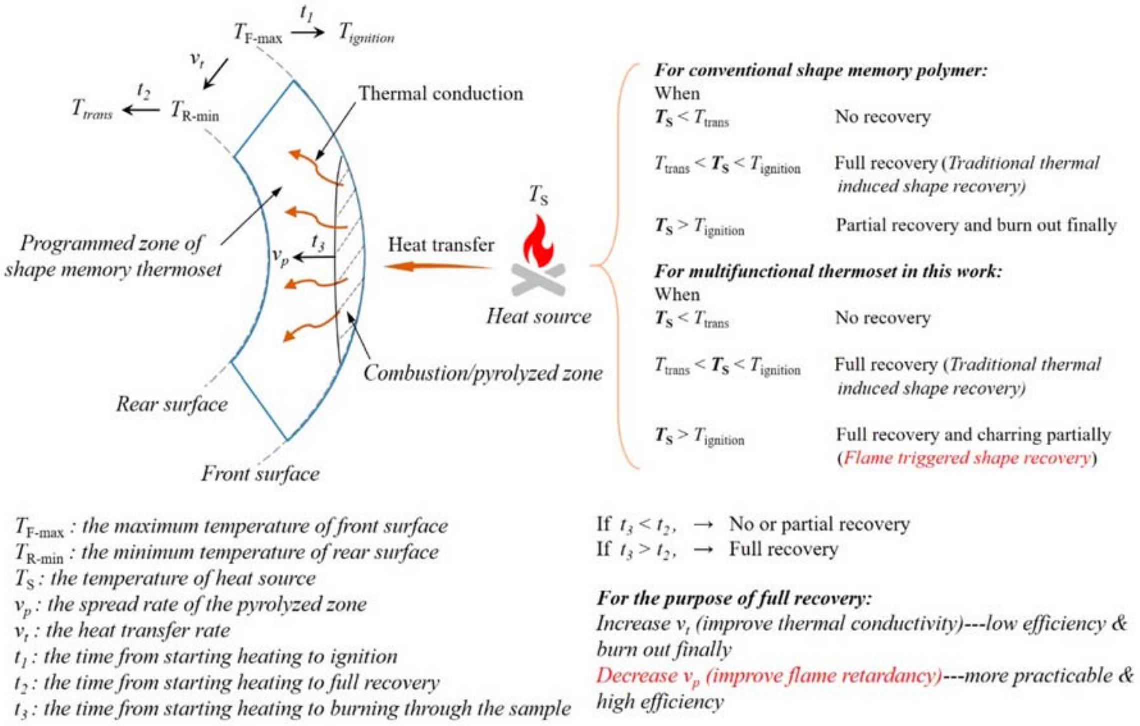

Figure 6. Schematic illustration of the scientific principle of the flame-triggered shape memory effect.

DGEBA, a new peak around 1745 cm^{-1} can be observed in the profile of the epoxy thermoset, which is attributed to the formation of ester linkages after curing with DOPO-MA. Notably, after the epoxy thermoset was milled into powders and recycled by hot compression, there is no any obvious difference among these three samples, indicating the maintaining of the functional groups and no degradation happened during the consecutive recycling experiments. Specifically, the remaining peaks of the carbonyl bond confirmed the successful transesterification reaction within the epoxy thermoset. Furthermore, the T_g value of the best performing recycled sample (recycling at 175 °C for 2 h) was determined by DMA and DSC respectively, as shown in Figures 4f and S11, respectively. We can see that the T_g values (136.3 °C by DMA and 107.6 °C by DSC) are only slightly different from those of the original sample. It demonstrates that the recycled samples have recovered to nearly the pristine performance, in consideration of the testing errors. In addition, the fracture surface of the recycled sample exhibited a similar rupture morphology to that of the original epoxy thermoset (Figure 4g). As shown by the TGA test in Figure S13, there is no weight loss observed below 250 °C. This indicates that the as-prepared epoxy thermoset is thermally stable at the highest recycling temperature (175 °C). The epoxy thermoset was recycled three times with the optimum parameters (175 °C and 2 h) to explore the repeatability of recycling. As shown in Figure 4e, the recycling efficiencies of the second and third cycles are about 34% and 22%, respectively, which are lower than that of the first recycling. This is understandable for any recyclable thermosets.

2.4. Reuse as Reinforcing Fillers. In addition to the recycling discussed above, in this part, we show a more feasible way to reuse the epoxy thermosets in real world conditions. Because of its intrinsic high stiffness and reversible transesterification characteristics, the milled thermoset powders can act as reinforcing fillers for polyester based composites. In this case, a widely used polyester copolymer, PEVA, was selected to blend with different amounts (10 wt % for PEVA-1 and 30 wt % for PEVA-2) of the epoxy powders and then was hot-pressed for achieving transesterification at the PEVA−epoxy powder interface, as shown in Figure 5a. After the inclusion of the epoxy powders, the yield strength and tensile modulus of elasticity of the PEVA composites were significantly improved (Figure 5b), while there was a certain decrease in the breaking strength and elongation. This phenomenon is common in the field of polymer composites, which is caused by the restriction of fillers on the motion and slippage of molecular chains under the tensile stress. This conclusion was also evidenced by the SEM images of the fracture surfaces of PEVA composites (Figures 5g and S14). As compared to the considerable smooth surface of pure PEVA, the PEVA composites presented more rough surfaces with irregular protrusions. The newly formed covalent ester linkages at the interfaces can effectively transfer the load from the weak PEVA chains to robust epoxy powders, leading to the enhanced modulus and yield strength.

Similarly, the storage modulus of the PEVA composites are much higher than that of the pure PEVA over the full temperature range (Figure 5c). It increased from 605 MPa for the pure sample to 1785 MPa for PEVA-1 and 2336 MPa for PEVA-2 at −40 °C, showing 295% and 386% improvements, respectively. From the tan delta curves in Figure 5d, we can find that the peaks of the tan delta were shifted to higher temperature region as the content of the epoxy fillers increases, indicating higher T_g values of the PEVA composites (from −13.2 °C to −9.2 °C and −8.5 °C, respectively). In addition, the peak values of the tan delta curves were reduced after adding the epoxy fillers, which indicates that energy loss caused by the movement of polymer chain segments was decreased. These two results both suggested that our previous statements that the motion of the PEVA chains was restrained by the formed ester bonds at the interface of the PEVA composites. For further investigation of the effect of the epoxy powder fillers, the thermal properties of the PEVA and its composites were characterized by DSC (Figure 5e and f). For incompatible binary polymer blends, there always presents two separate glass transition regions assigned to each component. As for the PEVA composite, the increases in T_{g1} values and melting points (T_m) and the decreases in crystallization temperatures (T_c) can be attributed to the restrained motions of the PEVA molecular chains by introducing the epoxy component. The T_{g2} values of the epoxy component slightly decreased in contrast to that of the pure epoxy thermoset, suggesting easier segmental motion of the epoxy thermoset by grafting the low melting point PEVA molecules.

PEVA is not only highly flammable but also easy to drop off when burning because of its low melting point, which always leads to rapid spreading of fire and a larger loss of lives and properties. In this study, because of the thermoset nature and intrinsic flame retardancy of the DOPO-MA cured epoxy thermoset, the epoxy powders reinforced PEVA composites exhibited an improved antidripping performance, as shown in Figure S15. The pure PEVA sample was burned out shortly along with a heavy dripping behavior. In contrast, the dripping performance of the PEVA-2 sample was obviously reduced. After it burned for a few seconds, there was no dripping behavior observed, despite the fact that the sample was not extinguished because of the low content of the flame retardant DOPO group in the PEVA-2 sample (about 6 wt %). This restrained dripping behavior during combustion can reduce the fire spreading and leave more time for people to escape from the fire ground.

2.5. Mechanism and Performance Comparison.

A schematic has been drawn to illustrate the scientific principle of this work, as shown in Figure 6. Because the bending mode contains both tensile and compressive deformation, here, we chose it as a representative for the illustration. When a programmed shape memory sample is heated by an external heat source, the temperature at the front surface begins to increase. When the maximum temperature of the front surface ($T_{\text{F-max}}$) is over the ignition temperature (T_{ignition}) of the material, it will be ignited and will keep decomposing and burning. The time that this process lasts is set as t_1. The combustion/pyrolyzed zone will spread to the inner structure of the sample depending on the thermal conduction and boundary conditions. We define the spread rate of the pyrolyzed zone as ν_p and the time from starting heating to burning through as t_3. Meanwhile, the heat will transfer from the high-temperature front surface to the low-temperature rear surface and tries to achieve thermal balance, the rate of which is defined as ν_t. When the minimum temperature of the rear surface ($T_{\text{R-min}}$) reaches the shape recovery transition temperature (T_{trans}), the sample will complete the shape recovery process in full. This time is labeled as t_2. Clearly, the comparison of t_2 and t_3 is an indicator for whether the sample will complete the shape recovery or not. If t_3 is longer than t_2, the sample can be recovered. Otherwise, it could be burned. Therefore, for the purpose of full recovery, it seems that we can chose to increase the ν_t by improving the thermal conductivity and reduce the ν_p by enhancing the flame retardancy. However, as is well-known, the thermal conductivity of polymers is relatively low, and it is difficult to make a significant improvement. In addition, even though the sample can fully recover to its permanent shape, it will burned itself out eventually, which means a suffocating limitation in real world applications. An effect is, thus, to improve the fire retardancy of the shape memory polymer, which is possible because of the advancement in flame retardant science and technology. Indeed, our results demonstrate the high feasibility of the method to achieve flame-triggered shape memory effect of polymer materials. Certainly, the size of the shape memory sample and the power of the heating source also have an influence on the shape recovery process. However, this is a problem in applications and can be fixed in practice.

To fully illustrate the superiority of the as-prepared thermoset, we defined a concept of work temperature window of thermal induced shape memory polymer. As for conventional shape memory polymers, the work temperature window is limited to the difference between the T_{trans} (e.g., T_g, T_m) and the T_{ignition}, as shown in Figure 7a. Specifically, the shape memory effect of polymers cannot be triggered when the temperature is lower than the T_{trans}. When the temperature is higher than T_{ignition}, the shape memory polymer will be ignited and burned out, which always leads to the fire hazard and limited application. In contrast, the intrinsic flame retardancy makes the as-prepared thermoset difficult to be ignited and easy to extinguish, and it exhibits the flame-triggered shape memory effect. Essentially, flame is a type of high temperature, which means that the shape memory work window for the as-prepared thermoset is far larger than that for conventional shape memory polymers. Figure 7b outlines the latest

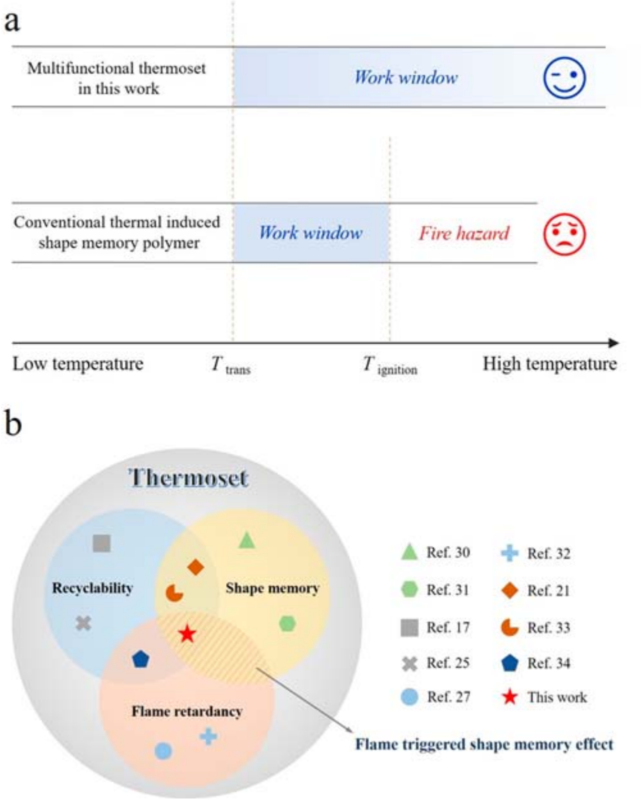

Figure 7. Comparisons with the published reports. (a) Illustration of the comparison of shape memory work temperature window between the as-prepared thermoset and the conventional shape memory polymers. (b) Comparison of the multifunctionality of the as-prepared thermoset with some typical reports.

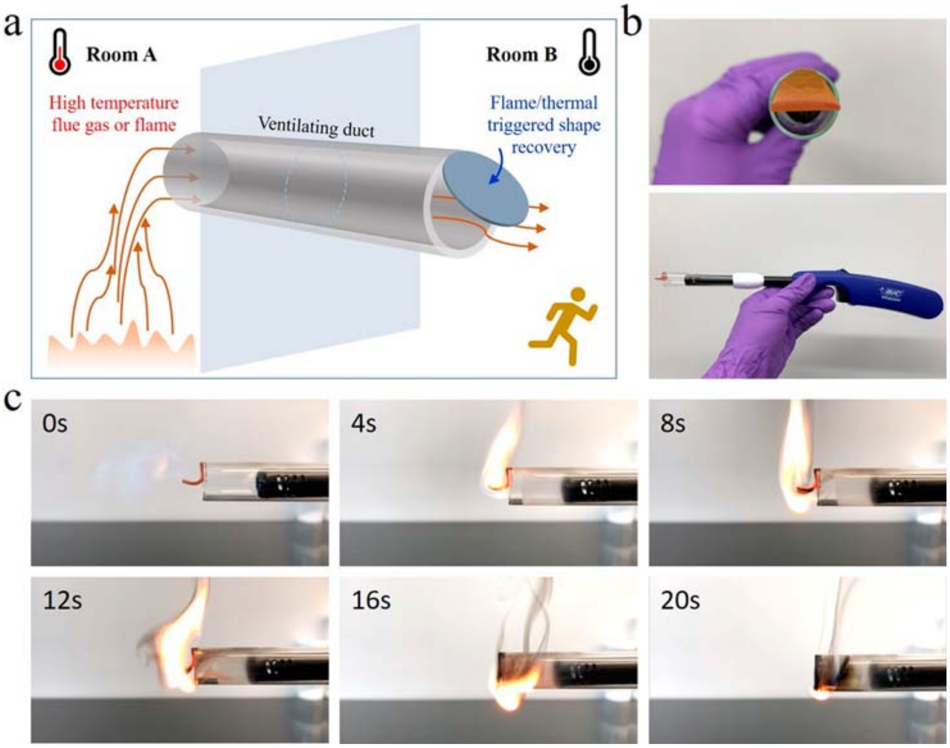

Figure 8. Prototype design of a potential fire damper by using the shape memory thermoset. (a) A schematic of the principle of the shape memory fire damper in a building on fire. (b) Photographs of a prototype of the shape memory polymer fire damper. (c) The working process of the epoxy thermoset fire damper triggered by lighter flame.

development and research on thermosets. Because of the inherent cross-linking network, most of the thermosets possess the thermal induced shape memory effect. The researchers mainly focused on the development of new thermoset systems besides epoxy resin in recent years.[30,31] Because of the intrinsic flammability, how to improve the flame retardancy of epoxy thermosets always has great scientific and practical significance.[27,32] For the purpose of economic and environmental consideration, more and more researchers have devoted themselves to develop the recyclable thermoset.[17,25] Some of them have reported some multifunctional thermosets that have both shape memory effect and recyclability.[21,33] Most recently, there are few papers reported the preparation of recyclable thermoset with flame retardancy.[34] However, as far as we know, there are no papers reporting both shape memory effect and flame retardancy in one thermoset, let alone a report of a thermoset integrated with shape memory, flame retardancy, and recyclability at the same time. In this work, we first accomplished the integration of these three important properties into one thermoset. As a benefited from the base performance—shape memory effect and flame retardancy—the as-prepared thermoset exhibited a more advanced property, flame-triggered shape memory effect. It can be predicted that this multifunctional thermoset will show strong potential in the related fields, such as aerospace, and the flame-triggered shape memory effect of which will show the application in a fire-protecting system.

2.6. Prototype Fire Damper. Here, we propose a simple prototype design of a potential fire damper based on the developed shape memory epoxy thermoset (Figure 8). In this design, a lighter was used to simulate high-temperature flue gas or flame suffered from a fire disaster that happened in room A (Figure 8a). A glass tube was used as an analogy of the ventilating ducts in real buildings. A bending programmed epoxy thermoset sheet attached on the rim of the glass tube acted as the fire damper (Figure 8b). As shown in Figure 8c, after the lighter was on, the flame began to ignite and heat the epoxy thermoset sheet. When the time reached 8 s, the bent epoxy sheet started the shape recovery process. After 20 s, the epoxy sheet fully recovered to the original straight position and cut off the spurting of flame, thus mostly prevented the fire from spreading in room B and allowed the people in room B have more time to escape. A clear advantage of this design is that only a cheap epoxy thermoset sheet is required to act as the sensor and actuator simultaneously, rather than the expensive commercial fire damper with a series of complicated machineries, which is feasible and highly desirable in certain fields.

3. CONCLUSION

In summary, a multifunctional shape memory epoxy thermoset with flame-triggered shape recovery was developed. This new epoxy thermoset has comparable mechanical properties and T_g value to conventional ones but shows excellent shape memory performance and flame retardancy. Thanks to this, a simple prototype of a potential fire damper made by the shape memory epoxy thermoset was demonstrated. The thermoset fire damper was not burned out; instead, it mostly suppressed the transport of flame and flue gas through the shape recovery process that triggered by flame and flue gas themselves. Furthermore, the epoxy thermoset can be efficiently recycled into a new sample through a ball milling-hot pressing process, and the tensile strength of the best recycled sample can reach as high as 85.4% of the original sample. The milled thermoset powders were also reused as fillers to reinforce a polyester copolymer—PEVA. Specifically, the PEVA composites exhibited about four times higher storage modulus compared to that of pure sample. These fascinating recycling performances are attributed to the reversible transesterification of the inherent dynamic ester bonds in the thermoset network. Together with the flame-triggered shape memory concept, this highly recyclable epoxy thermoset shows a good potential as a new type of SMPs for broad applications.

4. EXPERIMENTAL SECTION

4.1. Synthesis of Curing Agent and Epoxy Thermoset. The multifunctional curing agent was synthesized according to previous report,[35] as shown in Figure S1. First, 108.0 g (0.5 mol) of (9,10-dihydro-9-oxa-10-phosphaphenanthrene10-oxide (DOPO) (TCI, ≥97.0%) and 400 mL of toluene/THF (Sigma-Aldrich) mixture (1:1, V/V) were poured into a three-necked bottle equipped with a condenser and a magnetic stirrer. The system was heated to 95 °C and kept stirring under a nitrogen gas atmosphere to completely dissolve DOPO. After that, 49.0 g (0.5 mol) of maleic anhydride (MA) (TCI, ≥99.0%) was introduced into the bottle 5 times in 1 h. The system was then stirred continuously at 95 °C for 12 h under nitrogen atmosphere for complete reaction. After the mixture was cooled to room temperature, the precipitate was collected by vacuum filtration and washing with THF and ethanol. The filter cake was vacuum-dried at 100 °C for 12 h, and then the white powder product was obtained (Figure S2).

The epoxy thermoset was prepared by the following steps. The DOPO-MA was dried at 105 °C overnight before curing. Five grams (0.0147 mol) of diglycidyl ether of bisphenol A (DGEBA) (Sigma-Aldrich) was weighted in a mortar and heated to 80 °C, and then, 2.31 g (0.0074 mol) of DOPO-MA curing agent was added. The mixture was ground for 10 min, while it is hot. Zinc acetylacetonate hydrate (0.194 g, Sigma-Aldrich) was introduced and mixed for another 10 min. After that, the white mixture was poured into proper molds and cured at 140 °C for 8 h. The opaque mixture obviously changed into yellow transparent solid after curing (Figure S5), indicating complete reaction.

4.2. Materials Characterization. Fourier transform infrared spectroscopy (FTIR) tests were conducted on a Nicolet 6700 FTIR spectrometer (Thermo Scientific, USA) using Attenuated Total Reflection mode by collecting 32 scans from 500 to 4000 cm^{-1}. Thermal behavior of the epoxy thermoset was studied by using a PerkinElmer 4000 differential scanning calorimeter (DSC) (MA, USA). Samples (5−10 mg) were heated and cooled at a linear heating rate of 10 °C min^{-1}; the holding time was 5 min, and the second heating−cooling cycle was conducted. The purging rate of nitrogen gas was 30 mL min^{-1}. The morphologies of different samples were taken using a scanning electron microscope (SEM) (JSM-6610 LV, JEOL, USA). The samples were placed on a copper plate, and then coated with platinum before imaging. The accelerating voltage was 15 kV. Thermomechanical performance of the epoxy thermoset (30.42 × 5.74 × 1.21 mm^3) was evaluated by a Q800 dynamic mechanical analyzer (DMA) (TA Instruments, DE, USA) in multifrequency-strain mode with a heating rate of 3 °C min^{-1}. The amplitude was 20 μm, and the frequency was 1 Hz. The compression and tensile tests were performed by employing an eXpert 2610 MTS (ADMET, Norwood, MA, USA) equipped with a temperature-regulated oven. As for compression test, room temperature and 150 °C were chosen to investigate the evolution of compression behavior of the epoxy thermoset (4.67 × 4.52 × 6.2 mm^3) from glassy to rubbery state. The compression rate was 0.5 mm/min. The cured epoxy thermoset plate were cut into rectangular specimens (59.96 × 5.02 × 2.76 mm^3) for tensile test, and five parallel runs were performed for each sample. The crosshead speed was 1.0 mm/min for all samples.

4.3. Shape Memory Experiments. As shown in Figure S6, first, the cuboid sample with initial height h_0 was placed in between the MTS clamps (eXpert 2610, ADMET, Norwood, MA, USA) and heated to 150 °C for 1 h for achieving thermal equilibrium. Then the sample was compressed to a certain height h_1 at a speed of 0.5 mm/min. The height h_1 can be obtained according to the corresponding compressive programming profile (Figure S7). After that, the compressed sample was rapidly cooled to room temperature by spraying water with wash bottle. The height of the programmed sample was measured and noted as h_2 after removing the load. The free shape recovery test was conducted in an oven at 150 °C for 30 min. The height of the recovered sample was recorded as h_3. Therefore, the shape fixity ratio (F) and recovery ratio (R) can be calculated by the following equations:

$$F = \frac{h_0 - h_2}{h_0 - h_1} \times 100\%$$

$$R = \frac{h_3 - h_2}{h_0 - h_2} \times 100\%$$

To clearly illustrate the shape memory performance of the epoxy thermoset upon flame triggering, bending programming was selected to conduct the experiment. For the sake of simplicity, the rectangular slice samples (41.98 × 5.59 × 2.19 mm^3) were heated by a heat gun and then were bent using pliers. The samples were naturally cooled while maintaining the bent position. As for flame-triggered recovery, a lighter was used to ignite the programmed sample. The whole recovery process was recorded by a camera.

Recycling. First, the epoxy thermoset was manually broken into small pieces before being added into the ceramic containers of a planetary ball mill machine (Across International PQ-N2 Planetary, Livingston, New Jersey, USA). Then, the thermoset pieces were ground at 400 rpm for 8 h to obtain the epoxy thermoset powders. The powders were poured into a steel mold (Figure S10) and hot pressed through a pushing bar under a certain pressure (14 MPa) at different temperatures. To systematically evaluate the recyclability of the epoxy thermoset, the recycling temperatures were set to be 130, 150, and 175 °C, and the recycling time varied from 1, 2 and 4 h. Three recycling cycles in total were carried out. The recycling efficiency (η) was defined as the ratio of tensile strengths of the recycled samples (σ_r) to those of original samples (σ_o).

$$\eta = \frac{\sigma_r}{\sigma_o} \times 100\%$$

For reusing as fillers, the calculated amount of the thermoset powders were dispersed in 50 mL THF by sonication for 1 h. The poly(ethylene-*co*-vinyl acetate) (PEVA) (40 wt % vinyl acetate, Sigma-Aldrich) particles were then added to the homogeneous mixture. The system was kept stirring to completely dissolve the PEVA. The suspension was then poured into a glass dish and vacuum-dried at 100 °C overnight. After that, the obtained samples were hot pressed by a Laboratory Presses (Model 944226, DAKE, USA) at 140 °C for 2 h to achieve the transesterification reaction within the PEVA-epoxy powder interface. Finally, the flat panel was cut into dumbbell-shaped (L_0/80.79 × L_1/25.15 × W/4.57 × T/0.44 mm) and rectangular specimens (26.03 × 6.07 × 0.42 mm^3) for tensile and DMA tests, respectively.

Fire Damper Experiment. To simply simulate a fire damper, the bottom of a glass tube with diameter of 15 mm was cut off first. Then a lighter was sheathed in the glass tube, and the interface was wrapped by Teflon tape. After that, a circular epoxy thermoset sheet was programmed into a bent shape and was then attached onto the rim of the glass tube by using a glue, as shown in Figure 6b. When conducting the fire damper experiment, the trigger of the lighter was pulled and kept in working pattern to completely trigger the shape recovery process of the circular epoxy thermoset sheet.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b03092.

Combustion of the conventional epoxy thermoset (AVI)
Ignition and self-extinguishing of the DOPO-MA cured epoxy thermoset (AVI)

Flame-triggered process of the conventional epoxy thermoset (AVI)

Flame triggered shape recovery of the DOPO-MA cured epoxy thermoset (AVI)

Action of the fire damper prototype made by the DOPO-MA cured epoxy thermoset (AVI)

Combustion of the pure PEVA (AVI)

Combustion of the PEVA-2 composites (AVI)

Synthetic routes, photos, and SEM images; DSC curve and FTIR spectra of DOPO, MA, and DOPO-MA; schematic and profile of compression programming-recovery process; photos and SEM images of as-prepared thermoset, thermoset powder, and the recycled sample; TGA result of the thermoset; SEM images and dripping behavior of PEVA and its composite; tensile programming and free shape recovery of pristine and recycled samples; and possibility of chemical recycling (PDF)

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Notes

The authors declare no competing financial interest.

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