

Effect of a linear monomer on the thermomechanical properties of epoxy shape-memory polymer

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Abstract

The effect of a linear monomer on thermomechanical properties and shape recovery behavior of an epoxy shape-memory polymer is studied. These shape-memory polymers are prepared from epoxy base resin, hardener and linear epoxy monomer. As the content of the linear monomer increases, the glass transition temperature (T_g) determined using differential scanning calorimetry ranges from 37 to 96 °C. A decrease in rubber modulus is seen from dynamic mechanical analysis for the polymers, which reveals decreasing crosslink density with increasing linear monomer content. Tensile test results show that the elongation at break and strength depends on the content of linear monomer at T_g or $T_g - 20$ °C, while the linear monomer content has minor influence on elongation at break and strength at $T_g + 20$ °C. Finally, investigation on shape recovery behavior reveals that full recovery can be observed for each polymer when the temperature is equal to or above T_g . Also, increasing the linear monomer content results in a decrease in both shape recovery ratio (below T_g) and shape recovery speed (at T_g). These results are interpreted in terms of various crosslink densities attributed to the increasing linear monomer content.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

As a novel class of smart materials, shape-memory polymers (SMPs) are stimuli-responsive materials, which have the capability of recovering their original shape upon application of external stimulus [1]. The molecular structure of an SMP network includes two components—hard segment and soft segment. The hard segment is responsible for the permanent shape with a higher glass transition temperature (T_g) or melting temperature (T_m), while the soft segment enables the fixation of the temporary shape with a lower T_g or T_m . During the shape-memory cycle, the hard segment remains hard and provides the polymer with the shape-memorizing capability, while the soft segment softens upon heating above T_g or hardens on cooling below T_g and provides the elastic recovery properties of the polymers [2, 3].

One of the most common stimuli for SMP materials is temperature, and heating of the sample can be achieved

using water [4, 5], solution [6, 7], infrared radiation [8], electric current [9, 10] or magnetic fields [11]. SMP have been proposed for various applications, such as heat-shrinking films or tubing [12], sensors [13], actuators [14], medical and biological equipment [15, 16]. The broad range of applications needs a diverse set of polymer properties. This thus requires systematic studies to relate the structural changes with specific property needs.

Shape-memory behavior can be observed in several polymers, including polyurethane-based polymers [17–19], styrene-based polymers [9, 10, 20], epoxy-based polymers [21, 22] and others. Out of these SMP, thermoset epoxy SMP possesses unique thermomechanical properties together with an excellent shape-memory effect. Such materials have great potential applications in the field of smart structures. Furthermore, epoxy resin is a good candidate material for further study because its formulation could be adjusted to vary its properties to meet specific needs. Controlling macroscopic

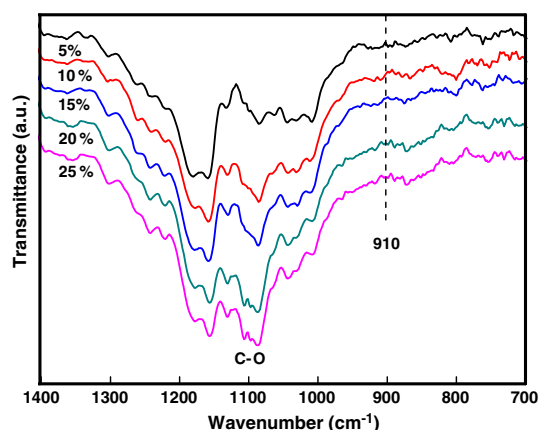


Figure 1. FT-IR spectra of the epoxy shape-memory polymers.

properties through the variation of network parameters plays an important role in investigation of SMP. Kim studied the effect of soft/hard segment phase separation and soft segment crystallization on the shape-memory property in polyurethane SMP [23]. Hu discussed how the molecular weight of the polymer network influences the shape-memory effect in polyurethane shape-memory films [19]. Studies have also been performed on the relation of network structure and shape recovery in a co-polymer of methyl methacrylate and poly(ethyleneglycol) dimethacrylate [24]. However, little work has been done to investigate the systematic tailoring of thermomechanical performances for SMP. Consequently, this study aims to construct the relationship between network structure and thermomechanical properties in an epoxy-based SMP material to help in the design of specific applications for shape-memory polymer materials.

2. Experimental details

The polymer matrix consists of an epoxy base resin and hardener, mixed in a ratio of 100 g resin to 100 g hardener. An active linear epoxy monomer is co-polymerized with the polymer matrix to adjust its molecular structure. The detailed chemical composition of the SMP matrix is proprietary to our lab, although the structure is known to be a thermoset crosslinked network. Additionally, it is known that the linear monomer is composed of a long linear chain of C–O bonds. The epoxy base resin and the linear monomer have an epoxy group number ratio of 1:1 in one molecule, a molecular weight ratio of 2:5 and a density ratio of 1:1. A linear monomer content of 5, 10, 15, 20 and 25 wt% was used. The pre-polymer mixture was degassed in a vacuum oven at 50 °C to obtain a bubble-free pre-polymer. The pre-polymer solution was then injected into a mold composed of two glass slides separated by a silica gel rod spacer with a thickness of 3 mm. Glass slides were cleaned with alcohol. A three-step thermal cure process was performed for the pre-polymer at 80 °C for 3 h, 130 °C for 3 h and then 150 °C for 5 h.

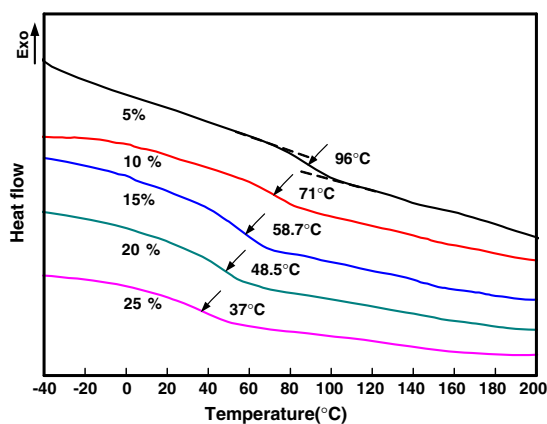


Figure 2. DSC curves of the epoxy shape-memory polymers.

3. Results and discussions

3.1. FT-IR study

The difference in structure of the networks was investigated using an FT-IR spectrometer (Nicolet Magna IR-560) in a reflection mode from 4000 to 400 cm^{-1} . The FT-IR spectrum of the epoxy SMP polymers from 700 to 1400 cm^{-1} is shown in figure 1.

Firstly, it should be noted that there is no absorption for each polymer at 910 cm^{-1} which corresponds to the characteristic absorption of the epoxy group. This clearly indicates that the linear monomer enters the polymer matrix network structure via chemical reaction of its epoxy groups. In addition, all polymers show absorptions at 1154 and 1090 cm^{-1} which are assigned to the C–O stretching. A close look at the figure reveals that the absorptions of C–O bonds become stronger with increasing linear monomer content in the polymer network. The outstanding structural characteristic of the added epoxy monomer lies in the long linear structure composed of C–O bonds. Both of these epoxy groups at chain ends of the linear monomer are linked to the hard segments of the matrix polymer network during the curing process, which contributes to an increased molar ratio of the C–O group in the co-polymer network. Therefore, the incorporated linear monomer results in an increase of C–O bonds in the whole network. Further support for this connection in the polymer network has been provided by thermal and mechanical tests as discussed in the following.

3.2. Thermal analysis

The glass transition is the essential transition from freezing to free motion states of segments in a polymer network, which is revealed by T_g . T_g is one of the major characteristic parameters of thermomechanical deformation and shape recovery in SMP materials. In this study, thermal properties of the polymers were characterized using differential scanning calorimetry (DSC, Netzsch204, Germany) from -40 to 200 °C with a heating/cooling rate of 10 °C min^{-1} .

Figure 2 shows the DSC thermograms of the polymers with the T_g being marked. As shown in the figure, T_g is 96,

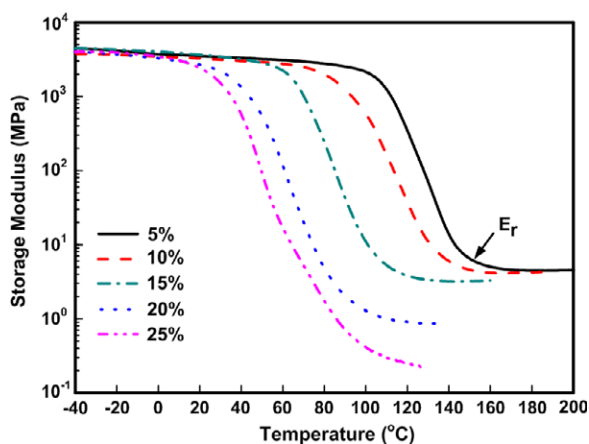


Figure 3. Storage modulus of the epoxy shape-memory polymers as a function of temperature.

71, 58.7, 48.5 and 37 °C for samples with a linear monomer content of 5, 10, 15, 20 and 25 wt%, respectively. The above results reveal that T_g decreases as the monomer content increases. Furthermore, this is a demonstration that T_g of the polymer can be altered by controlling the amount of linear monomer content in weight fraction.

In a thermoset SMP network, chemical crosslink points are linked by flexible segments, and the crosslink points and flexible segments act as hard segment and soft segment, respectively. The molecular structural characteristic of the linear monomer is a long molecular chain consisting of C–O bonds, which makes the linear monomer act as soft segment in the epoxy SMP network. Therefore, with increasing linear monomer content, the average molecule weight between crosslink points increases, which results in the decreasing crosslink density of the network. The deduction, that increasing linear monomer content leads to decreasing crosslink density, will be demonstrated further by the following result of the DMA test. Thus, on increasing linear monomer, the crosslink points are far more linked together with higher flexible segment mobility and resulting in a decrease in T_g . Previous work has shown that the crosslink density of networks was highly influential on T_g , which depends on the flexibility of segments in the polymer network [25]. Therefore, the increase of the linear monomer content leads to the increasing of the flexibility of networks, and therefore a decrease of T_g .

3.3. Dynamic mechanical analysis (DMA)

DMA is a key technique to reveal the change of molecular motion for SMPs, which contacts the macro-performance with the structure tightly at the molecular level. The DMA test was performed on a DMA Q800 (NETZSCH DMA 242) in a tension mold from -40 to 200 °C at a rate of 5 °C min^{-1} with a constant frequency of 5 Hz, using rectangular samples with dimensions of $30 \times 5 \times 1$ mm³. Figure 3 presents the storage modulus as a function of temperature obtained from the DMA test.

For a good shape-memory material, a large and sharp drop in the storage modulus around the glass transition is most

Table 1. Rubber modulus and corresponding crosslink density obtained from DMA.

Polymers with linear monomer content (wt%)	E_r (MPa)	N (nm ⁻³)
5	7.88	0.454 458
10	6.39	0.389 842
15	4.80	0.361 054
20	1.61	0.145 025
25	1.06	0.106 215

important, which can be seen from figure 3 since the modulus systematically decreases with increasing soft segment content by almost 2–3 orders of magnitude, whereas the elastic ratio, which is defined as the glass/rubber modulus ratio, is often quoted to estimate the magnitude of the change in modulus as the polymer undergoes shape recovery. Figure 3 shows that no considerable change in glass modulus is observed while the rubber modulus decreases for the polymers as the linear monomer content increases from 5 to 25 wt%. It is obvious that the increasing linear monomer leads to the decreasing rubber modulus and results in an increase in elastic ratio. The decrease in rubber modulus contributes to the increasing spacing between the crosslinking net points with increasing linear monomer content, corresponding to a lower steric hindrance and resulting in a drop in rubbery modulus [1]. A large elastic ratio is beneficial for showing good shape-memory capability since it gives larger shape fixity upon cooling and realizes a larger strain with a small stress at high temperature [23].

It should be noted that the rubber modulus is an important characteristic parameter of the crosslinking density of the networks [25]. The rubber modulus obtained from DMA can give a quantitative estimate of crosslink density for these polymer networks based on their assumption of the uniform three-dimensional crosslink distribution [26]. The theory of rubbery elasticity relates temperature, rubber modulus and average crosslink density (N) through $N = E_r/3kT$, where k is Boltzmann's constant and T is the temperature corresponding to E_r [23]. The estimated crosslink density of the networks can be seen in table 1. As expected, crosslink density decreases with decreasing rubber modulus attributed to the increasing linear monomer content. This result is consistent with previous studies [24].

In addition, as shown in figure 3, the glass and rubbery region extend shorter respectively with increasing linear monomer content, which can be explained by decreasing crosslink density and corresponding insufficient reinforcing effects of hard segments. Large and longer glass and rubbery moduli are desired for structural material in the sense that it keeps the resistance to low temperature deformation large and load-bearing capacity while showing shape-memory effect at higher temperature.

3.4. Static tension test

An isothermal quasi-static tension test was carried out on a Zwick Z010 (Zwick GmbH, Ulm, Germany) equipped with a

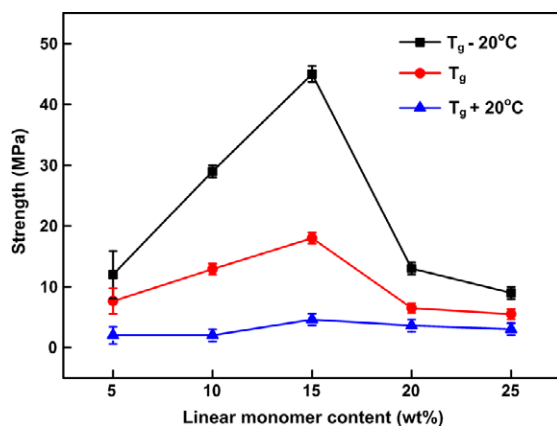


Figure 4. Relationships between strength and linear monomer content at different temperatures.

thermal chamber. Samples were cut by laser from polymer sheets 2 mm in thickness according to the size of standard samples (ASTM D638, Type IV). The tensile speed was 10 mm min^{-1} . In order to remove the temperature effect on the mechanical properties, the testing temperatures were set at $T_g - 20^\circ\text{C}$, T_g and $T_g + 20^\circ\text{C}$ for each polymer, respectively, which ensures all networks are in an equivalent state of macromolecular motion.

To investigate the effect of the linear monomer on the mechanical behaviors, strength and elongation at break (ϵ_B) of the polymers at different temperatures are summarized in figures 4 and 5, respectively. Figure 4 shows the tensile strength increases and then decreases with the increasing linear monomer content at T_g or $T_g - 20^\circ\text{C}$, showing a peak value for the polymer with 15 wt% linear monomer content. While at $T_g + 20^\circ\text{C}$, no considerable change can be found in strength with increasing linear monomer content. As shown in figure 5, with increasing linear monomer content, ϵ_B increases at T_g or $T_g - 20^\circ\text{C}$ while ϵ_B shows a similar value at $T_g + 20^\circ\text{C}$. ϵ_B reveals ductility of the polymers. It is obvious that the polymer networks show a broad range of mechanical properties ranging from a small-strain response to a large-strain response when temperature is below or equal to T_g . Further, it should be noted that ductility changes as a function of T_g of the polymers, and the polymer with a lower T_g value shows a higher ductility.

From the DMA test, the increasing linear monomer content lowers the crosslink density of the polymer network, which is the primary affected factor for the variety of mechanical properties of the polymers. Since crosslink points are totally responsible for carrying the load, the decrease in tensile strength is expected on decreasing crosslink density. However, in this study, tensile strength increases with increasing linear monomer content from 5 to 15 wt%, which can be attributed to the relatively high crosslink density of the network. The excessively higher crosslink density of the network leads to the higher brittle property, which may limit the capability of the carrying load and result in the lower tensile strength. The same trend of tensile strength with increasing monomer content was found in other polymers [27]. Further, the molecular chain between crosslink points determines the

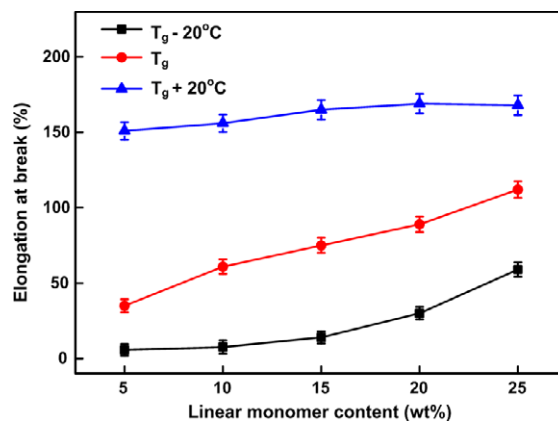


Figure 5. Relationships between ϵ_B and linear monomer content at different temperatures.

ductility of the polymer which is revealed by ϵ_B . Then, an increase in ϵ_B with increasing linear monomer content can be attributed to the inherent high flexibility of the linear monomer. When the temperature is below T_g , most movements of segments in the polymer network are frozen, while an increase in temperature above T_g favors higher segment mobility. When temperature rises from below T_g to above T_g , the flexible segments exercise easily in each polymer especially. This may lead to the effect of linear monomer content on ϵ_B and strength being minor.

Prior work had demonstrated that, as the crosslink density decreases, ϵ_B increases but with a sacrifice of lower strength [28]. However, in this study, the selected linear monomer results in an increase in both strength and ϵ_B when its content varies from 5 to 15 wt% when temperature is below or equal to T_g . Our results suggest that the mechanical properties of the epoxy SMP system can be optimized through molecular network structure to meet the required use of different potential applications.

3.5. Shape-memory behaviors

Samples for shape-memory behaviors were cut by laser from the thin polymer sheets as a rectangular strip (about $30 \times 10 \times 1 \text{ mm}^3$), referred to as the permanent shape. The straight bar-shaped samples were heated up to $T_g + 20^\circ\text{C}$ in an oven and held for 20 min for full heating. Then, samples became elastic and were bent into a 'U' shape around a mandrel with a radius of 2 mm at a bending rate of 10° s^{-1} . The measurement of bend angle is similar to that of shape recovery angle in the following. The bent samples fixed on the mandrel were subsequently cooled to 0°C at a rate of $10^\circ\text{C min}^{-1}$, and then held for 20 min to ensure the samples released from the mandrel retaining the U shape. To study the shape recovery behaviors, each bent sample cooled at 0°C was put in an oven at a certain temperature, and the temperature was set at $T_g - 20^\circ\text{C}$, $T_g - 10^\circ\text{C}$, T_g , $T_g + 10^\circ\text{C}$ and $T_g + 20^\circ\text{C}$ for the polymer. Thereby, with the temperature being held constant at T_g , it is more convenient to supply straight information about the effect of linear monomer content on shape-memory behaviors for the polymers. The shape recovery process of the

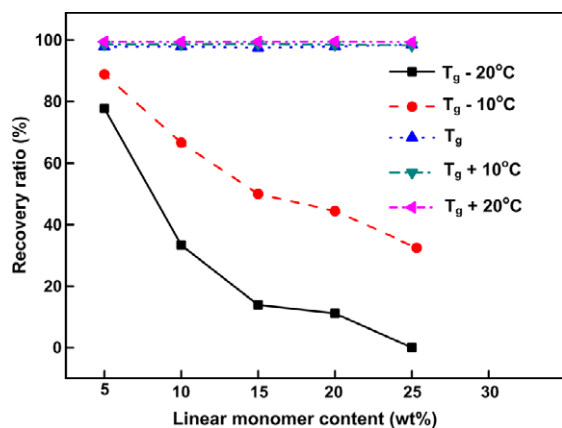


Figure 6. Shape recovery ratio versus linear monomer content at different temperatures.

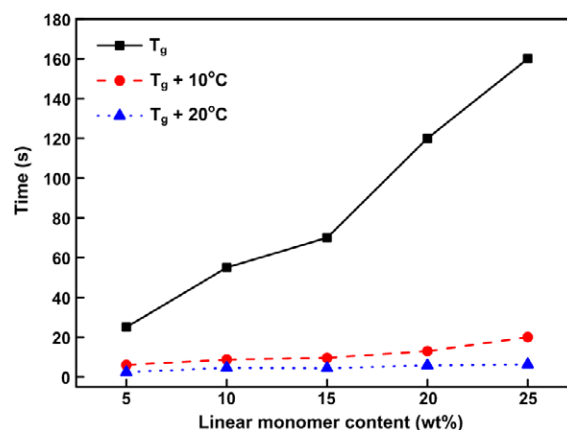


Figure 7. Time for full recovery versus linear monomer content relation at different temperatures.

bent samples was recorded by a video cassette recorder. Shape recovery angle is determined by measuring the angle between the straight ends of the bent specimen [29, 30].

Shape recovery ratio is obtained through calculating the ratio of shape recovery angle to 180° . In addition, shape recovery speed is evaluated by the time of full recovery. Figure 6 shows the shape recovery ratio versus linear monomer content for different active temperatures. As shown in the figure, the full recovery (near 100%) is observed at higher temperatures, e.g. T_g , $T_g + 10^\circ\text{C}$, $T_g + 20^\circ\text{C}$. But at temperatures lower than T_g ($T_g - 20^\circ\text{C}$ and $T_g - 10^\circ\text{C}$), the shape recovery ratio decreases with increasing linear monomer content. Shape recovery ratio represents the maximum recoverable strain. When temperature is below T_g , the maximum recoverable strain decreases with the increasing linear monomer content, while the linear monomer content has no influence on the maximum recoverable strain as the temperature is equal to or above T_g .

Figure 7 shows the time of full recovery of each polymer at temperatures of T_g , $T_g + 10^\circ\text{C}$ and $T_g + 20^\circ\text{C}$. As shown in the figure, full recovery time increases with increasing linear monomer content at T_g for each polymer. While, as the temperature is at $T_g + 10^\circ\text{C}$ or $T_g + 20^\circ\text{C}$, full recovery time keeps a stable value on increasing linear monomer content. Time for full recovery reveals the shape recovery speed. Furthermore, the increasing linear monomer content decreases shape recovery speed at T_g , while the various linear monomer content has a minor effect on shape recovery speed as the temperature is above T_g .

In the present epoxy SMP, the flexible macromolecule segments entangle together randomly before deformation, which is higher in entropy. After pre-deformation (heating, bending and cooling), the entangled molecular chain of SMP is in an orderly arrangement, which is a metastable structure with low entropy. Then, the strain energy is stored by the constraining effect of the crosslink points on segments, which are frozen in the bent shape by the transitory molecular interactions. Upon subsequent heating, the stored internal energy was released in the form of recovery force and the low entropy state drives individual chains toward their initial

state, facilitating shape memory [26]. The increasing linear monomer content in the network leads to a loose connection of net points by segments which results in a lower constraint effect of the crosslink points on segments and then the decreasing recovery force. The decreasing recovery force leads to a decrease in both shape recovery ratio (below T_g) and shape recovery speed (at T_g). T_g is a crucial parameter for the transition of segments from the frozen state (below T_g) to the mobility state (above T_g) for a polymer. The higher segment mobility above T_g 'releases' the stored strain energy more easily and completely than that below T_g . This may lead to no considerable change in both the shape recovery ratio and shape recovery speed above T_g . A particular benefit of the epoxy SMPs is their controllable activation temperature range that is linked to T_g which can be manipulated by changing the composition of the co-polymer.

4. Conclusions

A thermoset epoxy SMP system is prepared from epoxy base resin, hardener and linear epoxy monomer. The tailored thermomechanical properties together with adjusted shape-memory behaviors are systematically studied in this paper. With increasing linear monomer content, a decrease in T_g and an increase in elastic ratio can be observed for the polymers from DSC and DMA studies, respectively, as the increasing linear monomer leads to crosslink density decreasing for the polymers.

From tensile tests, the content of the linear monomer determines the elongation at break and strength, respectively, at T_g or $T_g - 20^\circ\text{C}$ but shows minor influence on elongation at break and strength at $T_g + 20^\circ\text{C}$. Finally, investigation on shape recovery behavior reveals each polymer shows a full recovery as temperature is equal to or above T_g , while increasing the linear monomer content results in a decrease in both shape recovery ratio (below T_g) and shape recovery speed (at T_g). Due to the adjusted thermomechanical properties and shape recovery behavior, the epoxy polymer is intended to be a possible shape-memory structural material.

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