Shape memory polymers from benzoxazine-modified epoxy

Sarawut Rimdusit¹, Montha Lohwerathama¹, Kasinee Hemvichian², Pornnapa Kasemsiri³ and Isala Dueramæ¹

¹ Polymer Engineering Laboratory, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, 10330, Thailand
² Chemistry and Material Science Research Program, Office of Atoms for Peace, 16 Vibhavadi Rangsit Road, Chatuchak, Bangkok 10900, Thailand
³ Department of Chemical Engineering, Faculty of Engineering, Khon Kaen University, Khon Kaen, 40002, Thailand

E-mail: sarawut.r@chula.ac.th

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Abstract

Novel shape memory polymers (SMPs) were prepared from benzoxazine-modified epoxy resin. Specimens consisting of aromatic epoxy (E), aliphatic epoxy (N), Jeffamine D230 (D) and BA-a benzoxazine monomer (B) were evaluated. The mole ratio of D/B was used as a mixed curing agent for an epoxy system with a fixed E/N. The effects of BA-a content on the thermal, mechanical and shape memory properties of epoxy-based shape memory polymers (SMPs) were investigated by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), flexural test and shape recovery test. The results revealed that the obtained SMPs exhibited a higher flexural strength and flexural modulus than those of the unmodified epoxy-based SMP at room temperature and at 20°C above glass transition temperature (Tg). The presence of 1 mol BA-a as a curing agent provided the specimen with the highest Tg, i.e. about 72°C higher than that of epoxy-based SMP cured by Jeffamine D230. All SMP samples needed only a few minutes to fully recover to their original shape. The samples exhibited high shape fixity (98–99%) and shape recovery ratio (90–100%). In addition, the recovery stress values increased with increasing BA-a mole ratio from 20 to 38 kPa, when BA-a up to 1 mol ratio was added. All of the SMP samples exhibited only minimum change in their flexural strength at the end of a 100 recovery cycles test.

(Some figures may appear in colour only in the online journal)

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]. One of most common stimuli for SMP materials is temperature, and heating of the sample can be obtained using water [2], solution [3], infrared radiation [4] or electric current [5]. SMPs have been used in many applications including packaging, textiles, electronics, medication, transportation, construction, and aerospace due to their light weight, low cost, ease of processing, and great flexibility in terms of material design [1, 6, 7]. Recently, SMP-based epoxy was applied as a shape memory polymer composite actuator that had outstanding actuation properties [8]. The actuator could be used in various fields such as robotics, biomimetics and microsystems: in particular, spring actuators are the most widely used, due to their simplicity of fabrication [9].

Generally, thermostets are widely used as SMP materials because thermostet SMPs have chemical cross links, and can...
be softened but do not melt at elevated temperatures [10]. Thermoset resins are preferred to thermoplastics in some applications, i.e. spacecraft, due to their better mechanical performance and environmental endurance [11]. Epoxy resin is one of the most popular thermosets that has been used in structures and can be applied for extreme applications. Shape memory epoxies have attracted much attention from academic and industrial researchers because they possess excellent shape memory performance. They are commercially available and are comprised in the range of large deformations, low recovery stresses and low glass transition temperature [1].

Recently, Xie et al [12] developed methods to tailor the $T_g$ of epoxy SMPs. Starting with an amine cured aromatic epoxy system, the SMP samples were prepared by introducing flexible aliphatic epoxy chains. The authors also found that the $T_g$ of the epoxy SMPs ranged from room temperature to 89°C. However, shape memory epoxy polymers are not suitable for many practical applications that require more stringent characteristics such as high glass transition temperature, high strength, high stiffness and good shape recovery [13]. The ability to fine tune the glass transition temperature and the mechanical property of the SMPs is thus an important requirement to suit their particular applications. There are two major methods that are used to meet this requirement, i.e. chemical structure modification and blending with the other polymers or resins. The latter one is preferable due to ease of processing and tailored properties.

Benzoxazine resin is a newly developed class of thermosetting resin derived from ring-opening polymerization of its precursors. The polymer possesses various good properties such as high thermal stability and excellent mechanical properties, thus showing high potential in many applications. Polybenzoxazines have some reported outstanding properties such as high glass transition temperature, high thermal stability, low melt viscosity before cure resulting in high process ability, as well as low water absorption. Furthermore, polybenzoxazines possess excellent mechanical performance and wide molecular design flexibility [14–16]. The resin has also been reported to act as a curing agent of epoxy and to yield synergism in some properties of the resulting copolymers with epoxy [16, 17].

Consequently, the purpose of this study is to develop polybenzoxazine–epoxy-based SMPs with improved thermal stability and mechanical properties for use at elevated service temperature, and for greater load-bearing applications. Some essential properties, such as glass transition temperature, flexural modulus, flexural strength and shape recovery performance, are investigated.

2. Experimental details

2.1. Materials

The materials used in this research are benzoxazine resin (bisphenol-A-aniline type, BA-a), aromatic epoxy, aliphatic epoxy and diamine curing agent. BA-a type benzoxazine resin based on bisphenol-A, formaldehyde and aniline was synthesized according to the patented solventless technology [18]. The BA-a resin is a yellow clear solid at room temperature. Bisphenol-A (polycarbonate grade) was provided by Thai Polycarbonate Co., Ltd (TPCC). Para-formaldehyde (AR grade) was purchased from Merck Co., Inc. and aniline (AR grade) was obtained from Panreac Quimica S.A. Co. The diglycidyl ether of bisphenol-A epoxy monomer (EPON 826) and neopentyl diglycidyl ether (NGDE) were available from Aditya Birla Chemicals (Thailand) Ltd. The epoxy curing agent, poly-(propylene glycol)bis(2-aminopropyl) ether (Jeffamine D230), was purchased from Sigma-Aldrich Co. All chemicals were used as received. The chemical structures of the epoxy components and the BA-a are shown in figure 1.

2.2. Resin preparation

The BA-a monomer was mixed with aromatic epoxy (EPON 826), aliphatic epoxy (NGDE) and the curing agent (Jeffamine D230) to provide epoxy-based SMP at various molar ratios of BA-a:D230 as listed in table 1. The mixture was heated at 70°C in an aluminum pan for about 10 min to yield a homogeneous mixture. The molten resin was then poured into an aluminum mold and was thermally cured in an oven. The fully cured specimens were then cut into various shapes for each specific test.

In the nomenclature of the mixtures, the notations E, N, D and B stand for EPON 826, NGDE, Jeffamine D230 and BA-a, respectively. The digits after the notation give the molar ratio of the monomer in the same order, i.e. ENDB 1/1/0/1 represents EPON 826, NGDE, Jeffamine D230 and BA-a mixture with the molar ratio of 1:1:0:1, respectively.

2.3. Sample characterizations

A dynamic mechanical analyzer (NETZSCH, model DMA 242) was used to obtain the storage modulus ($E'$), loss modulus ($E''$) and loss tangent (tan $\delta$) of the polymeric specimens. The specimen, with dimensions of 10 mm $\times$ 50 mm $\times$ 3 mm, was tested using a three-point bending mode at a frequency of 1 Hz and heating rate of 2°C min$^{-1}$ from 0 to 250°C. The crosslink density of the obtained polymer network was calculated from the storage modulus ($E'$) at a rubbery plateau and the glass transition temperature ($T_g$) was taken as the maximum point on the loss modulus curve.

To investigate the effect of the BA-a resin on the flexural strength and flexural modulus of the polymers at room
temperature and 20 °C above $T_g$ based on ISO178:2001, a universal testing machine (Instron Co., Ltd model 5567) with a thermal chamber was used. The dimensions of a specimen were 10 mm $\times$ 50 mm $\times$ 2 mm. The test method was a flexural mode with a supporting span of 32 mm. The test was performed using a crosshead speed of 1.0 mm min$^{-1}$.

The shape recovery performance is an essential property of the SMP samples. Therefore, a systematic shape recovery test of the SMP specimens upon bending load was performed. The procedure for the thermo-mechanical bending cycling of the SMPs includes the following steps (see also figure 2): first, the specimen in its permanent shape is kept in an oven for 5 min at $T_g + 20^\circ$C; then the SMP is bent to a storage angle $\theta_0$ in a ‘U’ shape with a radius of 2 mm in the soft rubbery state, and then the SMP is kept at room temperature with the external constraint to freeze the elastic deformation energy for 5 min; the SMP specimen fixed to the apparatus is then put in an oven at elevated temperature, and then it recovers to an angle $\theta_N$. Five specimens were used in each test. The method used to quantify the precision of deployment is illustrated in figure 2, where $r$ denotes the radius of the mandrel, $t$ represents the thickness of the SMP specimen, $\theta_0$ is the original storage angle of the specimen in the storage state during the first bending cycle, and $S(x_0, y_0)$ is a point selected to determine $\theta_0$. $\theta_N$ is the residual angle in the recovery state during the $N$th thermo-mechanical bending cycle ($N = 1, 2, 3, \ldots$). $R(x_N, y_N)$ is a testing point in order to calculate $\theta_N$.

$$\theta_N = \arccot x_N \quad (N = 1, 2, 3, \ldots, 0 \leq \theta_N \leq 180^\circ). \quad (1)$$

The value of the shape recovery ratio is calculated by

$$R_N = \frac{\theta_0 - \theta_N}{\theta_0} \times 100\% \quad (N = 1, 2, 3, \ldots) \quad (2)$$

where $R_N$ denotes the shape recovery ratio of the $N$th thermo-mechanical bending cycle. $S(x_0, y_0)$ and $R(x_N, y_N)$ are measured by a vernier caliper with a resolution of 0.01 mm. Finally, $\theta_N$ and $R_N$ are obtained through equations (1) and (2). In the following tests, the radius $r$ of the mandrel and the thickness of the SMP specimen are 2 mm and 1.5 mm, respectively [19, 20].

3. Results and discussion

3.1. Dynamic mechanical properties

The dynamic mechanical properties of benzoxazine-modified epoxy SMPs are presented in figures 3–6. The thermal transition events in polymers can be described in terms of free volume. The changes of free volume can be monitored as molecular changes or physical changes, such as a volumetric change, internal movement of polymer molecules by the heat adsorption or heat emission during that change, the decrease of stiffness and the increase of mobility by a change in relaxation time [21].
The plot of the loss modulus as a function of temperature of the benzoxazine-modified epoxy SMP samples is illustrated in figure 3. The $T_g$ values for the benzoxazine-modified epoxy SMPs were 47°C in ENDB 1/1/1/0, 72°C in ENDB 1/1/0.8/0.2, 80°C in ENDB 1/1/0.6/0.4, 85°C in ENDB 1/1/0.4/0.6, 92°C in ENDB 1/1/0.2/0.8, and 119°C in ENDB 1/1/0/1. An incorporation of BA-a resin in the epoxy-based SMP resulted in an increase of the $T_g$ with increasing BA-a fraction in the alloys. This may be due to the more rigid molecular structure and possibly much higher intramolecular and intermolecular forces in the polybenzoxazine compared with the epoxy. This observation is in good agreement with previous work reported by Rimdusit and Ishida [16].

Figure 4 illustrates a plot of storage modulus, a material stiffness, as a function of temperature of the benzoxazine-modified epoxy SMP samples. The storage moduli of the solid polymer in its glassy state (35°C) were 3.18, 3.90, 4.34, 4.44, 4.62 and 4.70 GPa at BA-a contents of...
0, 0.2, 0.4, 0.6, 0.8 and 1 mol ratio, respectively. The storage modulus tended to increase with increasing BA-a content in the alloys as a result of the more rigid characteristics of the BA-a resin. The effects of BA-a resin on the storage modulus in the rubbery plateau region of the polymer alloys are illustrated in figure 5. The plateau moduli in the rubbery plateau region of the polymer alloys as a result of the more rigid characteristics of the BA-a resin. The effects of BA-a resin on the storage modulus in the rubbery plateau region of the polymer alloys was closely related to the rubbery plateau modulus. For a tight network structure, i.e. rubbery plateau modulus greater than 10^5 Pa such as in our SMPs, the non-Gaussian character of the polymer network becomes more and more pronounced and the equation from the theory of rubbery elasticity no longer holds. The approximate relation expressed in equation (3) below proposed by Nielsen [22] is thus preferred and is reported to better describe the elastic properties of a dense network, e.g. in an epoxy system.

$$\log \left( \frac{E'}{3} \right) = 6 + 293 \left( \frac{\rho}{M_c} \right)$$

where $E'$ (Pa) is the storage modulus in a rubbery plateau region, $\rho$ (g cm$^{-3}$) is the density of the material at room temperature, and $M_c$ (g mol$^{-1}$) is the molecular weight between crosslink points. As displayed in table 2, the density values at room temperature of benzoxazine-modified epoxy SMPs at 0, 0.2, 0.4, 0.6, 0.8 and 1 mol are 1.14, 1.15, 1.16, 1.17, 1.18 and 1.19 g cm$^{-3}$; the crosslink density values are $2.90 \times 10^{-3}$, $3.25 \times 10^{-3}$, $3.62 \times 10^{-3}$, $3.79 \times 10^{-3}$, $3.81 \times 10^{-3}$ and $4.29 \times 10^{-3}$ mol cm$^{-3}$, respectively. It was observed that the crosslink density tended to increase with an increase in BA-a content. The crosslink density is one parameter that relates to the $T_g$ of the copolymer and the heterogeneous polymer network as expressed by the Nielsen equation [23, 24].

$$T_g - T_g(0) = \frac{3.9 \times 10^4}{M_c}.$$  \hspace{1cm} (4)

The number average molecular weight between cross-linked points is $M_c$. $T_g(0)$ and $T_g$ are the glass transition temperature of the uncross-linked polymer and the glass transition temperature of the polymer, respectively. According to the Nielson equation (equation (4)), $M_c$ is inversely proportional to the cross-linked density. This parameter is one key factor affecting $T_g$ of the polymer networks. Figure 6 illustrates the $T_g$ from the loss modulus and the cross-linked density of SMP alloys at various compositions. As seen from this figure, the $T_g$ of the polymer network increases when its cross-linked density in the alloys increases, which is in good agreement with our DMA results. Additionally, the molecular rigidity of the benzoxazine fraction can also enhance the $T_g$ of the resulting hybrid polymer network, which is in good agreement with our previous work [16, 17].

### 3.2. Mechanical properties

The mechanical properties of benzoxazine-modified epoxy SMPs play an important role in their effective utilization. In this work, the mechanical properties of the SMP samples were investigated in the glassy state (room temperature) and the rubbery state ($T_g + 20^\circ C$). Generally, SMPs are commonly used over these temperatures.

Figures 7(a) and (b) exhibit plots of the flexural strength and flexural modulus of the benzoxazine-modified epoxy SMPs at room temperature as a function of the BA-a content. The flexural strength values of the benzoxazine-modified epoxy SMPs are 59.5 MPa in ENDB 1/1/1/0, 102.2 MPa in ENDB 1/1/0.8/0.2, 122.2 MPa in ENDB 1/1/0.6/0.4, 131.1 MPa in ENDB 1/1/0.4/0.6, 149.1 MPa in ENDB 1/1/0.2/0.8, and 164.3 MPa in ENDB 1/1/0/1. It can be observed that the flexural strength of the benzoxazine-modified epoxy SMPs increases with increasing BA-a content. The flexural modulus values of the benzoxazine-modified epoxy SMPs are 1.8 GPa in ENDB 1/1/1/0, 3.3 GPa in ENDB 1/1/0.8/0.2, 3.7 GPa in ENDB 1/1/0.6/0.4, 3.8 GPa in ENDB 1/1/0.4/0.6, 3.9 GPa in ENDB 1/1/0.2/0.8, and 4.4 GPa in ENDB 1/1/0/1. The addition of BA-a resin results in a systematic increase of the modulus of the obtained SMP. This could be due to the addition of the more rigid BA-a structure into the epoxy-based SMP increasing the stiffening of the resulting polymer alloys. The flexural strength of the thermosetting resin was influenced by a number of interrelated parameters including $T_g$, molecular weight between crosslinks, free volume, chemical structure, network regularity and perfection, and many other contributing factors [17].

Moreover, the mechanical properties of benzoxazine-modified epoxy SMPs in the rubbery state are also important parameters that affect the deployment ability of the SMP samples. The flexural strength of the benzoxazine-modified...
Figure 7. Flexural strength (a) and flexural modulus (b) of the benzoxazine-modified epoxy SMP samples at various compositions at room temperature.

Flexural SMT was measured using flexural tests with a universal testing machine, and a forced air convective environmental chamber was used for elevated temperature tests. The dependence of flexural strength on BA-a content was investigated at a testing temperature of 20°C above \( T_g \). Figure 8(a) exhibits the plot of the flexural strength as a function of the BA-a content of benzoxazine-modified epoxy SMPs at \( T_g + 20^\circ C \). The flexural strength values in the rubbery state for the benzoxazine-modified epoxy SMPs are 0.6 MPa in ENDB 1/1/1/0, 0.9 MPa in ENDB 1/1/0.8/0.2, 0.9 MPa in ENDB 1/1/0.6/0.4, 1.0 MPa in ENDB 1/1/0.4/0.6, 1.4 MPa in ENDB 1/1/0.2/0.8, and 2.5 MPa in ENDB 1/1/0/1. The flexural strength in the rubbery state of the benzoxazine-modified epoxy SMPs increases with increasing BA-a resin fraction from 0 to 1 mol. Figure 8(b) exhibits the plot of the flexural modulus as a function of the BA-a content for the benzoxazine-modified epoxy SMPs at \( T_g + 20^\circ C \). The addition of BA-a resin also results in a systematic increase of the modulus in the rubbery state with increasing amount of BA-a resin. The flexural modulus values of benzoxazine-modified epoxy SMPs are 5.9 MPa in ENDB 1/1/1/0, 9.5 MPa in ENDB 1/1/0.8/0.2, 10.3 MPa in ENDB 1/1/0.6/0.4, 10.2 MPa in ENDB 1/1/0.4/0.6, 14.5 MPa in ENDB 1/1/0.2/0.8, and 35.1 MPa in ENDB 1/1/0/1.

At \( T_g + 20^\circ C \), the SMP system with 1 mol of BA-a content without Jeffamine D230 exhibited the highest flexural strength and flexural modulus. These results suggest that BA-a exhibits a stronger positive effect on the mechanical properties of epoxy over Jeffamine D230 curing agent. Furthermore, macromolecular chain motion of the benzoxazine-modified epoxy SMP plays a critical role in mechanical resistive loading. From our results, the mechanical properties of the benzoxazine-modified epoxy SMP were clearly dependent on the BA-a and Jeffamine D230 composition. The motion of the macromolecular chains was likely to be more hindered by the presence of BA-a than Jeffamine D230, helping the benzoxazine-modified epoxy SMP to resist external loading; this resulted in a significant improvement in mechanical properties.
3.3. Shape memory properties

3.3.1. Effect of BA-a content on shape fixity of epoxy SMP.

The shape fixity is one key parameter used to describe the extent of a temporary shape being fixed during shape memory. Shape fixity may be fixed upon rapid cooling of deformed material to room temperature or below glass transition temperature. A high glassy state modulus ($E'_g$) will provide a material with high shape fixity during simultaneous cooling and unloading, whereas a high rubbery modulus ($E'_r$) provides high elastic recovery at high temperature. In addition, a sharp transition from glassy state to rubbery state makes the material sensitive to temperature variation. A high elasticity ratio ($E'_g/E'_r$), especially a difference of two orders of magnitude, allows easy shaping at $T > T_g$ and great resistance to deformation at $T < T_g$ [25]. High glassy modulus is not always mandatory for high shape fixity but is desirable, whereas a high rubbery modulus ($E'_r$) implies high elastic recovery at high temperature [25]. In this study, the modulus ratio ($E'_g/E'_r$) was taken as $E'_{g,T_g-50^\circ C}/E'_{r,T_g+50^\circ C}$ where $E'_{g,T_g-50^\circ C}$ and $E'_{r,T_g+50^\circ C}$ are the storage moduli at temperatures of $50^\circ C$ below $T_g$ and $50^\circ C$ above $T_g$. The modulus ratios of our benzoxazine-modified epoxy SMPs are summarized in table 3. It can be observed that the storage modulus increased with increasing mole ratio of BA-a resin whereas the $E'_{g}/E'_r$ ratio tended to decrease with an increase in the mole ratio of the BA-a. The modulus ratio can be used to represent the shape fixity of the samples. The relationship between shape fixity and modulus ratio can be described by the following mathematical model [25, 27]:

$$\text{Shape fixity (R)} = 1 - \frac{E'_r}{E'_g}$$

(5)

where $E'_g$ is the glassy modulus ($T_g - 50^\circ C$), $E'_r$ is the rubbery modulus ($T_g + 50^\circ C$). It is to be noted that the modulus ratio can be used to predict shape fixity when the SMP behaves as a linear elastic material in the range of temperature under investigation. A high elasticity ratio ($E'_g/E'_r$) allows easy shaping at $T > T_g$ and a great resistance to deformation at $T < T_g$. The polymer material has to be designed to meet the above criteria for shape memory applications. The shape fixity values of benzoxazine-modified epoxy SMPs are also summarized in table 3. The samples showed excellent shape fixity values of about 98–99%. This range of values corresponds to those reported by Leonardi et al [6] for the shape fixity of an epoxy (DGEBA type) network consisting of n-dodecylamine (DA) units as physical crosslinks and m-xylendiamine (MXDA) units as chemical crosslinks. The prepared epoxy SMP at a molar ratio of 6:4:1 (DGEBA/DA/MXDA) was reported to have a shape fixity value of 98% [6].

3.3.2. Shape recovery ratio at different active temperatures.

Shape recovery is used to reflect how well an original shape of the sample has been memorized. Shape recovery characterizes the ability of an SMP to recover the accumulated strain during the deformation step after subsequent cooling upon reheating to the rubbery state. A systematic shape recovery test of the specimen upon bending was performed. In this study, the shape recovery was tested following the previous report by Leng et al [26]. The shape recovery process of the bent samples was recorded by a video camera and their shape recovery angles were determined by measuring the angle between the straight ends of the specimens [13, 19, 26]. Rectangular specimens were used to investigate the recovery phenomenon. As shown in figure 9, the ENDB 1/1/0.8/0.2 sample was heated up to its transition temperature ($T \geq T_g$) in an oven, i.e. 73 C in this case. Then, the sample became elastic and was bent into the u-shape of the mandrel. The fixed sample was subsequently cooled to room temperature, and then held for 20 min to ensure that the sample retained its u-shape. In the next step, the bent sample was placed in a heating chamber at different temperatures for further study on its shape recovery performance. Our SMP samples showed similar shape recovery performance, as illustrated in figure 10.

We investigated the shape recovery ratio ($R_N$) of the SMP at different temperatures. The measurement of recovery angle versus time was conducted at $T_g - 20^\circ C$, $T_g - 10^\circ C$, $T_g + 5^\circ C$, $T_g + 10^\circ C$ and $T_g + 20^\circ C$. The predeformed temperature of the SMP was set as the $T_g$ of the SMP. The original storage angle $\theta_0$ was selected as 180°. The shape recovery ratio was obtained by calculating the ratio of the shape recovery angle to 180°. The value of the shape recovery ratio was calculated by

$$R_N = \frac{\theta_0 - \theta_N}{\theta_0} \times 100\%$$

(6)

where $R_N$ denotes the shape recovery ratio of the Nth thermo-mechanical bending cycle. $\theta_0$ is the original storage angle of the specimen. $\theta_N$ is the residual angle in the recovery state during the Nth thermo-mechanical bending cycle ($N = 1$). Figure 11 shows a plot of the shape recovery ratio at $T_g - 20^\circ C$, $T_g - 10^\circ C$, $T_g + 5^\circ C$, $T_g + 10^\circ C$ and $T_g + 20^\circ C$. The experimental results demonstrated that the epoxy modified with benzoxazine ranging from 0 to 1 mol ratio presented fast responsive behavior in response to temperature within 150 s. This observation indicated that the shape-recovered ratio did not depend on BA-a content, and the value was observed to be almost 100% at higher testing temperatures, e.g. $T_g$, $T_g + 10^\circ C$, $T_g + 20^\circ C$, whereas at temperatures below $T_g$ ($T_g - 20^\circ C$) the recovery ratio decreased with increasing BA-a content. At $T < T_g$, with the relatively high stiffness of the SMP, the mobility of the SMP-based benzoxazine-modified epoxy in the high compressive strain state is limited by the
strong constraint of the structure of the SMP system as a result of the addition of the more rigid BA-a structure into the epoxy-based SMP.

Moreover, the recovered ratio for 1 molar ratio of BA-a content clearly decreased at every temperature and the shape recovery ratio decreased with increasing BA-a content. Therefore it appears that the shape recovery behavior can also be observed within the range of $T_g - 20^\circ C$ and $T_g$, which is associated with the partial glass transition. However, the shape recovery ratio dropped sharply when the active temperature decreased to $T_g - 20^\circ C$, suggesting that the shape recovery effect cannot be released below an active temperature of $T_g - 20^\circ C$. Deformations of the low temperature phase, occurring above a critical stress, were recovered completely during the solid–solid transformation to the high temperature phase. As the driving force for shape recovery in a polymer is the elastic strain generated during the deformation, deformation at high temperature is much easier due to the lower rubbery modulus of the polymer which makes orientation of the polymer more feasible. However, the orientation will be partly relaxed before the structure is frozen in during the subsequent cooling cycle. On the other hand, deformation at low temperature is more difficult due to the higher glassy state modulus of the polymer, but chain orientation will remain at a higher degree as the relaxation process is slowed down.

The $R_N$ values of all samples were 95–100% and were significantly higher than those of shape memory polymers from polyurethane–benzoxazine systems [28] which were reported to be 72–84%. The $R_N$ value of some epoxy-based SMPs was 99% [29]. Based on the results, active temperatures of $T_g$ and $T_g + 20^\circ C$ provide a recovery ratio of about 90–99% within 150 s. Therefore, these temperatures, i.e. $T_g$ and $T_g + 20^\circ C$, are selected to be used as the conditions for measurement of the recovery times of benzoxazine-modified epoxy SMP samples.

3.3.3. Effect of BA-a content on shape recovery time. The shape recovery times for benzoxazine-modified epoxy at different active temperatures, i.e. $T_g$ and $T_g + 20^\circ C$, are shown in figures 12 and 13. Below $T_g$, the SMP specimen deploys very slowly due to a partial glass transition and an energy dissipation of the SMP. According to the results, all samples need a few minutes to recover their original shape, which indicates a good shape memory performance. Figure 12 illustrates the relationship between recovery angle and recovery time of benzoxazine-modified epoxy SMP specimens at $T_g$. The slope of the curves in figure 12 was found to be relatively constant and maximum in the temperature range of 50–150°. Below and above this range, the slope was observed to be lower. This implies that the epoxy-based SMP has a relatively low recovery rate at the initial and terminal stages. At the incipient stage, the release of constrained force was followed by heavy friction among molecules, so that the slope was found to be relatively high. After the incipient stage, the friction force reduced under the gradual adjustment of segments. At the terminal stage, the shape recovery rate became slow once again because most of the constrained force had been released, with little of it remaining [30].

Figure 13 shows the plot of recovery angle as a function of recovery time for benzoxazine-modified epoxy SMP specimens at $T_g + 20^\circ C$. As can be seen in figure 13, the epoxy-based SMP cured by a mixture of curing agents between benzoxazine resin and Jeffamine D230 at various mole ratios could deploy quickly within the initial 30 s, and then the deployment velocity was reduced quickly due to the termination of strain energy dissipation. A similar observation was also reported in carbon fiber reinforced styrene based SMPs [19]. The shape recovery time of the benzoxazine-modified epoxy SMPs having BA-a content of 0–1 mol ratio...
Figure 10. Shape memory behavior of a benzoxazine-modified epoxy SMP sample at ENDB 1/1/0/1: (a) original shape, (b) temporary shape and (c) recovered shape at \( T_g + 20^\circ C \).

was observed to range from 40 to 140 s, i.e. the shape recovery time was found to increase with increasing amount of BA-a resin. Shape recovery depends on both the structure of the polymer and the thermo-mechanical conditions of shape memorization [26]. This result implies that the addition of BA-a can alter the shape recovery time, therefore broadening the applications of the epoxy-based SMPs.

The shape recovery speeds of the benzoxazine-modified epoxy SMP samples were evaluated by the time period of their full recovery. Figure 14 illustrates the relationship of the shape recovery time and BA-a content at the active temperature (\( T_g \) and \( T_g + 20^\circ C \)). According to the results, all of the samples took only a few minutes to completely recover to their original shape, suggesting good shape recovery performance. At \( T_g \), the shape recovery time of the specimens increased with an increasing amount of BA-a content. The benzoxazine-modified epoxy SMP samples with 0, 0.2, 0.4, 0.6, 0.8 and 1.0 mol ratio of BA-a took 40, 57, 88, 112, 131 and 173 s, respectively, to fully recover. At \( T_g +20^\circ C \), the shape recovery time also increased with an increase in BA-a content. The benzoxazine-modified epoxy SMPs samples with 0, 0.2, 0.4, 0.6, 0.8 and 1.0 mol ratio of BA-a took 40, 57, 61, 72, 83 and 142 s, respectively to recover. This observation suggested that on increasing the active temperature, the shape recovery time decreased as expected, whereas an increasing amount of benzoxazine resulted in an increased recovery time at the same temperature. This could be because the shape recovery of the SMPs depended on the relaxation of chain segments. At high temperature, the movement of chain segments became intense, which caused an increase in the recovery force on the samples. As a consequence, the shape recovery time of the specimens decreased with an increase in active temperature. Furthermore, with addition of benzoxazine resin in the epoxy
SMP, the movement of the chain segments would be more restricted due to an increase in crosslink density, which would result in a decrease of molecular weight between crosslink points, as shown in table 2. Hence, benzoxazine-modified epoxy SMP samples with higher BA-a content provided a lower shape recovery time.

3.3.4. Effect of BA-a content on recovery stress. To be suitable for potential applications in the area of actuators and reconfigurable structures, two key performance criteria for SMP-based devices are recovery stress and response time [12]. The recovery stress quantifies the tendency of the SMP to return to its original shape. The test was conducted by restricting the strain of a deformed SMP. When the SMPs were heated and deformed, elastic stress was generated and the elastic stress was stored when the SMPs were cooled below $T_g$. If the deformed and fixed SMPs were reheated above $T_g$, the stress stored in the SMPs was released as shape recovery stress [31].

First, maximum stress was applied at $20\,^\circ{\text{C}}$ above $T_g$. The strain at the maximum stress point was maintained by cooling down to room temperature. As a consequence, the stress was reduced to zero at this stage and the sample was held at room temperature for 15 min, then it was heated to $20\,^\circ{\text{C}}$ above $T_g$ by maintaining the strain. In the final stage, the sample was held at $20\,^\circ{\text{C}}$ above $T_g$ for 15 min [32].
Figure 16. Recovery stress as a function of BA-a content of the benzoxazine-modified epoxy SMP samples at various compositions.

Figure 17. Flexural strength versus number of recovery cycles from consecutive shape memory cycles of the benzoxazine-modified epoxy SMP samples at various compositions: (●) ENDB 1/1/0/1, (■) ENDB 1/1/0.8/0.2, (♦) ENDB 1/1/0.6/0.4, (▲) ENDB 1/1/0.4/0.6, (▼) ENDB 1/1/0.2/0.8 and (▲) ENDB 1/1/0/1.

3.3.5. Mechanical properties of the samples after repeated recovery cycles. In order to evaluate the degradation of the SMPs based on benzoxazine-modified epoxy, the relationship between the flexural strength and the number of bending cycles was determined at $T_g$. The test results in plots of flexural strength and number of recovery cycles are shown in figure 17. All of the benzoxazine-modified epoxy SMP samples can fully recover to their original shape at 100 cycles. However, there is a small difference of flexural strength between the first and subsequent cycles. The SMP samples with 0, 0.2, 0.4, 0.6, 0.8 and 1 mol ratio of BA-a showed flexural strengths at the 100th cycle of about 0.60 ± 0.03, 0.86 ± 0.03, 0.91 ± 0.01, 1.00 ± 0.03, 1.39 ± 0.06 and 2.49 ± 0.15 MPa, respectively. A small change of flexural strength values was also observed, as seen in figure 17. This phenomenon can be explained by fatigue of the material during repeated shape recovery processes. However, the benzoxazine-modified epoxy SMPs maintained their flexural strength after testing up to 100 cycles. This indicates an excellent cycling capability of the obtained SMP alloys due to the excellent thermal stability of benzoxazine-modified epoxy polymer and its chemical crosslink nature.

4. Conclusions

Enhanced thermo-mechanical performance of epoxy SMPs was achieved by alloying with BA-a resin. The incorporation of the BA-a contributed to higher storage modulus in the glassy state, higher crosslink density, enhanced flexural strength and greater flexural modulus at room temperature than epoxy-based SMPs cured solely by Jeffamine D230. In addition, the flexural strength and flexural modulus in the rubbery state were found to increase with increasing amount of BA-a resin. The obtained SMPs also showed excellent shape fixity values of about 98–99%. In addition, the recovery stress of the benzoxazine-modified epoxy SMPs was also observed to be larger than that of epoxy-based SMPs. The various compositions of benzoxazine-modified epoxy SMPs, at different active temperatures, i.e. $T_g$ and $T_g + 20^\circ$C, needed only 2–3 min to recover their original shapes. Interestingly, the obtained SMPs also provided outstanding shape recovery ratio values close to 99–100%, indicative of good shape.
memory performance. Finally, the addition of benzoxazine resin as a co-curing agent for epoxy enables control of the shape recovery time, which makes the obtained samples attractive as good candidates for shape memory material to be used in a broader range of applications.

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