Herein we propose a facile strategy to prepare 3D-printable tunable shape memory polymer blends (SMPs) by melt-blending a commercial thermoplastic elastomer, SEBS, with polyethylene wax and low-density polyethylene. The SMPs are easy to process via traditional polymer processing apparatuses and suitable for a commercial fused deposition modeling 3D printer.

Shape memory polymers (SMPs) are smart materials that can change shapes upon exposure to various external stimuli such as heat, light, ultrasound, and chemical substances.1–5 Among different categories of SMPs, heat-activated SMPs, driven predominantly by entropic elasticity, are one of the most common types.6–9 Conventional heat-activated SMPs, consisting of a crosslinked network and only one reversible thermal transition, can memorize one temporary shape, which is defined as dual shape memory effect (dual SME).1 Based on tailoring chemical compositions via chemosynthesis,10–13 altering phase structures via polymer blending,14 constructing semicrystalline polymer networks via a crosslinking reaction15–18 or building macrostructures via later-assembly,19–21 multiple shape memory polymers (multi-SMPs) with multiple discrete thermal transitions are prepared. Multi-SMPs feature the ability to memorize more than one temporary shape in each shape memory cycle.22–24 Recently, Xie reported that polymers with a crosslinked network and a broad reversible thermal transition have the potential to realize the multiple shape memory effect (multi-SME) at arbitrary deformation temperatures (T_d) as long as T_d < T_G is sufficiently apart, which was defined as tunable SME.24,25 Compared with multi-SMPs, the number of temporary shapes tunable SMPs can memorize is variable and the T_d < T_G can be adjusted optionally, thus tunable SMPs can realize more complex and free actions through tunable shape changes.

Additive manufacturing, also known as three dimensional (3D) printing, is a remarkable burgeoning technique that allows materials to be deposited in a layer-by-layer manner to form objects with sophisticated 3D structures and high resolution, driving major innovations in the fields of manufacturing, architecture, and healthcare, etc.26–29 The combination of SMPs and 3D printing endows printed objects with custom-designed structures, as well as the capability to change shape in response to external stimulus. Up to now, some work on 3D printing with SMPs has been performed. Zarek et al. prepared photo-curable resins with dual SME based on polycaprolactone and isocyanatooctyl methacrylate via an alcohol–isocyanate reaction, then printed active structures using a commercial stereolithography printer.30 Li et al. synthesized methyl acrylate-co-styrene copolymers (“building blocks”) with different glass transition temperatures via living radical polymerization. They printed 3D structures, which showed good multi-SME, with various building blocks using a fused deposition modeling (FDM) printer.31 More recently, Xie et al. printed several 2D structures using a series of light-curable monomers. Such 2D structures can be turned into 3D structures spontaneously when immersed in water or wax.32 In comparison with the existing 3D-printable dual SMPs or multi-SMPs, 3D-printable tunable SMPs have the possibility to implement a highly complex and sequential shape change process vividly in a pre-programmed way. Thus, it may have promising prospects in a broad range of fields, such as intelligent actuations, biomedical devices, as well as flexible electronics and aerospace applications. However, to the best of our knowledge, there is no research yet into 3D printing with tunable SMPs.

In this work, we proposed a facile blending strategy to prepare tunable shape memory polymer blends with the feasibility of 3D printing. Such tunable shape memory polymer blends consist of three components: styrene-\(\text{b}\)-(ethylene-co-butylene)-\(\text{b}\)-styrene (SEBS), polyethylene wax (PEW) and low-density polyethylene (LDPE). All the raw materials are industrial supplies with low cost and no solvent was involved throughout the entire manufacturing process. The blends have good tunable SME and were easily extruded as monofilaments with targeted diameters via
traditional polymer processing apparatuses. The monofilament was further applied to a commercial FDM 3D printer and smart objects with different structures were 3D printed.

The mixing ratio of three components has an important effect on the properties of this material (Tables S1–S7, ESI†). To obtain both satisfactory shape memory properties and good processability, our 3D-printable shape memory material was prepared by mixing PEW and LDPE granules as well as SEBS powders with a specific mixing ratio of 30 : 50 : 20 (SEBS : PEW : LDPE, mass ratio) using a twin screw extruder. To demonstrate the typical shape memory process of this ternary blend, the extruded filament was cut into pellets and then hot pressed into rectangular sheets (30 mm × 5 mm × 0.5 mm). Afterwards, we performed operational testing on the sheet as follows: (1) the sample with permanent shape 0 (S0) was twisted at 95 °C and fixed at 80 °C for 5 minutes to yield the first temporary shape 1 (S1). (2) The sample with S1 was twisted at 80 °C and fixed at 65 °C for 5 minutes to yield the second temporary shape 2 (S2). (3) The sample with S2 was twisted at 65 °C and fixed at 0 °C for 5 minutes to yield the third temporary shape 3 (S3). It should be emphasized that different parts of the sample were deformed at different deformation temperatures (Td,s) during this programming process. (4) A programmed sheet with S3 was reheated to 65, 80 and 95 °C in sequence, and the shapes at 65, 80 and 95 °C during the recovery process were abbreviated as S2, S1 and S0, respectively. The qualitative shape memory process is illustrated vividly in Fig. 1a. It is found that all the temporary shapes were easy to yield and shapes S0, S1 and S2 were strikingly similar to S0, S1 and S2, indicating that this ternary blend has good ability to memorize at least three temporary shapes and recover to preceding shapes. It is also worth noting that upon reheating to 65, 80 and 95 °C, the recovery time from S3 to S2, from S2 to S1 and from S1 to S0 is 15, 11 and 6 seconds, respectively, demonstrating that the blend has good thermal sensitivity. We also quantitatively evaluated quadruple shape memory behavior using a fixing ratio (Rf) and a recovery ratio (Rr) determined by bending angle during the bending testing.33 Rf describes the capability of the thermal switch to fix the temporary shapes, and Rr denotes the capability of the sample to be restored to its previous shapes during the thermomechanical bending cycle.

The same part of a sample was bent three times at three deformation temperatures Td1, Td2 and Td3 are 95, 80 and 65 °C, respectively, the same with the aforementioned qualitative experiment) and the bending angles as well as the corresponding temperatures are shown in Fig. 1b. The Rf values corresponding to S1, S2 and S3 were 78%, 82% and 95%, and the Rr values corresponding to S2, S1 and S0 were 85%, 81% and 78%. Both of the qualitative and quantitative results suggest that our ternary blend has a good quadruple shape memory effect.

In order to exhibit the tunable shape memory property of this ternary blend, various Tds were chosen to perform dual, triple and quadruple shape memory testing. To avoid destroying the physical crosslinked SEBS-network of this ternary blend, the maximum temperature chosen in these experiments is 95 °C.

We firstly selected 80 °C as Td to conduct dual shape memory testing. Both Rf and Rr values were 97%, certifying excellent dual SME of this ternary blend (Fig. 2a). We selected 90 °C as Td1 and 60 °C as Td2 to perform triple shape memory testing (Fig. 2b). Rf values of the first and second temporary shape were 98% and 93% and the Rr values were 86% and 92%, proving that this ternary blend has pretty good triple shape memory behavior. According to the above-mentioned experimental result, this ternary blend has good quadruple SME when we chose 95, 80 and 65 °C as Tds (Fig. 1b). To further certify the tunability of this ternary blend, we selected three different Tds to carry out quadruple shape memory testing. When Tds were 95, 75 and 60 °C (Fig. 2c), the Rr values were 93%, 79% and 95% and the Rf values were 88%, 84% and 84%. When Tds were 95, 75 and 50 °C (Fig. 2d), the Rr values were 95%, 83% and 87% and the Rf values were 72%, 83% and 85%. Taken all together, this ternary blend can memorize at least three temporary shapes and Tds can be tailored flexibly in a broad temperature range, demonstrating that this blend has good tunable SME. We noticed that the fixation and recovery capability changed when we chose different Tds, therefore we changed Tds to conduct dual shape memory testing and corresponding thermal simulation testing. It is found that there is a positive correlation between Rf (Rr) values and enthalpy values (Fig. S1 and Table S8, ESI†). From this perspective, the Rf (Rr) value of each shape can be altered freely so long as we regulate the enthalpy distribution rationally during the shape.

![Fig. 1](https://example.com/fig1.png)

(a) Photographs showing the quadruple shape memory effect of the ternary blend. (b) Quantitative quadruple shape memory results of the ternary blend measured by bending testing.
According to Xie’s research,1,2,4 polymers with a crosslinked network and a broad reversible thermal transition might possess tunable SME. To investigate the essence of the broad thermal transition, successive nucleation and annealing (SNA) thermal fractionation was carried out on the blend sample. SNA thermal fractionation enhances the potential molecular fractionation that occurs during crystallization based on dissimilarity of the crystalline properties, which means that slight differences of thermal transition will be magnified using this technique.35,36 In this work, we performed SNA thermal fractionation according to the following procedures: the sample was heated to 200 °C and held for 5 min to eliminate thermal history, then cooled to 0 °C to create a standard thermal history. Subsequently, a sample was reheated to the first seeding temperature (T1) and held for 10 min to anneal residual unmelted crystals. Then the sample was cooled to 0 °C again to accomplish sufficient crystallization. The fractionation temperature range was from 105 to 30 °C at an interval of 5 °C, which means the first T1 was 105 °C and the last T1 was 30 °C. After a thermal fractionation process, the sample was reheated from 0 to 200 °C at 2 °C min⁻¹ and the final DSC melting curve was obtained, as shown in Fig. 3c. It can be seen that there is a distribution of multiple individual melting peaks induced by such thermal treatment on the final DSC trace at about 30–110 °C, confirming that the broad thermal transition of this ternary blend stems from the heterogeneous microstructures instead of slow response to thermal treatment. Essentially, each individual melting peak on the final DSC trace corresponds to a series of lamellae with similar thickness, which forms in the annealing temperature range (105–30 °C). Each of the individual thermal transitions on the final melting curve in Fig. 3c could be considered as a thermal switch with a specified transition temperature and has potential to memorize a corresponding temporary shape.

According to this result, we deduced that multiple temporary shapes can be memorized in a shape memory cycle. To verify foregoing speculation, multi-stage recovery testing was conducted as follows: the sample was firstly deformed to a bending
angle of 180° at 95 °C and cooled to 0 °C to fix this temporary shape. Then it was reheated from 0 to 95 °C slowly. The bending angle was recorded in real time at an interval of 5 °C throughout the whole recovery process. As shown in Fig. 3d, a continuous shape recovery behavior of this ternary blend was observed when reheated gradually from 0 to 95 °C, indicating that each temperature section has the corresponding melting (crystallization) component and these components do not interfere with each other (Fig. S8, ESI†). Based on the analysis above, we may conclude that this ternary blend with a broad thermal transition can memorize multiple temporary shapes well and we can alter $T_{ds}$ optionally so long as there are adequate individual thermal switches between any two $T_{ds}$. Consequently, very free tunable SME could be realized only via the reasonable selection of $T_{ds}$.

To demonstrate the applicability of a 3D printing SMP process, this ternary blend consisting of SEBS/PEW/LDPE was extruded as a monofilament with a diameter of 1.65 ± 0.1 mm. The monofilament was applied to a FDM 3D printer directly. It is found that the ternary blend has good processability and is suitable for 3D printing. The effect of LDPE on the processability and 3D printing properties was discussed in the ESI† (Fig. S9). Several proof-of-concept models were 3D printed to exhibit tunable shape memory behavior. A workflow that illustrates the process of fabricating a 3D structure based on a commercial FDM 3D printer is shown in Fig. 4a. Firstly, digital models were pre-designed in a computer with the software SketchUP (Trimble Navigation, America) and then exported as standard triangle language (STL) file types. The STL files were modified with the native printer software Maxform (Clopx, China) and exported as gcode file types. Then the gcode files were imported into the FDM 3D printer. Under a FDM system, the filament made of raw materials with a specified diameter was fed into the printer via a pinch roller. The scale of our 3D printer’s platform was 210 × 210 mm and the temperature of this platform was set to 100 °C for the purpose of sticking the finished part. The diameter of the nozzle was 0.4 mm and its temperature was set to 220 °C to ensure that the material could be extruded smoothly in a controlled X–Y–Z movement onto the previous layer of the object being built. A flower with eight petals and a star with three arms were obtained successfully via 3D printing. Shape memory testing was performed as follows: first of all, the flower was immersed in a water bath at a constant temperature of 95 °C until the flower was softened sufficiently and then two petals of flower were closed by force. Subsequently, the flower with two gathering petals was cooled to 80 °C while holding the stress for 3 min. After the stress was released, another two petals closed artificially. Then the flower with four gathering petals was cooled to 65 °C while holding the stress for another 3 min. Finally, the rest of the four petals were closed by force and the flower with eight gathering petals was cooled to 0 °C while holding the stress for the same time. A “closed” flower was gained through these steps. The “closed” flower was immersed in a water bath of 65, 80, and 95 °C in
sequence. Finally, the flower bloomed successively, as shown in Fig. 4b. Then we selected different $T_{d1}$ ($T_{d2}$ and $T_{d3}$ are 90, 75 and 60 °C, respectively) and performed a similar operation on the star with three arms. The star also demonstrated good multi-SME, as shown in Fig. 4c. The experimental results prove that this ternary blend can be 3D printed to fabricate objects with tunable SME and various topological structures simultaneously. Compared with conventional thermoplastic-shaping techniques like simple casting or molding, 3D printing sheds light on the rapid prototyping of tunable shape memory materials with complicated, specific and personalized structures, which may have an excellent prospect in the fields of flexible electronics, electrical actuators, intelligent biomedical scaffolds, etc.

### Conclusions

In summary, we have successfully designed tunable SMPs consisting of SEBS, PEW and LDPE based on a facile melt blending strategy. The heat-driven tunable SMPs are easy to process and suitable for a commercial FDM 3D printer. Smart objects with different structures have been 3D printed. These SMPs have the potential for large-scale fabrication as all the raw materials are industrial supplies with low cost and little pollution and the preparation strategy is very facile.

### Conflicts of interest

There are no conflicts of interest to declare.

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### Notes and references