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Investigation of the Long-Term Storage Stability of Shape Memory Epoxy Prepolymer

*Xue Wan, Yang He, and Jinsong Leng**

Epoxy-based shape memory polymers (ESMPs) are important types of thermoset shape memory polymers due to their unique thermomechanical properties, which have great potential in applications ranging from smart actuators to deformable structures. The long-term storage stability is important for ESMPs, especially when pursuing the same batch of materials for alternatives. Stable storage of ESMP preplomyers in the long term and taking it out for curing when needed are of great benefit to engineering applications which highly require the same batch of materials for high production efficiency, such as in deployable space structures, semiconductor, and electronic packaging. However, this important storage stability of ESMP has not been studied so far. Herein, a series of ESMPs with tunable glass transition temperatures (T_gs) ranging from 100 to 170 °C is prepared. The effect of long-term storage at low temperatures on rheological, thermal, thermomechanical, mechanical, and shape memory properties is systematically investigated. The ESMP after storage shows an improvement of crosslinking density, T_gs, and mechanical strength, while maintaining chemical structures and excellent shape memory properties. This feasible method of low-temperature storage realizes overall long-term stability and enhancement of strength in ESMPs, making it more promising for engineering applications.

1. Introduction

Shape memory polymers (SMPs) are types of stimuli–responsive materials that could revert to their original shapes from temporary shapes when exposed to an external stimulus, such as heat, humidity, electrical current, light, magnetic field, etc.[1–6] Due to their characteristics of shape-changing capability, high recovery strain, low weight, and ease of processing, SMPs have been explored for applications in deployable structures, biodegradable stent, flexible electronics, smart textiles, and soft robotics.[7–14] SMPs are categorized into thermoplastic and thermoset in general, corresponding to physical and chemical crosslinking networks, respectively.[15,16] Thermoplastic SMPs have an advantage of larger deformation strain and reprocessibility,[8] while their shape recovery ratio usually is not good as thermoset, although there are some exceptions.[17] Thermoset SMPs show higher glass transition temperature (T_g), mechanical strength, and shape memory property than thermoplastic counterparts because thermoset has high-density covalently crosslinking networks.[18] In addition, thermoset SMPs could be manufactured by curing liquid monomers with crosslinkers or adding crosslinking points on the basis of thermoplastic. The properties of thermoset SMPs could be easily tuned by materials selection and weight ratio of monomers and crosslinkers, and the nature of fluid monomers makes it easy to manufacture complex shapes. Benefiting from these advantages, thermoset SMPs are more desirable in large-scale engineering application as structural materials.[19–21]

As an important type of thermoset SMPs, epoxy-based shape memory polymers (ESMPs) have aroused sustained academic interest in decades.[22–28] Various chemistry strategies were utilized to fabricate ESMPs by different choices of monomers and hardeners. This enabled ESMPs to possess a wide variety of T_gs, excellent shape memory performance, insulating properties, high modulus, and high-temperature-resistant performance. Not only as structural materials for engineering applications, ESMPs have also been extended to multifunctionalities, such as self-healing,[29] recyclability,[30] and multishape systems.[31,32] A prototypical example of ESMP with a high T_g was obtained by curing an epoxy base resin, a hardener, and a linear epoxy monomer.[33] The effect of gamma irradiation on thermomechanical properties of this type of ESMP was systematically investigated.[34] The excellent anti-irradiation performance combined with self-deploying properties showed great potential as aerospace structures. Liu et al. modified ESMP with organic montmorillonite to increase the mechanical strength, recovery speed, and T_g, while maintaining high shape recovery rate.[35] Similarly, Seok Bin et al. chose carbon fiber to reinforce ESMPs to make shape memory composites and utilized a constitutive equation model to explain shape memory performance.[36] Jo et al. fabricated ESMPs (T_g: 120–135 °C) for deployable space structures with high toughness.[37] As ESMPs behave as promising candidates as deployable engineering structures, the long-term storage stability or shelf life is quite crucial for their practical applications. However, there are very few studies on the long-term storage

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stability of ESMPs and their prepolymers. Some researchers found that a storage period of 0.5 or 2 months had no effect on recovery strain of epoxy-based shape memory composites and shape memory polyurethane foam stored under constraint at room temperature (RT).[19,38] Some focused on the effect of chemical crosslinking extent on the long-term storage stability of acrylate-based SMPs.[39] However, the regulation method is complicated and it is hard to meet the requirements of large scale. In addition, a lot of ground experiments are required to verify stabilities before putting ESMP structures to be applied in realistic situations. Thus, long-term storage stability is quite important for ESMP, which means that it is stable in the storage period and achieves the same or better overall properties after curing when needed. To achieve this goal, it is better to prepare as much ESMP as possible, especially from the same batch to obtain same properties for long-term use in engineering. In addition, it is important to monitor the storage stability of the epoxy resin. In this study, we present a novel method of low-temperature long-term storage for ESMP prepolymers. Different from previous storage methods, we store various ESMPs with tunable T_gs in their oligomer state. Systematic investigation of long-term storage stability in low temperatures of ESMPs was focused upon. The overall properties, including rheological, thermal, mechanical, and shape memory capabilities were analyzed in detail. We surprisingly found that the strength of ESMP increased in the initial storage period of 5 months, while maintaining excellent shape memory properties. This research helps fill the blank of long-term storage stability of ESMPs for engineering applications.

2. Results and Discussion

The process of making ESMP at some storage intervals is shown in **Figure 1**. Although the storage was under low temperature, the chemical reactivity between epoxy monomers and hardeners still existed. A slight density of crosslinking networks is formed during this period followed by complete thermal curing at high temperature. We speculated that this low-temperature storage was beneficial for final properties of epoxy, because the transition from epoxy monomers to 3D networks happened gradually and gently.

All ESMPs with different T_gs consisted of the same components; hence, the viscosity showed no obvious difference. We chose ESMP 150 as a representative for investigation of rheological properties in long-term storage period. The curve of apparent viscosity versus shear rate is shown in **Figure 2**a. All the epoxy resins were Newtonian fluids as they showed a constant viscosity independent of shear rate. The viscosity increased significantly as the storage time prolonged. The viscosity at 10 months was almost 21 times higher than at 0 month. This evident increase reflected that the epoxy monomers and hardener started to react during storage in a refrigerator. It should be pointed out that although the viscosity rose up remarkably, it had a strong dependence on temperature. As shown in Figure 2b, the viscosity of ESMP 150 stored for 7 months significantly decreased as the temperature increased. This was convenient for making the ESMP sample. After long-term storage, it was difficult to pour high viscous resin into the mold quickly. The process could be easier when the resin is heated to an elevated temperature to decrease the viscosity.

Figure 3 shows the long-term evolution of thermomechanical properties of EMSP 100. As shown in the dynamic mechanical analysis (DMA) curve of tan δ and storage modulus as a function of temperature, respectively, the variation of T_g and storage modulus are shown in Figure 3a,b, and the detailed values are shown in Figure 3c,d. We classified the storage period into three main regions according to the variation of thermomechanical properties. In the first stage, the T_g of ESMP 100 showed an increase of 8.1 °C from ≈95 °C at 0 month to 103 °C at 1 month. It indicated that in the first month during storage in the refrigerator, the crosslinking reaction between the epoxy resin and the hardener occurred. This was also proved by a slight increase in the crosslinking density, which is discussed in the later paragraph. As the T_g reflected the extent of crosslinking density, the crosslinking networks after storage became denser. In addition, the process

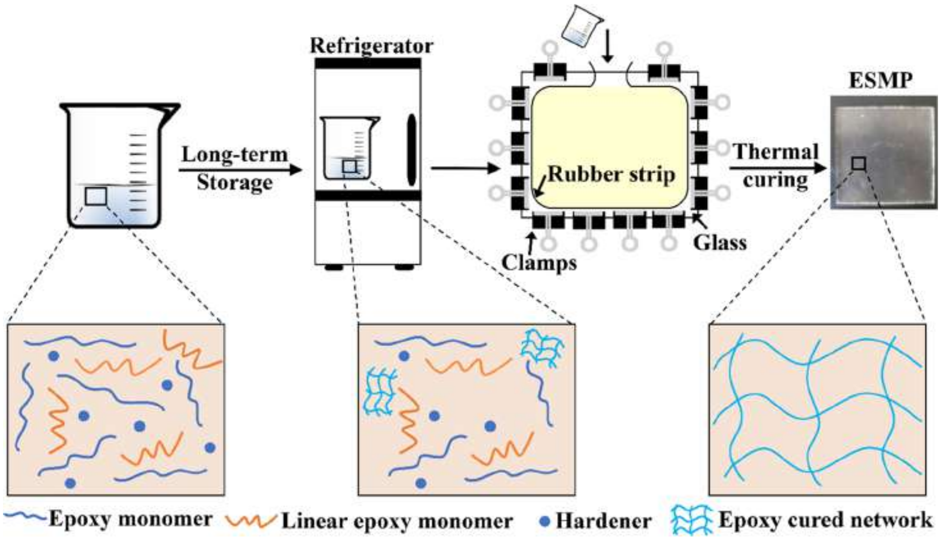

Figure 1. Schematic process of making ESMP during long-term storage in a low-temperature refrigerator at some intervals.

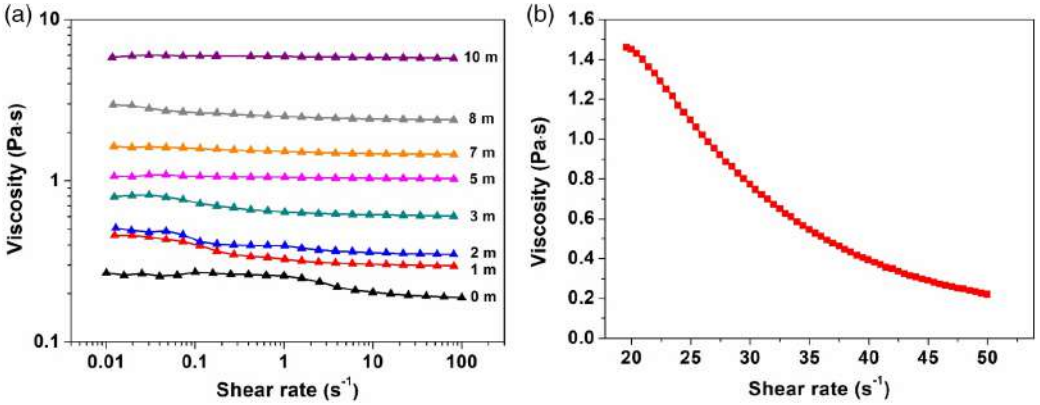

Figure 2. Rheological properties of ESMP 150. a) Apparent viscosity as a function of shear rate during long-term storage. b) Apparent viscosity of ESMP at 7 m as a function of temperature.

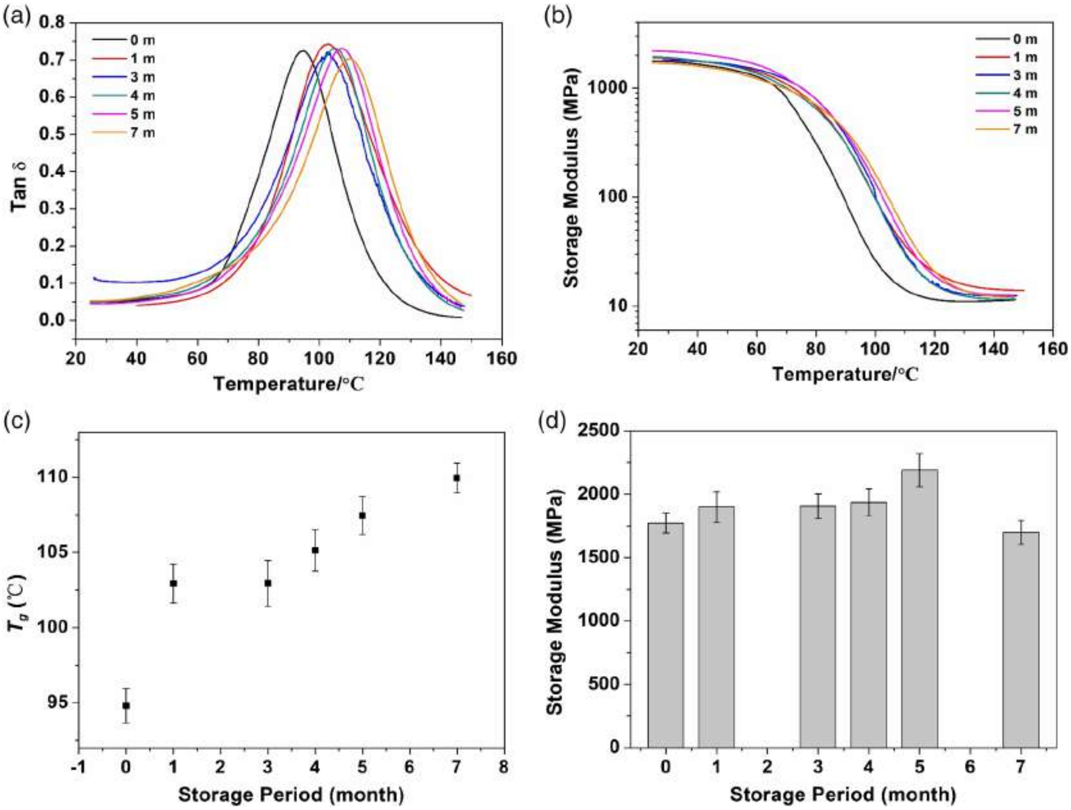

Figure 3. Long-term thermomechanical properties of ESMP 100. a) DMA curve of tan δ; b) DMA curve of storage modulus; c) T_g variation; and d) storage modulus versus storage period.

of low-temperature storage was similar to stepwise curing, which led to a more complete transition from epoxy monomers to macromolecules; hence, the T_g rose up. In the second stage, the T_g also showed an increasing trend but with a slower growth at around 4.5 °C. This was because the reactivity was higher in the first month and decreased in the next few months. As the storage time passed by, the number of reactive groups decreased over time. Both in the first and second stage, the storage modulus increased with a total percentage of about 23%, which was in accordance with the variation of T_g. In the third stage between 5 and 7 months, although the T_g continued to grow, the storage modulus saw a significant decrease, even lower than the initial value at 0 month. It indicated that in this period, the storage period was too long for the ESMP 100 to maintain the original performance, so it may reach the pot life. This will also be discussed later by combining with the change of crosslinking density in long-term storage time.

Figure 4 shows the long-term evolution of thermomechanical properties of EMSP 150. It exhibited three similar regions like ESMP 100, which were 0–1 month, 1–5 months, and after

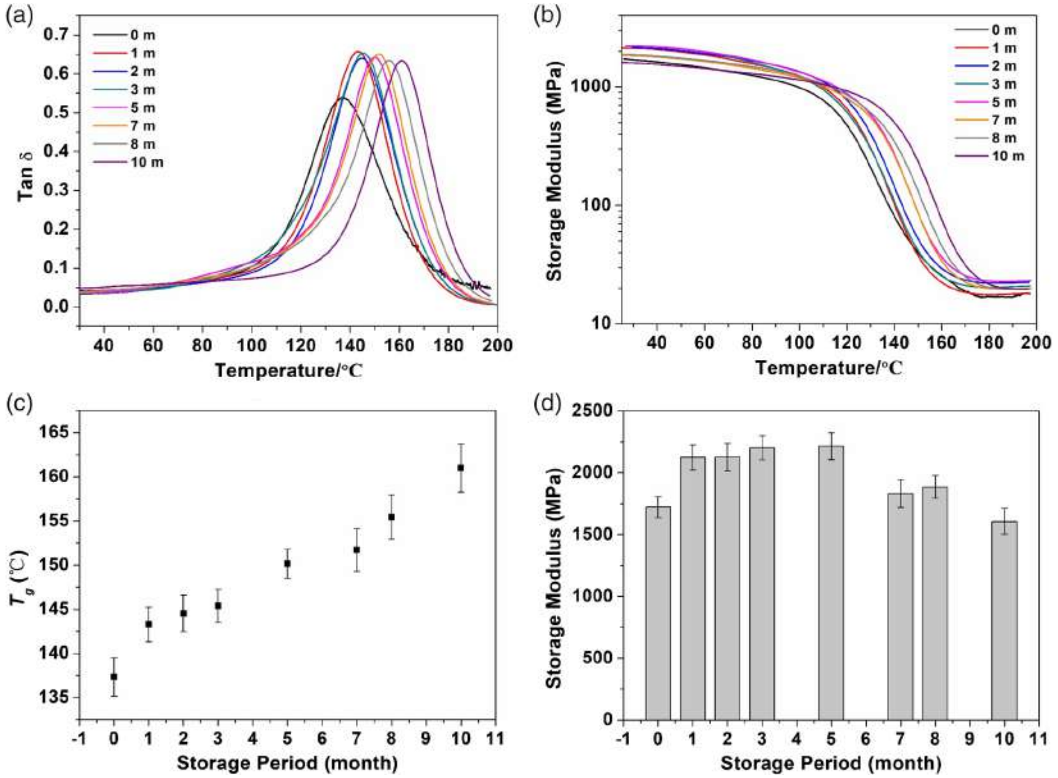

Figure 4. Long-term thermomechanical properties of ESMP 150. a) DMA curve of tan δ; b) DMA curve of storage modulus; c) T_g variation; and d) storage modulus versus storage period.

5 months. The T_g and storage modulus increased by ≈6.0 °C and 23%, respectively, in the first period, reflecting the reacted groups that started to form crosslinking networks. Until 5 months, both the T_g and storage modulus showed a steady growth, whereas the storage modulus had an inflection point at 5 months.

ESMP 170 also had similar characteristic in long-term storage, as shown in **Figure 5**. In the first month, the T_g and storage modulus saw an evident increase of around 7.4 °C and 20.6%, respectively. In the next two stages, although the T_g rose up, the growth rate was not as large as ESMP 100 and 150. This was because the ESMP 170 itself already had a higher crosslinking density compared with the ESMP 100 and 150. Thus, during long-term storage, the room for growth of ESMP 170 was not that high. The afore mentioned thermal results reflected that the higher the crosslinking density that already existed in ESMP, the smaller the increment of T_g and storage modulus after long-term storage.

From the results of T_g variation, it was clear that ESMP 170 had higher crosslinking density than ESMP 150 and 100. This is also verified by Fourier transform infrared spectroscopy (FTIR) spectrum, as shown in Figure S1 (Supporting Information). ESMP 100 had a stronger absorption peak of the epoxy group at 910 cm^{-1} because of the more addition of the linear epoxy monomer in its component. All the ESMPs exhibited a characteristic peak at 1080 cm^{-1}, which corresponded to C–O stretching. The long-term monitoring of chemical structures of ESMP is shown in Figure S2-4, Supporting Information. We found no evident change of characteristic peaks, indicating that the ESMP had long-term chemical stability.

The crosslinking density of cured ESMP could be calculated from Equation (1) to (2) based on the rubber's state and the detailed calculation is as follows.[25]

$$E = \frac{3\rho RT}{M_c} \tag{1}$$

E: storage modulus at 20 °C above extrapolated temperature when storage modulus decreases gently, ρ: polymer density, R: gas constant, T: absolute temperature, and M_c: average molecular weight among crosslinking points.

$$\frac{E}{3RT} = \frac{\rho}{M_c} = \frac{m}{VM_c} = \frac{M_c N}{VM_c} = \frac{N}{V} \tag{2}$$

m: polymer mass of every unit volume, N: crosslinking density, and V: unit volume.

Take ESMP 150 as an example to calculate the crosslinking density at different storage months. The initial crosslinking density was 1.51×10^{-3} mol cm^{-3} and then increased to 1.58×10^{-3} mol cm^{-3} at 1 month. It showed the highest value of 2.02×10^{-3} mol cm^{-3} at 5 months and then decreased to 1.69×10^{-3} mol cm^{-3} at 10 months. It reflected that the crosslinking density increased in both the first (0–1 month) and second (1–5 months) stage of storage and then decreased at the final stage (more than 5 months). In addition, the crosslinked structure was uniform according to the DMA results of ESMP.

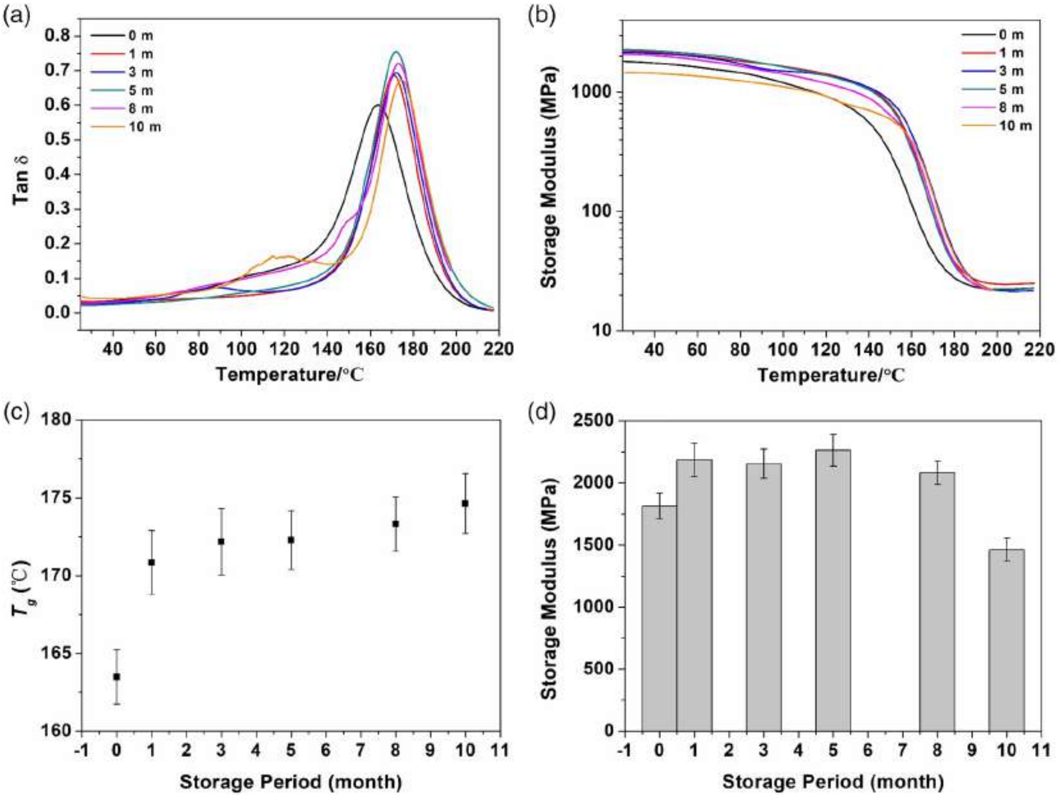

Figure 5. Long-term thermomechanical properties of ESMP 170. a) DMA curve of tan δ; b) DMA curve of storage modulus; c) T_g variation; and d) storage modulus versus storage period.

To investigate the influence of long-term low-temperature storage on mechanical properties, tensile tests were conducted on the ESMP at RT. **Figure 6** shows the stress–strain curves and representative static mechanical properties. It was obvious that ESMP 100 with a relatively lower crosslinking density exhibited lower Young's modulus and tensile strength, but higher elongation at break, whereas ESMP 150 and 170 showed brittle fracture. This was due to the higher content of the linear epoxy monomer that existed in ESMP 100, thus increasing the toughness. For the respective ESMP, the tensile strength and Young's modulus increased until 5 months, in a consistent manner with the variation of storage modulus. This also confirmed from another angle that during the initial storage, the epoxy monomer and hardener gradually reacted and formed crosslinking networks, which has also been proved by the calculated crosslinking density mentioned earlier. This result of the highest crosslinking density at 5 months was consistent with the highest values of T_g, storage, and Young's moduli also at 5 months. This could be explained by the theory of slow curing of oligomers and prepolymers for long-term storage, as reported by Chen et al.[40] and Fernández-Francos et al.[41] When stored at a relatively low or frozen temperature in a refrigerator, the epoxy monomer and hardeners would still react from each other because of the existence of the functional group, although the reaction extent was much lower than at room or higher temperature. This reflected that the crosslinking density increased with storage time in the first few storage periods, reached the best in some middle time point, and finally deteriorated for longer time. This deterioration at longer time was because there was pot life or shelf life of the epoxy mixture, which has already been reported by Chen et al.[40] in similar storage experiments.

Thus, it deteriorated mechanical properties in this period. However, we could see during the whole long-term storage that ESMP generally exhibited stable and even better static mechanical properties during the first few months. Interestingly, the relationship between increment of mechanical properties and storage period as the crosslinking density varied could be inversely speculated. This stability and excellent mechanical properties were promising for ESMP to be applied in engineering applications.

Due to better ductility of ESMP 100, we chose it to quantitatively analyze the shape memory properties in several shape memory cycles. The detailed shape memory curves in five cycles are shown in **Figure 7**a–e, at a storage time of 0, 2, 4, 5, and 7 months. We calculated the shape memory properties, that is, R_f and R_r by Equation 3–4, and the results are shown in **Table 1**. All the values of R_f and R_r were close to 90% and 100%, respectively. We calculated the average R_f and R_r in the five cycles and compared them between different storage times, as shown in Figure 7f. After storage for 7 months, R_f and R_r decreased by only 2 and less than 1%, respectively, which was a negligible change. We measured the recovered strain and shape recovery time in the reheating process and calculated the ratio of these two values which was denoted as shape recovery speed. The average shape recovery speed was 7.38×10^{-2}, 7.43×10^{-2}, and $5.88 \times 10^{-2}\%\ \mathrm{min}^{-1}$. This reflected that in the 5 months, the

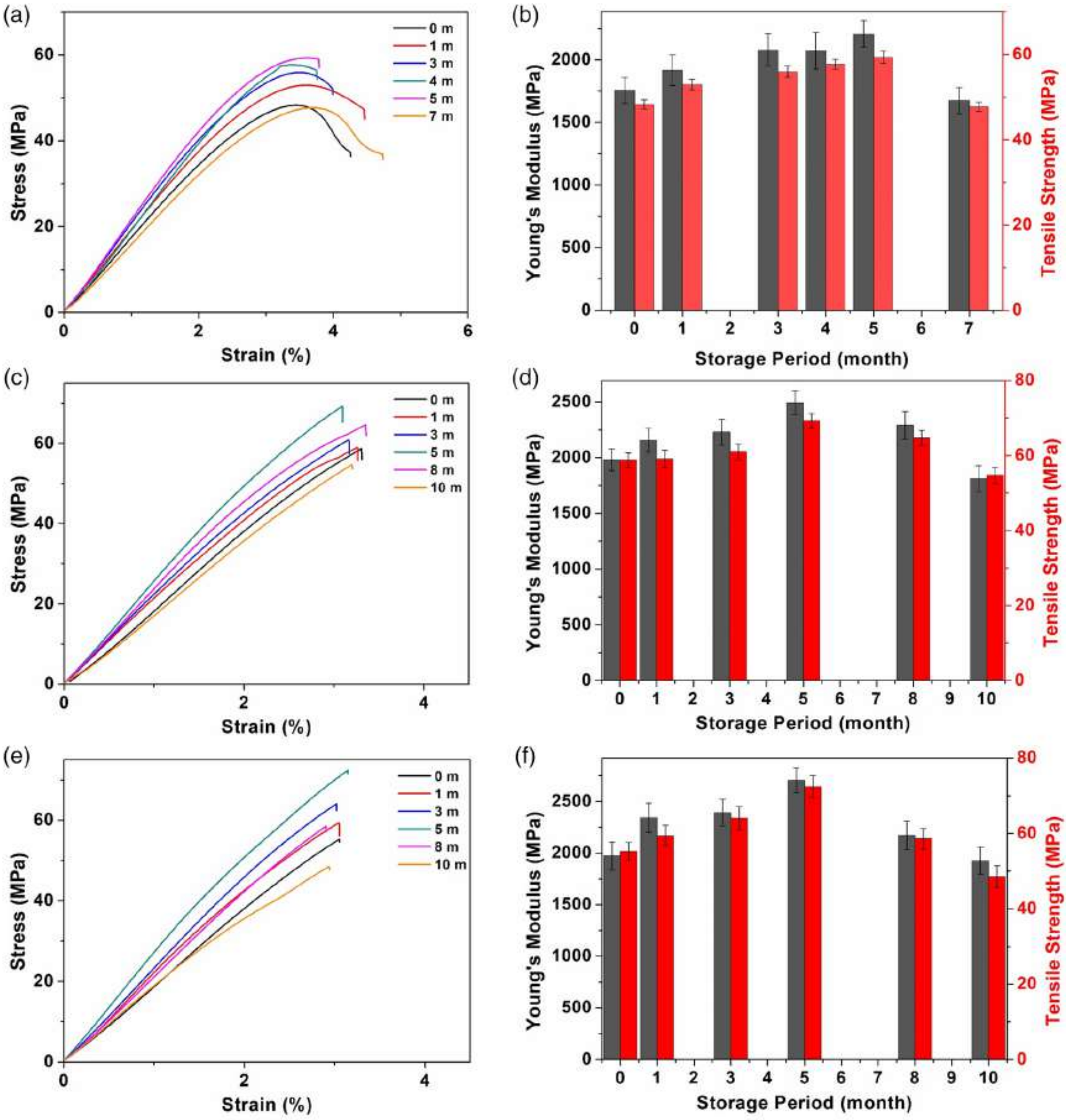

Figure 6. Long-term static mechanical properties of ESMP. Stress–strain curve and variation of tensile properties of a–b) ESMP 100; c–d) ESMP 150; and e–f) ESMP 170.

long-term storage did not have an obvious effect on shape recovery speed. The slightly decreased shape recovery speed only occurred at a longer storage time of 7 months, where the other performances also deteriorated. It reflected that the shape memory properties were excellent even in the fifth shape cycle after storage for long term that exhibited promise as deployable structures. We visually demonstrated the qualitative shape recovery performance of ESMP 150 stored in 7 months. We endowed the sample with a temporary shape with bending curvature and it completed full shape recovery within 17 s at 160 °C, as shown in **Figure 8**a. The calculated shape recovery ratio based on shape recovery angle is shown in Figure 8b, which revealed that it had excellent shape memory properties after the long-term storage period.

3. Conclusion

In this article, the influence of long-term storage of ESMP prepolymers at low temperature on overall properties was investigated systematically. A series of ESMP with T_g ranging from 100 to 170 °C was taken out from their preolymer state and cured at specific storage time. The viscosity of ESMP increased remarkably, which reflected that the epoxy mixture gradually formed crosslinking networks with the increase in storage time. We analyzed that the improvement in thermal, thermomechanical, and static mechanical properties in a storage period of 5 months is attributed to the increase in crosslinking density. The stable chemical structures were characterized by the FTIR spectrum during the whole storage period, proving very stable

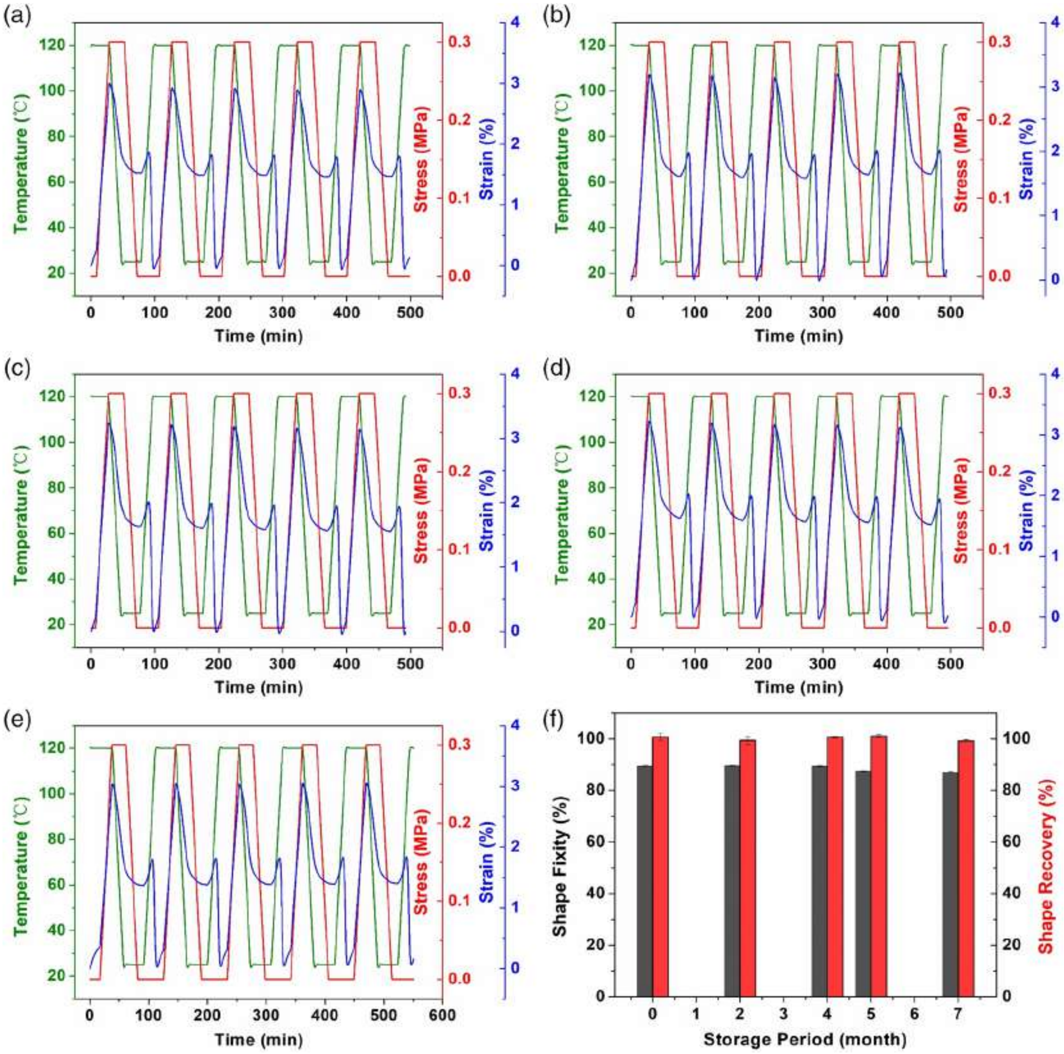

Figure 7. Long-term shape memory cycles of ESMP 100 in storage times of a) 0 m; b) 2 m; c) 4 m; d) 5 m; and e) 7 m. f) Variation of shape memory properties versus storage period.

Table 1. Shape memory properties of ESMP 100 during long-term storage.

Storage period (month)	Shape memory properties [%]									
	First cycle		Second cycle		Third cycle		Fourth cycle		Fifth cycle	
	R_{f1}	R_{r1}	R_{f2}	R_{r2}	R_{f3}	R_{r3}	R_{f4}	R_{r4}	R_{f5}	R_{r5}
0	89.4	100.0	89.5	99.2	89.5	100.0	89.4	100.0	89.4	99.5
2	89.3	99.5	89.6	100.0	89.5	100.0	89.5	96.6	89.5	99.4
4	89.0	100.0	89.5	100.0	89.5	100.0	89.7	100.0	89.6	100.0
5	87.6	100.0	87.6	100.0	87.7	100.0	87.4	100.0	87.2	100.0
7	86.4	98.6	86.7	99.4	87.2	99.6	87.3	99.4	87.5	99.1

compositions for long term and large batch use. This research proved the stability of ESMP prepolymer in long-term storage at low temperature. More importantly, ESMP stored in 10 months possessed almost undiminished shape memory properties and excellent repeatability in five continuous shape memory cycles. This epoxy system containing all formulated components is of great significance for fields requiring high production efficiency, such as deployable space structures, semiconductors, and electronic packaging. Although we focused on ESMP, such a feasible method will also apply to other types of materials and their prepolymers with characteristics of forming crosslinking networks in the low-temperature storage environment.

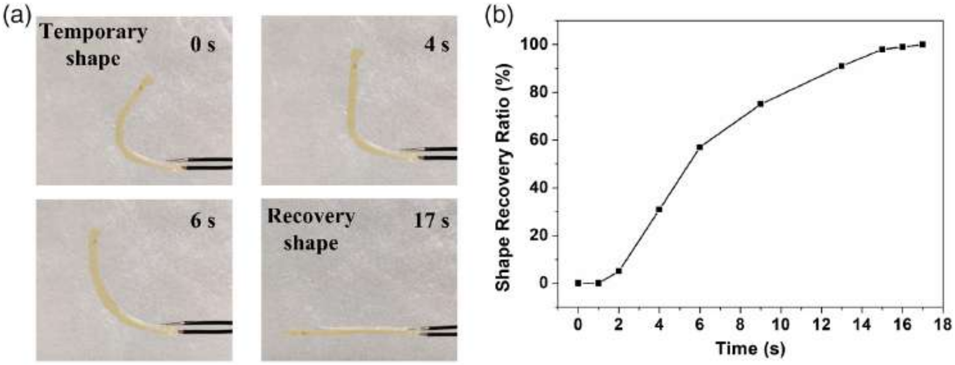

Figure 8. Macroscopic shape memory characterization of ESMP 150 with storage time of 7 m: a) visual demonstration within 17 s at 160 °C and b) shape recovery ratio versus time.

4. Experimental Section

Sample Preparation: A series of ESMP with a T_g ranging from 100 to 170 °C were prepared according to our previous studies.[33] The T_gs of ESMPs were tuned by the weight ratio of monomers, which reflected different crosslinking densities. The liquid ingredients were mixed thoroughly at RT and then stored in a refrigerator at −18 °C for about 10 months. The nomination of ESMP 100, ESMP 150, and ESMP 170 represented T_gs at ≈100, 150, and 170 °C, respectively. The stored ESMP was taken out from the refrigerator at a set of intervals and mixed through mechanical stirring for 10 min at RT. Then, it was degassed in a vacuum oven to remove bubbles. Next, it was poured into a mould with a thickness of 2 mm followed by thermal curing. Finally, the sample was demolded and cut into required pieces by a laser cutting machine for further characterization.

Rheological Test: All ESMPs were degassed in vacuum to remove bubbles prior to the rheological test. A DHR-2 rheometer (TA Instruments) with parallel-plate geometry was used for tests at 25 °C. Viscosity tests were conducted over shear rates ranging from 0.01 to 100 s^{-1}. The independence of viscosity on temperature was evaluated in a temperature range from 20 to 50 °C at a shear rate of 10 s^{-1}.

Thermal Test: The thermomechanical properties were determined by DMA using Q800 (TA instrument) under the film tension mode. The sample was heated at a rate of 5 °Cmin^{-1} and the frequency was set at 1 Hz.

Static Mechanical Test: The static mechanical property was characterized using a universal Zwick machine under tensional mode. Dog bone-shaped samples were cut into regular sizes according to ASTM D638. The samples were tested at a speed of 3 mm min^{-1} at RT.

Shape Memory Test: The shape memory properties were characterized by shape memory cycles using Q800, in a force-controlled mode.[2] A preload of 0.01 N was applied to avoid slippage. The test was programmed as follows. First, the sample was kept thermally balanced at T_d (deformation temperature above T_g) for 10 min to acquire the initial strain (ε_0). Then, the sample was stretched at a constant speed. Next, the sample was cooled to RT and the deformed strain was obtained (ε_d). Then, the stress was released, the fixed strain as ε_f was recorded, and kept isothermally for 5 min. Finally, the sample was reheated to T_d and kept isothermally for shape recovery. The recovered strain was recorded as ε_r. The shape fixity ratio (R_f) and shape recovery ratio (R_r) were calculated by the following equations.[22,42]

$$R_f(\%) = \frac{\varepsilon_f}{\varepsilon_d} \times 100\% \quad (3)$$

$$R_r(\%) = \frac{\varepsilon_d - \varepsilon_r}{\varepsilon_d - \varepsilon_o} \times 100\% \quad (4)$$

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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