

A Composite Elastomer with Photo-responsive Shape Memory and Programmable Hygroscopic Actuation Functionalities

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Electronic Supplementary Information

Abstract Developing hygroscopic actuators with simultaneous high elasticity, shape programmability and tunable actuating behaviors are highly desired but still challenging. In this study, we propose an orthogonal composite design to develop such a material. The developed composite elastomer comprises carboxyl group-grafted polystyrene-block-poly(ethylene-co-butylene)-block-polystyrene (SEBS-*g*-COOH) as the elastic substrate, and a synthesized azobenzene derivative as the functional filler (Azo12). By surface treatment using acidic and base solutions, the carboxyl groups on the surface can reversibly transform into carboxylate groups, which render the composite tunable hygroscopic actuating functionality. On another aspect, the added filler undergoes *trans*-to-*cis* isomerization when exposed to UV light irradiation, leading to liquefaction of the crystalline aggregates formed by Azo12 molecules. The liquefied Azo12 molecules can autonomously resotre their *trans* form and reform the crystalline structure. This reversible change in crystalline structure is utilized to realize the shape memory property, and 5 wt% of Azo12 addition is adequate for the composite to exhibit photo-responsive shape memory behavior without compromising much of the elasticity. The regulation of external geometry by shape memory effect is effective in altering the actuating behavior. The proposed method can be extended to designing different composites with the demonstrated functionalities.

Keywords Actuator; Shape memory; Photo-responsive; Hygroscopic responsive; Azobenzene

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INTRODUCTION

Many creatures in nature can sense the variation of environmental humidity and respond in way of shape change or locomotion. Inspired by them, synthetic hygroscopic actuators (HAs) have gained rapid development, which have great application potentials in fields including soft robotics, artificial muscles, smart sensors and devices, and so on.^[1–9] However, comparing with other types of actuators responding to temperature, light, electric field, and magnetic field, the exploration of HA remains far behind.^[10] To date, a main drawback of the developed HAs is their relatively low elasticity, which is possibly due to the existing of intermolecular interactions formed between the hygroscopic groups in dry environments that deteriorate network deformability. Liquid crystalline elastomers (LCEs) are widely used to develop HAs. However, the situation becomes complicated when LCEs meet water as they are apt to lose their responsivity when humidified.^[11,12] Furthermore, the developed methods

greatly compromise the network elasticity, leading to the significant change of mechanical behaviours of hygroscopic LCEs from elastic to brittle.^[13] Dielectric elastomers is also utilized to develop HAs, but the tensile strains of them reported to date are usually limited to below 50%.^[14] Considering that elasticity is closely related to the flexibility and complexity of their actuating behaviours, developing HAs with superior elasticity is of great importance and is still urgent.

Another challenge of developing HAs is the pursuing of re-programmable actuating behaviour. Here the re-programmable actuating behaviour refers to that the relevant aspects of actuation such as direction, speed, and amplitude of the actuation behavior can be modulated by post treatment. Most of the developed HAs can only exhibit monotonous actuating behaviours because of their chemically stable covalent crosslinking networks.^[15] Introducing dynamic intermolecular interactions or non-covalent crosslinking sites makes the resulting networks reprogrammable, but the time consumed for re-programming usually takes from minutes to hours, and the necessary input of heat or light energy inevitably arouses side reactions such as network degradation.^[16,17] Surface patterning methods are developed to post-modulate the actuating behaviours, but the erasing of the created patterns is quite difficult, and therefore the pro-

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gramming process is non-repeatable.^[18,19] Shape memory effect can also be introduced to regulate the external shapes and consequently the actuating behaviour of actuators. Shape memory effect refers to fixation and subsequent relaxation of temporal strains controlled by external stimuli, and the mechanism is the dynamic changes of intermolecular interactions in the network. Previous studies prove that the shape memory effect can effectively alter the external geometry and therefore the trajectory of the actuating behaviour.^[20–23] However, the existence of intermolecular interaction responsible for shape memory effect hinders the deformation of the network, which possibly leads to low tensile strains of the reported actuators. Moreover, most of the introduced shape memory effects in HAs are triggered by temperature variation, which would inevitably change the equilibrium water content in the network and arouse unavoidable deformation of HA.^[24] Therefore, it is necessary to introduce shape memory effect activated by nonthermal stimuli, which allows orthogonal stimulation of shape memory and actuating deformations. However, to the best of the authors' knowledge, such HAs are still quite rare.

In this work, we propose an orthogonal composite design to address the above-mentioned issues. The developed composite comprises carboxyl group-modified polystyrene-block-poly(ethylene-co-butylene)-block-polystyrene (SEBS-*g*-COOH) as the substrate and an azobenzene derivative as the functional filler. The carboxyl groups in SEBS-*g*-COOH can be reversibly transform to carboxylate groups and further recover to its initial protonated form by acid and base treatment. This allows the creation of surface patterns deciding the hygroscopic sensitivity and therefore the moisture-driven actuation behaviour of the composite.^[25,26] The azobenzene derivative possesses a methyl group at the 3-position and two dodecane short chains at 4- and 4'-positions. The short dodecane chains allow a good dispersion of azobenzene derivative in SEBS-*g*-COOH, and the methyl group facilitates the *trans*-to-*cis* isomerization of azobenzene derivative upon UV light exposure.^[27,28] In the following context, the azobenzene derivative is named as Azo12. The isomerization of Azo12 leads to liquefaction of the crystalline AD aggregates, which is utilized for strain fixation and relaxation during the UV light-triggered shape memory process. The incorporation of Azo12 has a very limited influence on the elasticity, as the composites still exhibit good extensibility. Since the shape memory and moisture-driven actuating functionalities are respective-

ly originated from the filler and the substrates, orthogonal regulation of the two components can be realized to achieve complex and flexible actuating behaviours of the composite. A scheme demonstrating the structure of the composite elastomer can be found in Fig. 1.

EXPERIMENTAL

Materials

Styrene-ethylene-butadiene-styrene copolymer (G1651 H, PS content: 33%, M_w : 174,000) was obtained from Kraton High Performance Polymers Co., Ltd. Maleic anhydride (MAH) was purchased from Innochem technology Co., Ltd. Dicumyl peroxide (DCP) was purchased from McLean Reagent Co., Ltd. Xylene, toluene, hydrochloric acid, and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd. Anhydrous ethanol (AR grade) was purchased from Chengdu Aike Reagent Co., Ltd. 1-Bromobutane, 1-bromododecane, *o*-cresol, and 4-aminophenol were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Nitrite was purchased from Fuchen (Tianjin) Chemical Reagent Co., Ltd. Ethyl acetate and *n*-hexane were purchased from Tianjin Fuyu Fine Chemical Co., LTD. Potassium hydroxide (KOH) was purchased from Guangdong Guanghua Technology Co., Ltd.

Synthesis of Azo12

Azo12 was synthesized according to the literature.^[29] Briefly, sodium nitrite (1.66 g, 20 mmol) dissolving in 25 mL water was added dropwise into a dilute hydrochloric acid (2.4 mmol, 25 mL) containing 4-aminophenol (2.18 g, 20 mmol). Afterward, the mixture was stirred for 15 min at 0 °C. Then, the mixture was added to a sodium hydroxide aqueous solution (20%, 8 mL) containing *o*-cresol (2.16 g, 20 mmol) at 0 °C. After stirring the mixture at room temperature for 16 h, hydrochloric acid was used to acidify the mixture to a neutral pH. The resulting product in the form of brown solid was filtered and washed using deionized water before drying. Column chromatography was applied to purify 4,4'-dihydroxy-3-methyl azobenzene on silica gel (eluent: ethyl acetate/petroleum ether=1:10, V:V).

4,4'-Dihydroxy-3-methyl azobenzene (0.228 g, 1.0 mmol) was dissolved in acetone together with 1-bromododecane (0.41 g, 3.0 mmol) and potassium carbonate (1.10 g, 8.0 mmol). The resulting mixture was stirred at 60 °C for 7 days using a magnetic bar. The mixture was further filtered after cooling to room temperature, which was then concentrated under reduced pressure. Lastly the residue was purified by

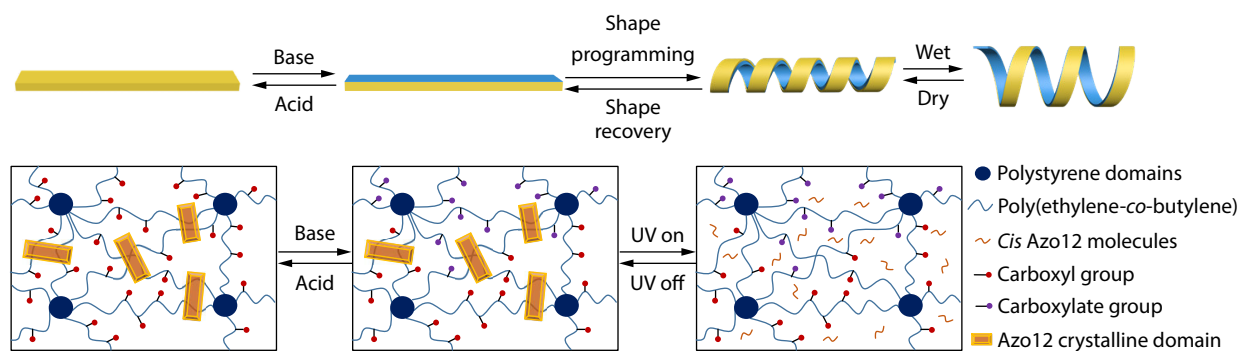


Fig. 1 A scheme showing the process to realize programmable moisture-driven actuating behavior and the underlying mechanism.

column chromatography on silica gel (eluent:ethyl acetate/petroleum ether=1:9) and recrystallized from acetone to obtain the final product.

Preparation of SEBS-*g*-COOH

SEBS (10 g) was dissolved in xylene in a round-bottom flask by magnetic stirring for 1 h at 100 °C. Maleic anhydride (MAH) previously dried at 120 °C for 12 h was added into the flask together with DCP, and the solution was heated to 140 °C under stirring. After 4 h the solution was cooled to 40 °C and the product was precipitated from the solution by adding anhydrous ethanol. The product was washed and filtrated repeatedly before drying in a vacuum oven at 120 °C for 12 h. The resulting material was further placed in air for at least 24 h to obtain the final product. The ¹H-NMR spectra of the products during synthesis can be found in Fig. S1 (in the electronic supplementary information, ESI).

Preparation of the Composites

The synthesized Azo12 and SEBS-*g*-COOH were together dissolved in toluene as the solvent at a mass ratio of 1:19. The mixture was stirred and heated to 80 °C for 4 h. Afterward, the solution was poured into a Teflon plate mould and placed in a 50 °C oven for 4 h. The residual solvent molecules were further removed by vacuum drying at 50 °C to obtain the final film.

Acid/Base Treatment

Filter papers are first immersed in KOH or HCl aqueous solution with certain concentrations for certain times before use. Afterward, the filter papers are placed on the surface of the composites at desired positions for certain time, followed by removal of the filter papers and the treated surfaces are cleaned by gently washing using deionized water to remove residual solutions. Finally, the composites are allowed to drying in a 50 °C vacuum oven for 12 h to accomplish the treatment process.

Evaluation of Shape Memory Property

The shape memory property of the material was evaluated using the following steps. The samples were firstly processed into long strips with a size of 20 mm × 4 mm × 0.2 mm. After exposing to UV light for a certain time, they were deformed into a bended shape or a stretched shape with certain strains (ε_m , the total strain). The deformation was kept using clamps for 8 h and then removed to obtain a temporary shape (ε_t). Further heating or irradiating the sample under UV light triggers the shape recovery process to obtain a recovered shape (ε_r , the recovered strain). The shape fixity ratio (R_f) and the shape recovery ratio (R_r) are determined using the following equations: $R_f = \varepsilon_t / \varepsilon_m \times 100\%$; $R_r = (\varepsilon_t - \varepsilon_r) / \varepsilon_t \times 100\%$.

Characterizations

¹H-NMR spectra were recorded on an NMR Bruker 600 MHz spectrometer. Contact angle measurement system (OCA 20, Dataphysics, Germany) with a drop volume of 2 μ L controlled by the system's own pipette is applied. Scanning electron microscopy (SEM) characterization uses a benchtop scanning electron microscopy (TM3030, Hitachi, Japan, accelerated voltage 15 kV). Differential scanning calorimetry (DSC) was determined by Q1000 (TA Instruments, New Castle, DE) with a scanning rate of 10 °C/min. Fourier transform infrared spectra (FTIR) were obtained using a Thermo Scientific FTIR spectrometer (PerkinElmer Frontier FTIR) in the range of 4000–400 cm^{-1} with a resolution

of 4 cm^{-1} and an accumulation of 16 scans per analysis. Dynamic mechanical properties were tested using Q800 (TA Instruments, New Castle, DE), the temperature range was set from room temperature to 125 °C, and the heating rate was 3 °C/min. Tensile tests were conducted on a Suns UTM2103 (Shenzhen, China) universal tensile testing machine. The strain rate was fixed at 100 mm/min and a sensor with a maximum measurement of 2000 N. X-ray diffraction (XRD) measurements were conducted on a Rigaku D/max 2550VB3+/PC X-ray diffractometer (Rigaku Co., Tokyo, Japan) operated with Cu K α irradiation at 40 kV and 40 mA, and the scan rate used was 3 (°)/min. The absorbance of the composite films was measured by using a UV-visible spectrophotometer (Shimadzu UV3600).

RESULTS AND DISCUSSION

SEBS-*g*-COOH is prepared by first grafting of maleic anhydride group to SBES, and then allows the conversion of maleic anhydride group to hydroxyl group by reacting with water existing in air.^[30] The successful synthesis of SBES-*g*-MAH and SEBS-*g*-COOH is verified by FTIR. As the results given in Fig. 2(a), compared with pure SEBS, the infrared spectra of SEBS-*g*-MAH after grafting showed a carbonyl characteristic absorption band at 1780 cm^{-1} , which proves the formation of SEBS-*g*-MAH. Further placing in air for 24 h the spectrum of the sample shows a C=O stretching vibration band located at 1710 cm^{-1} and the band at 1780 cm^{-1} can hardly be observed. This indicates that most of the maleic anhydride groups are converted to carboxyl groups. The composite in the form of thin film is prepared by dissolving SEBS-*g*-COOH and Azo12 in toluene followed by evaporating the solvent. Unless otherwise stated, the prepared film samples are 0.15 mm in thickness and are labelled as Azo-*x*, where *x* indicates the weight percentage of Azo12 in the composite. Fig. 2(b) presents the actual photos of a pile of Azo12 powder and a composite elastomer film before and after UV light irradiation. After 30 s irradiation with a light intensity of 550 mW/cm^2 , the Azo12 powder is thoroughly liquified with a simultaneous colour change from orange to red. The colour of the composite sample also changes from orange to red after UV light irradiation, which indicates the liquefaction of Azo12 in the composite. This is also verified by UV-Vis spectroscopy. Fig. 2(c) shows the absorption spectra of Azo-5 samples before and after different irradiation times. The characteristic peaks located at 361 nm is a strong π - π^* band and that at 454 nm is a weak n - π^* band. These two peaks can be clearly observed in the spectrum of the unirradiated sample. With increasing the irradiation time, the π - π^* peak gradually diminishes whereas the n - π^* nm peak strengthens, which is due to the *trans*-to-*cis* isomerization of Azo12. XRD spectra of Azo12 and the composite before and after UV light irradiation are presented in Fig. 2(d). The spectrum of SEBS-*g*-COOH only shows a broad peak located at $2\theta=19^\circ$, indicating the amorphous nature of it. The unirradiated Azo12 powder shows two sharp peaks located at $2\theta=10^\circ$ and 19.2° , and these two peaks are also observable in Azo-5. After irradiation, these peaks in both Azo12 powder and Azo-5 sample are all disappeared. DSC curves given in Figs. 2(e) and 2(f) also reveal the effect of UV light irradiation on the Azo12 crystalline aggregates. The curve of Azo12 shows a sharp melting peak at 55 °C, which can also be observed in Azo-5. The curve of SEBS-*g*-COOH only shows a broad peak at higher temperatures, which

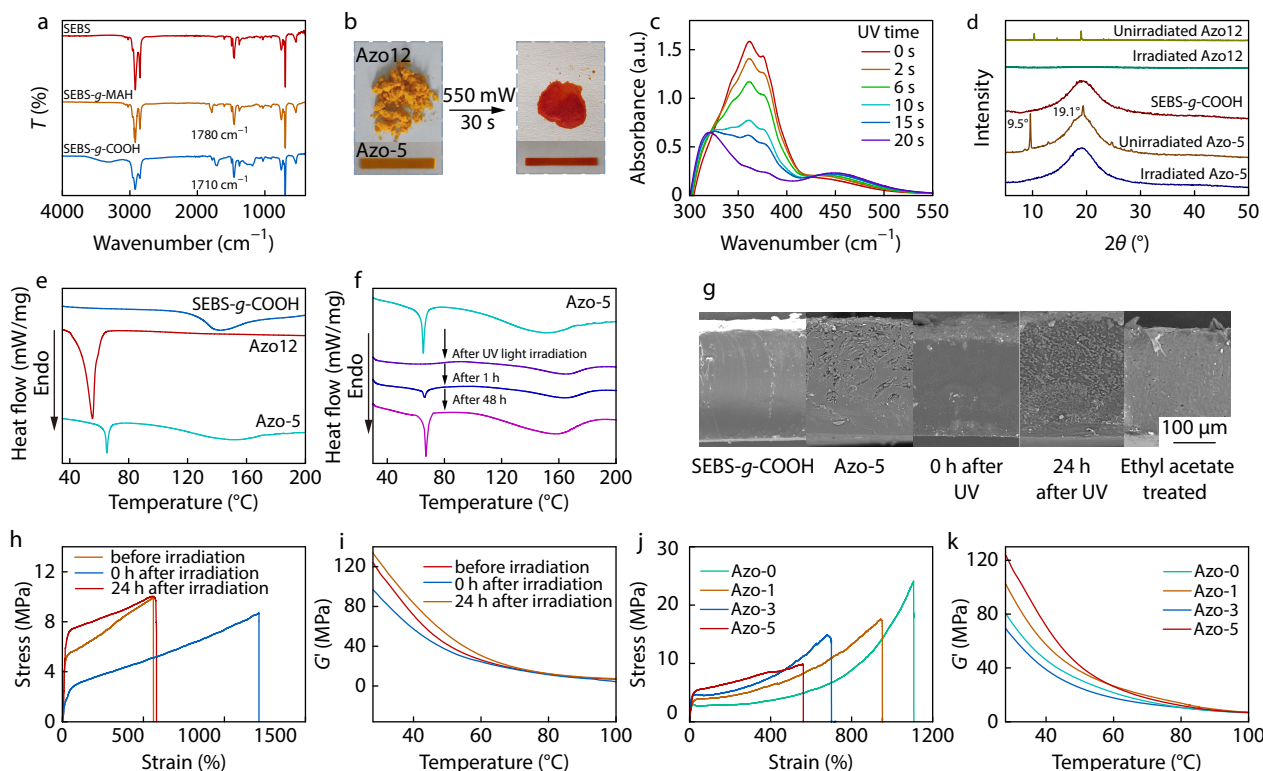


Fig. 2 (a) FTIR spectra of SEBS, SEBS-*g*-MAH, and SEBS-*g*-COOH; (b) Photos showing the changes in appearance of Azo12 powder and Azo-5; (c) UV-Vis spectra of Azo-5 before and different time after irradiation; (d) XRD patterns of SEBS-*g*-COOH, Azo12, and Azo-5 samples before and after irradiation; (e) DSC curves of SEBS-*g*-COOH, Azo12, and Azo-5; (f) DSC curves of Azo-5 before and different time after irradiation; (g) SEM images of SEBS-*g*-COOH, Azo-5, and Azo-5 at 0 h, 24 h after UV, and after ethyl acetate treated; (h) Tensile behaviors and (i) DMA curves of Azo-5 before and after irradiation; (j) Tensile behaviors and (k) DMA curves of composites with different Azo12 contents.

is attributed to the evaporation of water molecules from the amorphous network. The water loss of Azo-5 upon heating to 60 °C is 15.6% (Fig. S3 in ESI). The melting peaks in Azo-5 composite disappear after irradiation and reappear with time after ceasing irradiation. The XRD and DSC results together suggest that Azo12 molecules form crystalline aggregates in the composite, and the *trans*-to-*cis* isomerization of Azo12 molecules triggered by UV light irradiation leads to destruction of the aggregates. After ceasing irradiation, the *cis* isomers gradually transform into *trans* again, and the aggregates can reform with time. This is also verified by SEM. The images given in Fig. 2(g) show the morphologies of the cross-section of Azo-5 before and after irradiation. It can be clearly seen that Azo12 crystalline aggregates are separately inserted in the SEBS-*g*-COOH substrate. After UV light irradiation, Azo12 aggregates can no longer be observed, leaving the substrate exhibiting a smooth and homogeneous morphology. After 24 h ceasing irradiation the aggregates can be observed again. We also use ethyl acetate to treat the sample to dissolve Azo12 molecules and remove them from the composite, and the SEM image only shows micrometre-sized holes in the surface of the substrate. The above results again indicate that the Azo12 molecules form crystalline aggregates in the composite, which can be destroyed by UV light irradiation due to *trans*-to-*cis* isomerization of Azo12 molecules. The *cis* isomers of Azo12 gradually transform to their *trans* state again with time, leading to the reformation of crystalline domains.

The reversible solid-liquid transformation of Azo12 crys-

talline aggregates leads to prominent changes in mechanical properties of the composite. Fig. 2(h) shows stress-strain curves of Azo-5 samples before and after irradiation. The unirradiated sample breaks at 561% strain with a tensile strength of 9.91 MPa. After irradiation, the tensile strain increases to 1210% whereas the tensile strength mildly drops to 8.67 MPa. After waiting for 24 h, the tensile behaviour of the irradiated sample almost recover to the unirradiated state, with a tensile strength of 8 MPa and a fracture strain of 580%. Fig. 2(i) shows the changes of storage moduli (G') of samples before and after irradiation. All samples show notable drop of G' upon heating, and the difference lies in that the G' values of the samples at room temperature decreases from 124.1 MPa to 96.7 MPa caused by irradiation, which further recovers to 134.0 MPa for sample tested after 24 h of irradiation. The effect of Azo12 content on the mechanical properties is also investigated. Samples with 1 wt%, 3 wt% and 5 wt% of Azo12 are prepared and their tensile and dynamic mechanical behaviors are tested. Neat SEBS-COOH (Azo-0) is also tested for comparison. Fig. 2(j) shows that with increasing the Azo12 content, the composite exhibit deteriorated elasticity, as the values of the tensile strength and fracture strain for Azo-0 are 1102% and 23.87 MPa, which respectively drop to 558% and 9.88 MPa with 5 wt% of Azo12 addition. DMA curves given in Fig. 2(k) also reveals a similar tendency, as the G' value gradually decreases from 124.1 MPa to 69.3 MPa after incorporating Azo12 up to 5 wt%. These results indicate that the Azo12 crystalline aggregates do not participate in the network de-

formation to dissipate mechanical energy, and their reversible solid-liquid transformation can be utilized to temporally regulate the mechanical properties of the composite. In the following context, we use Azo-5 to conduct the experiments as a high Azo12 content guarantees prominent light-responsiveness of the composite.

The photo-responsive shape memory effect is next unveiled. A scheme and corresponding actual photos given in Fig. 3(a) together demonstrate a typical shape memory process of the composite triggered by UV light. An Azo-5 sample is first tailored into a long-strip shape, which is then treated by UV light irradiation and then programmed into a coiled shape by twining it on a rod. After 7 h the sample is removed from the rod and a temporal coiled shape is obtained. This temporary shape can be activated to recover to its initial straight shape by UV light irradiation. Fig. S4 (in ESI) also demonstrates the recovery process of a sample programmed into a paper plane-like temporary shape. The influences of relevant parameters on R_f and R_r are systemically investigated, and stretching deformation is applied to conduct the experiments. Figs. 3(b)–3(d) show the relationship between R_f and irradiation time. The samples together show a tendency that a longer irradiation time offers better shape fixation, and for a certain irradiation time samples with higher Azo12 contents show better R_f s. Similarly, Azo-5 shows faster and better shape fixation under stronger UV light irradiation, as the time required to reach 80% of R_f is shortened from more than 120 s to 10 s with the increase of intensity from 222 mW/cm² to 334 mW/cm². Samples with different thicknesses are prepared,

and the results show that thicker samples require longer times for fixation. Fig. 3(e) shows the relationship between R_f and fixation time for samples with different tensile strains. It is rational that a longer fixation time give rise to a higher R_f , as the destructed Azo12 crystalline domains are gradually reformed with time for strain fixation. An interesting phenomenon is that the composite exhibit higher R_f s with large tensile strains, as the value of R_f for samples after 60 s of irradiation and fixed with 200%, 400%, and 700% tensile strain for 24 h is 50%, 56% and 61%, respectively. This is possibly due to the morphological change of Azo12 aggregates in the network to adapt to network deformation, and more drastic deformations leads to more prominent morphological change of Azo12 for strain fixation. The decrease in thickness upon stretching may also favour strain fixation. For shape recovery, it can be clearly seen that samples exhibit faster and more complete shape recovery extents exposing to a stronger UV light, as the time taken for completing the recovery process can be shortened from longer than 60 s to 30 s and even 10 s when the irradiation intensity increases from 135 mW/cm² to 220 mW/cm² and 262 mW/cm², respectively. (Fig. 3f). All these results indicate that the shape memory effect originates from the liquefaction and re-crystallization of Azo12 molecules as reversible crosslinking. The liquefaction of Azo12 crystalline aggregates to unlock the network mobility, and therefore all the parameters favoring the liquefaction of Azo12 crystallinities such as longer irradiation time, a higher Azo12 concentration, stronger UV light intensity, and thinner samples lead to better strain fixation. After irradiation, a

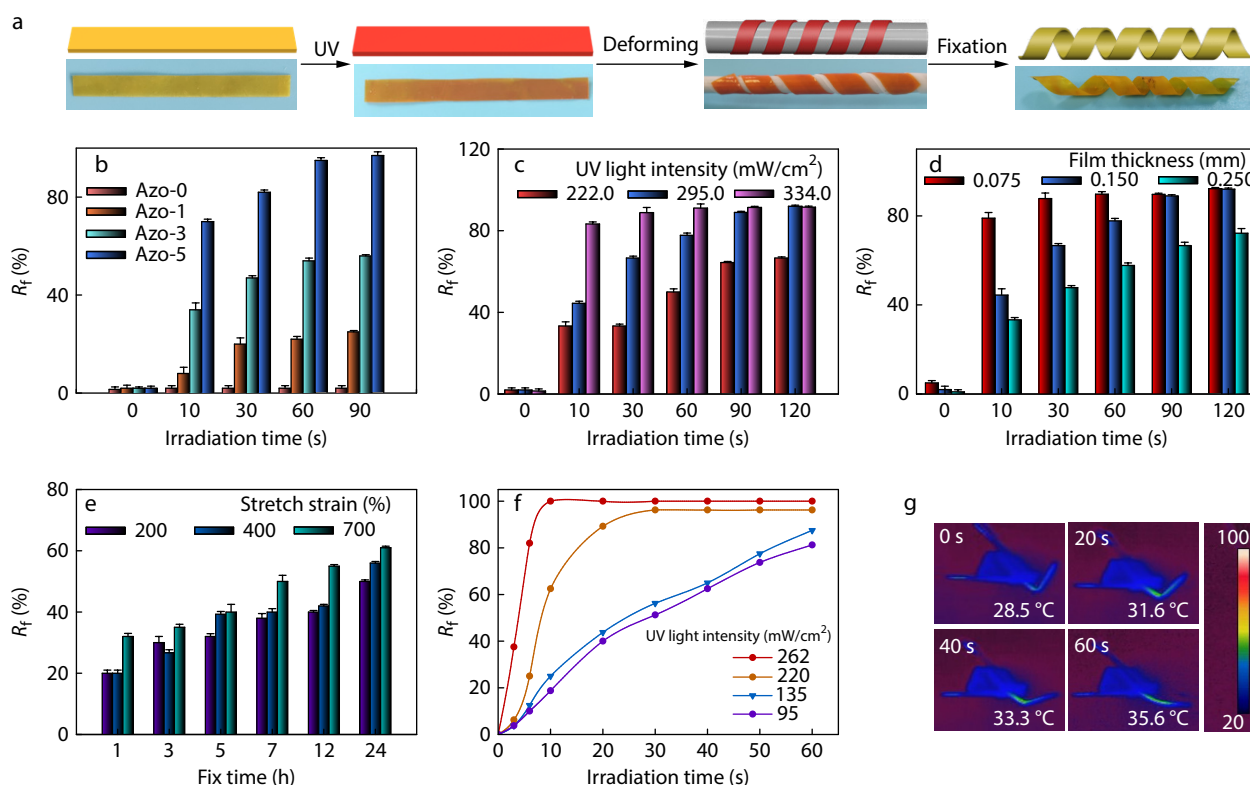


Fig. 3 (a) Scheme and actual photos demonstrating the shape memory process. The influences of (b) Azo12 content, (c) irradiation intensity, (d) film thickness, and (e) applied strain on R_f ; (f) The influence of irradiation intensity on R_f ; (g) Infrared thermal images showing the temperature change of a Azo-5 sample during UV light triggered shape recovery.

longer retention time allows more adequate crystallization of Azo12 molecules acting as crosslinking sites, resulting in better strain fixation. Since the Azo12 crystalline domains can also be destructed by heating to higher than T_m (Fig. S2 in ESI), the photo-thermal effect caused by the UV light source should be avoided. As the images given in Fig. 3(g), the temperature of the sample at the irradiated region only increases from 28.5 °C to 35.6 °C after 60 s irradiation. Considering that the T_m of Azo12 is 55 °C, these results verify that the shape memory effect is based on a nonthermal mechanism.

Fig. 4 shows 3 examples exhibiting shape transformation from 2D shapes into intricate 3D shapes by shape memory effect. All the 3 samples exhibit rectangular shapes in the initial stage, and after the proposed shape memory process they transform into a paper plane-like shape, a starfish-like shape, and a shape with alternative wavy strips, respectively. These temporary shapes are stable at ambient conditions, as after 12 h no shape change can be observed, even though the colour of the same changes from orange to bright yellow.

The moisture-driven actuating behavior that can be regulated by acid/base treatment, and the environmental humidity change is realized by using a commercial humidifier. As the photos given in Fig. 5(a), the untreated strip-like sample exhibits negligible shape change upon wetting and drying. After base treatment using potassium hydroxide (KOH) aqueous solution, the sample bends toward the untreated side within 110 s when humidified, which reversibly recover to its initial flat shape after 15 min of drying. The sample is further treated by acidic hydrogen chloride (HCl) solution, which becomes insensitive to humidity change again. These results indicate that the surface treatment can effectively “switch on” and “switch off” the moisture-driven actuation behavior. The cyclic actuating behaviors of samples after alternative base and acid treatment are presented in Fig. 5(b). KOH aqueous solutions with different concentrations are used and the HCl aqueous solution is kept at 12 mol/L. The results show that the sample treated using a higher concentration of base solu-

tion exhibits a larger actuating amplitude, and the largest bending angle obtained by treating the sample using 30 mol/L KOH solution can be as high as 92°. After acid treatment, all samples show negligible bending actuation, and this base-acid treatment cycle can be repeated for at least 3 times with good reproducibility. We also surveyed the actuating behaviours of samples with different compositions, and the results indicate that the Azo12 content has very limited influence on the actuating behavior. As the results given in Fig. 5(c), the actuating amplitude of the samples is quite approaching, which is 95°, 95°, 95° and 92° for Azo-0, Azo-1, Azo-3 and Azo-5, respectively. The above results together indicate that surface treatment is effective in enabling the film with moisture-driven actuating behaviors, which can be completely erased and reprogrammed with good repeatability.

The actuating mechanism is next investigated. The FTIR spectra given in Fig. 5(d) verify that the reversible transformation of carboxyl/carboxylate groups during surface treatment. The spectrum of SEBS-g-COOH shows strong absorption band near 1710 cm^{-1} , which is attributed to C=O stretching vibration. After treatment of KOH aqueous solutions with different concentrations, carbonyl stretching absorption band disappears and is replaced by two new bands at 1570 and 1400 cm^{-1} corresponding to the symmetric and antisymmetric stretching vibration of the carboxylate ions, respectively. Further treatment using a hydrogen chloride solution with a concentration of 12 mol/L, the band at 1710 cm^{-1} reappears and the bands at 1570 and 1400 cm^{-1} are absent. It should be noted that here the reflection mode is selected, which means the FTIR spectra only suggest the changes happening on the treated surface. Fig. 5(e) shows mass changes of the samples after alternative acid and base treatment. KOH solutions with different concentrations are utilized and the concentration of the acid solution is kept at 12 mol/L. It can be seen that the fractional weight change of the three samples individually treated by base solutions with concentrations of 5, 15 and 30 mol/L are 5.58%, 6.80% and 9.15%, respectively. After acid

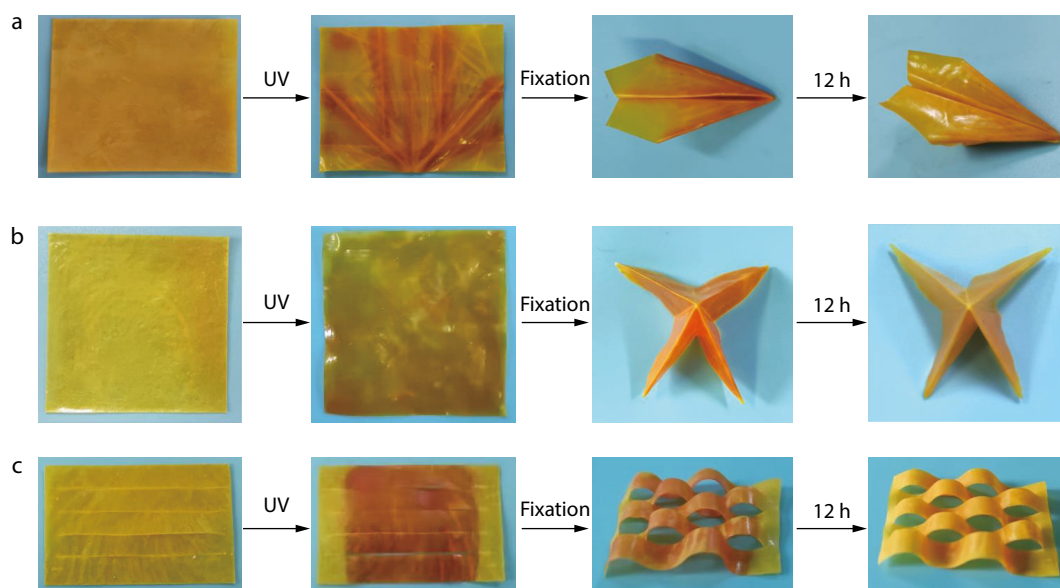


Fig. 4 Photos showing 3 examples exhibiting 2D-to-3D shape transformation based on shape memory effect.

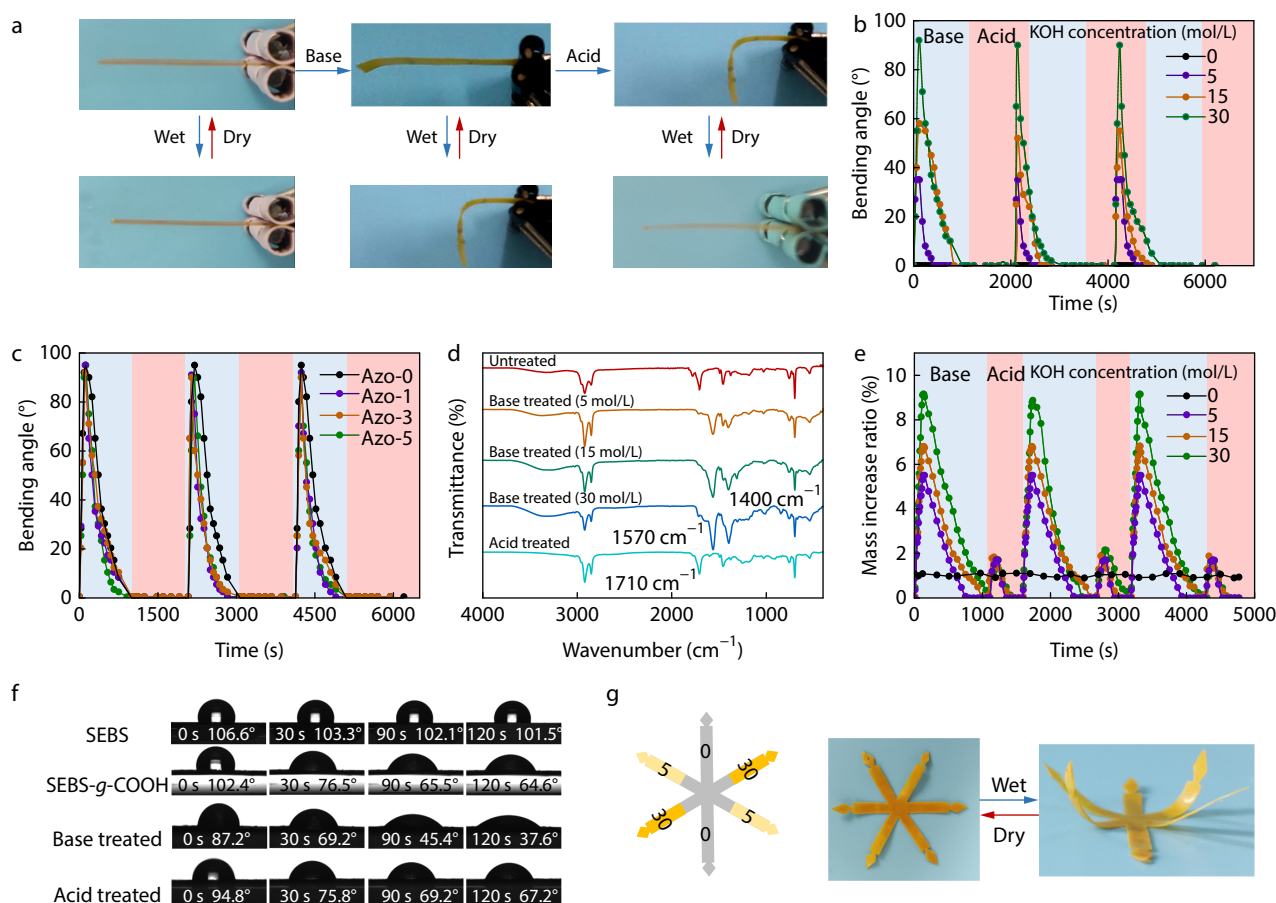


Fig. 5 (a) Photos of the programmable moisture-driven actuating behaviors of Azo-5 controlled by surface treatment; Cyclic actuating behaviors of (b) Azo-5 treated by base solutions with different concentrations and (c) composites with different Azo12 contents; (d) FTIR spectra of Azo-5 samples surface treated by acid and base solutions. (e) Fractional weight changes of Azo-5 samples after cyclic surface treatments. (f) WCA of SEBS, SEBS-g-COOH, base-treated Azo-5, and acid-treated Azo-5. (g) A Azo-5 sample demonstrating patternable moisture-driven actuating behavior.

treatment, the fractional weight change of the three samples decreases to lower than 2%. The influence of this group conversion on the surface hydrophilicity is surveyed by investigating the change of water contact angle (WCA). As shown in Fig. 5(f), the WCA value of the untreated sample is 106.6°, which eventually decreases to 101.5° after 2 min. After base treatment, the initial WCA is lowered to 87.2°, which further decrease to 37.6° after 2 min. Further acid treatment the WCA of the sample is quite approaching to the value of the untreated sample, which is 94.8° obtained after immediate contact and 67.2° obtained after a 2 min stay of the droplet on surface. All the above results together verify that surface treatments using acid/base solutions induce reversible conversion between carboxyl and carboxylate groups, which alters the surface hydrophilicity and water absorption capacity. The carboxylate groups enhance water absorption when humidified, which causes volume expansion and therefore bending deformation film toward the untreated side. The absorbed water molecules can be further released upon drying, leading to volume shrinkage and flattening of the sample. Surface treatment is advantageous in creating hygroscopic patterns with spatially differentiated sensitivities. One example is given in Fig. 5(g), where a planer sample with 3 pairs of arms

is first prepared. Afterward, the arms are surface treated using KOH solutions with different concentrations (0, 5 and 30 mol/L). Further upon wetting, the sample changes into a 3D shape with the arms' different extents of bending deformation.

After individual investigation of the photo-responsive shape memory and moisture-driven actuating behaviours, these two shape-changing functionalities are orthogonally combined to realize more complex and flexible deformations. This is realized by surface treatment of the samples to create hygroscopic patterns before utilizing the shape memory effect for shape programming. By manipulating the external geometry, the actuating amplitude and direction can be effectively altered. 4 Samples are presented in Fig. 6. The first sample is first shape programmed into a flower-like 3D shape. After surface patterning, the petals of it can reversibly bend toward different directions. The second sample with a programmed spiral shape, which can further deform to alter its inner diameter upon the variation of environmental humidity. The last two samples are first processed into delicate 2D shapes as the initial shape, which are further programmed into more complicated 3D temporary shapes resembling butterfly and chrysanthemum. When triggered by moisture, they

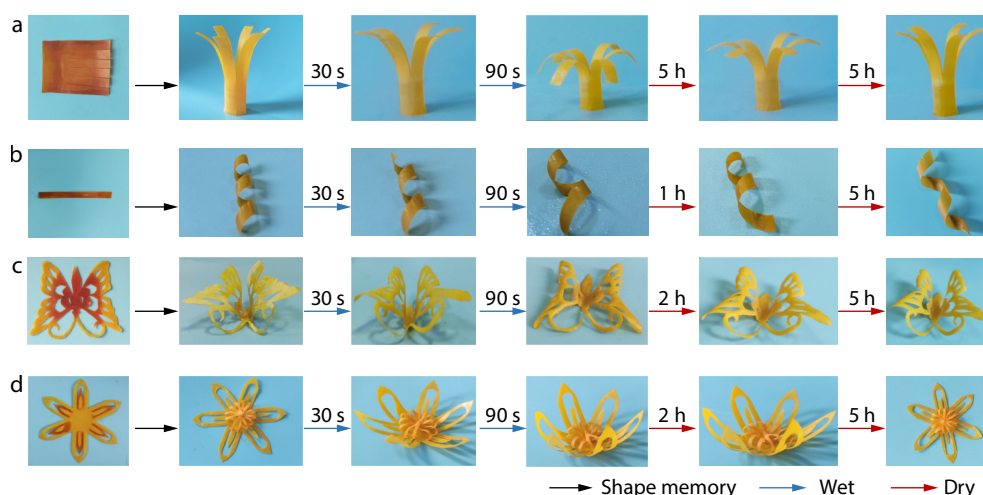


Fig. 6 Complex moisture-driven actuating behaviors of 4 Azo-5 samples with programmed 3D shapes.

exhibit deformations mimicking the wing flapping of a butterfly and blossoming of a flower. Moreover, one application scenario demonstrating the potential use of the actuator can be found in Fig. S5 (in ESI), where a hook made by the composite actuator can controllably grasp and lift the object in air stimulated by moisture.

CONCLUSIONS

This work reports an orthogonal composite design to enable programmable moisture-driven actuating behaviors. The prepared composite comprises SEBS-*g*-COOH as the elastomer substrate and Azo12 as the photo-responsive functional fillers. The reversible liquefaction and solidification of Azo12 crystalline domains can be effectively controlled by UV light irradiation, which renders the prepared composite excellent nonthermal shape memory effect. On another aspect, the carboxyl groups in the SEBS chains can be reversibly converted to carboxylate groups by surface treatment using base and acid solutions, which greatly alter moisture absorbing capability of the treated surface, leading to switching on and off of the hygroscopic actuating behaviour. We also show that these two types of shape change can be separately operated, as the Azo12 content has very limited influence on the actuating behaviour. We further show that by combining these two functionalities together, intricate hygroscopic actuating behaviours of 3D shaped composites can be obtained by first surface patterning and the shape programming before the stimulation of moisture. The proposed strategy can be extended to designing different composite materials with orthogonal shape memory and actuating functionalities.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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