Effects of benzoxazine resin on property enhancement of shape memory epoxy: A dual function of benzoxazine resin as a curing agent and a stable network segment

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Abstract. An ability of bisphenol-A/aniline based benzoxazine resin (BA-a) to simultaneously acts as a curing agent and a stable or rigid network segment for shape memory epoxy, i.e. a two component system, is demonstrated. This significantly simplifies a formulation of present shape memory epoxy systems, i.e. a three or four component system. A suitable content of BA-a in the aliphatic epoxy (NGDE)/polybenzoxazine (PBA-a) samples for good shape memory performance is in a range of 30 to 50 mol%. The storage modulus of the obtained NGDE/PBA-a shape memory polymers (SMPs) was increased from 3.57 GPa for 30 mol% BA-a content to 4.50 GPa for 50 mol% BA-a content. Glass transition temperature of the sample was also substantially increased with increasing BA-a fraction, i.e. from 51°C to 140°C. Flexural modulus and strength at room temperature of the samples at 50 mol% BA-a were found to be as high as 3.97 GPa and 132 MPa compared to the maximum values of 2.54 GPa and 100 MPa of SMP based on cyanate ester-epoxy. All samples exhibited a high value of shape fixity close to 100%. A presence of the BA-a in the samples also imparted a greater recovery stress ranging from 0.25 to 1.59 MPa. Consequently, the obtained NGDE/PBA-a copolymers are highly attractive for shape memory materials to be used in a broader range of applications particularly at elevated temperature and a higher recovery stress value.

Keywords: polymer blends and alloys, smart polymer, shape memory polymers, polybenzoxazine, aliphatic epoxy

1. Introduction

Shape memory polymers (SMPs) belong to a novel class of smart materials having been a topic of active research since 1980s, particularly in the past few years [1–7]. They possess an ability to return from a temporary shape to their permanent shape induced by external stimuli such as light, humidity, solvents, electric or magnetic fields, ionic strength, pH or most typically thermal activation [8]. Interestingly, SMPs have a number of advantages over shape memory metal alloys (SMAs) such as light weight, high elastic deformation with a strain value as high as 200%, a broad range of application temperatures which

can be tailored, ease of manipulation, potential biocompatibility and biodegradability as well as cost competitiveness [5, 9]. SMPs have a wide application range in self-deployable structures in spacecraft [1, 10], orthodontic applications, intelligent medical devices [5, 9] or smart textiles and apparels [11]. In general, SMPs can be either thermoplastics, i.e. polyethylene [2] and polyester [5] or thermosetting polymers such as epoxy [12, 13] or polyurethane [14, 15]. In case of SMP thermoplastics, their networks can be constructed with physical crosslinks by physical interactions. This characteristic will allow very easy reshaping or re-formation of this class of poly-

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mers. However, they can potentially melt at high temperature, and lose their memory properties over time [16]. Contrarily, chemical crosslinks by covalent bonds can be formed for thermoset SMPs; they soften but do not melt at elevated temperature [4, 17]. As a consequence, thermosetting SMPs, especially epoxy-based SMPs, have been highly attractive particularly in advanced applications [13, 18, 19]. To further broaden the useful property range of shape memory epoxy, epoxy-based shape memory copolymers and epoxy-based shape memory composites have also been developed [18–21]. Recently, Xie and Rousseau [20] had developed methods to tailor transition temperature (T_g) and shape recovery properties of SMPs based on aromatic epoxy as hard segments, aliphatic epoxy as soft segments and aliphatic amine as curing agents. The authors reported that all of their cross-linked epoxy samples showed good SMP characteristics, including excellent shape fixity with shape recovery close to 100% as well as easily tailored thermal transition temperatures ranging from room temperature to 89°C. However, in polymerization step of oxirane group containing epoxy, the resin requires a suitable curing agent. In general, epoxy curing agents, i.e. aromatic amines possess some drawbacks such as relatively low elongation and rather slowly curing for epoxy resin as well as serious toxicity concerning in some cases and corrosion to the processing apparatus [22]. In addition, they show no direct benefit to the shape memory performance of the obtained shape memory epoxy.

Benzoxazine resin, a novel class of thermosetting phenolics [23], has been developed in 1990s to solve various inherent problems occurred in traditional phenolics. For example, the resin can undergo ring-opening polymerization upon heating without strong acid or base catalysts; therefore, no condensation by-product is released during a curing process. This eliminates the formation of voids or air gaps in the fully cured products that normally occur in phenolic resin. A very low A-stage viscosity of the resin results in its high processing ability including ease of filler wetting and high filler loadings [24–26]. The polymer from this resin has been reported to show high thermal stability, excellent mechanical performance, good dimensional stability and relatively high glass transition temperature even though they exhibit relatively low crosslinking density [23, 27, 28]. More importantly, the benzoxazine resin has been shown to be able to blend with various types of resins or

polymers to provide even broader spectrum of the copolymer properties. As exemplified, benzoxazine resin had been shown to be able to function as a latent curing agent for epoxy resin and, in some cases, provide synergism in thermal and mechanical properties of the obtained benzoxazine/epoxy copolymers [27, 29–31]. Very recently, shape memory polymers between bisphenol-A/aniline based benzoxazine resin (BA-a) and shape memory polyurethane (SMPU) have been investigated by Erden and Jana [32]. From their investigation, the authors suggested that the BA-a can be either chemically bonded with SMPU chains by copolymerization or grafting reactions or blended with SMPU as a separate phase. Furthermore, the polybenzoxazine (PBA-a) can act as an additional hard phase for the SMPU due to its higher glass transition temperature and much greater storage modulus than the soft segment phase of the SMPU. An addition with only 17 wt% of the BA-a in the SMPU rendered a recovery stress and shape recovery ratio as high as 13 MPa and 93%, which was substantially higher than those of the starting SMPU, i.e. 6.8 MPa and 72%. In addition, Rimdusit *et al.* [7] have recently developed shape memory polymer copolymers based on bisphenol-A/ aniline based benzoxazine resin (BA-a), aliphatic-aromatic epoxy mixture, and Jeffamine D230 as the epoxy curing agent. Enhanced thermomechanical performance of the obtained epoxy SMPs was achieved by an addition of the BA-a fraction. 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. Moreover, the recovery stress of the obtained SMPs was reported to increase with increasing BA-a content up to 33 mol% with the reported recovery stress of about 38 kPa. It was 1.8 times higher comparing with 20.4 kPa of the unmodified shape memory epoxy.

The purpose of this study is to investigate the potential use of bisphenol-A/aniline based benzoxazine resin (BA-a) as a sole curing agent for aliphatic shape memory epoxy. Moreover, it is expected that the aromatic structure of the BA-a can act as a hard or stable phase for the aliphatic epoxy network thus eliminate the need for aromatic epoxy that is normally added in typical shape memory epoxy products. Twofold benefits are expected from this aliphatic epoxy/benzoxazine SMPs, i.e. (1) a potential improvement of thermomechanical properties and

recovery stress of the copolymer samples with an addition of the more rigid polybenzoxazine and (2) a simpler shape memory epoxy formulation from the dual function of the BA-a above. Some essential properties, such as glass transition temperature, flexural modulus, flexural strength, recovery stress and shape recovery performance will also be investigated.

2. Experimental

2.1. Materials

Materials used in this study was bisphenol-A/aniline-based benzoxazine resin (BA-a). The BA-a was synthesized according to the solventless technology [23, 33]. Bisphenol-A (polycarbonate grade) was provided by Thai Polycarbonate Co., Ltd. (Rayong, Thailand). Para-formaldehyde (AR grade) and aniline (AR grade) was purchased from Merck Co., Ltd. (Darmstadt, Germany) and Panreac Quimica, S.A. (Barcelona, Spain), respectively. Aliphatic epoxy (Neopentyl glycol diglycidyl ether; NGDE) was available from Aditya Birla Chemicals Thailand Ltd. (Rayong, Thailand). All chemicals were used as received. The NGDE/BA-a mixtures at different mole percent of the BA-a varied from 30 to 50 mol% were prepared. The mixture was heated at about 80°C in an aluminum pan and stirred for about 15 min to yield a homogeneous mixture. The molten resin was poured into an aluminum mold and was thermally cured at 80°C for 2 h in vacuum oven and 130°C/12 h, 140°C/4 h, 150°C/4 h and 160°C/2 h, respectively, in an air circulated oven. Then, the cured NGDE/polybenzoxazine (PBA-a) shape memory samples were cut into various shapes for each specific test.

2.2. Characterization methods

Curing behaviors of the BA-a, NGDE and NGDE/BA-a mixtures were studied using a differential scanning calorimeter (DSC) model 2910 from TA Instruments (New Castle, DE, United States). Each sample with a mass in a range of 3–5 mg was sealed in an aluminum pan with lid. The heating rate used was 5 and 10°C/min and the sample temperature was scanned from room temperature to 320°C under nitrogen purging with the gas flow rate of 50 mL/min. The degree of conversion of a sample was determined according to the relationship in Equation (1):

$$\text{Conversion [\%]} = \left(1 - \frac{H_{\text{rxn}}}{H_0}\right) \cdot 100 \quad (1)$$

where H_{rxn} is the heat of reaction of the partially cured samples and H_0 is the heat of reaction of the uncured resin mixture.

Chemical structure and network formation of all samples was studied by a Fourier transform infrared spectroscopy (FTIR), a Spectrum GX FT-IR spectrometer from Perkin Elmer with an ATR accessory (Waltham, Massachusetts, United States). All spectra were taken as a function of time with 64 scans at a resolution of 4 cm⁻¹ and wavenumber ranging from 4000–650 cm⁻¹. For viscous liquid NGDE/BA-a mixtures, a small amount of mixture was casted as thin film on a potassium bromide (KBr) window and its FTIR spectrum was obtained.

Dynamic mechanical analyzer (DMA) model DMA242 from Netzsch, Inc. (Bavaria, Germany) was used to determine a storage modulus (E') and loss tangent ($\tan \delta$) of the NGDE/PBA-a shape memory samples. The sample in rectangular shape, with a dimension of 10 mm×50 mm×3 mm, was tested using a three-point bending mode with 40 mm supporting span at the frequency of 1 Hz and a heating rate of 2°C/min from room temperature to the temperature beyond the glass transition temperatures (T_g) of each sample. The T_g was taken as the maximum peak on the loss tangent curve in the DMA thermogram.

Flexural properties of NGDE/PBA-a shape memory samples were measured according to ASTM D 790M using a universal testing machine (model 5567) from Instron (Thailand) Co., Ltd. (Bangkok, Thailand). The test method was a three-point bending load with a supporting span of 32 mm and tested at a crosshead speed of 1.0 mm/min. A dimension of a rectangular shape sample was 10 mm×50 mm×2 mm.

A systematic shape recovery test of NGDE/PBA-a shape memory samples under bending load was also performed. The procedure for the thermomechanical bending cycling of NGDE/PBA-a shape memory samples includes the following steps: firstly, the sample in its permanent shape was kept in an oven for 20 min at $T_g + 20^\circ\text{C}$; then the sample was bent to a storage angle θ_0 in a 'U' shape with the radius of 2 mm in the soft rubbery state, after that the sample was kept at room temperature with the external con-

straint to freeze the elastic deformation energy for 20 min. The sample fixed on the apparatus was then immersed into air circulated oven at elevated temperature, and it recovered to an angle θ_N [34]. The value of the shape recovery ratio (R_N) can be calculated by Equation (2):

$$R_N = \frac{\theta_0 - \theta_N}{\theta_0} \cdot 100\% \quad (2)$$

Shape fixity and recovery stress of NGDE/PBA-a shape memory samples were studied by a universal testing machine under three point bending mode. The experimental procedure for the shape fixity and recovery stress was performed using the same method as described in [35]. Firstly, a fixed shape was formed by applying force to a sample (10 mm×50 mm×2 mm) at $T_g + 20^\circ\text{C}$ and left to cool down to room temperature. The force was then removed completely to obtain a temporary shape. The deflection after unloading was then measured, and shape fixity (R_f) of each sample was determined. In addition, the sample was also heated up to $T_g + 20^\circ\text{C}$ by keeping the fixed deflection content, afterwards, deflection force of each sample during heating was measured and the corresponding recovery stress was obtained.

3. Results and discussion

3.1. Effects of BA-a contents on curing behaviors of NGDE/BA-a mixtures

Curing characteristics of aliphatic epoxy (NGDE)/benzoxazine resin (BA-a) mixtures at BA-a contents of 30, 40 and 50 mol% were studied by a differential scanning calorimeter (DSC) at a heating rate $5^\circ\text{C}/\text{min}$ as shown in Figure 1. The thermogram of the BA-a showed a curing exothermic peak located at about 210°C , while the NGDE showed no sign of any curing reaction in this temperature range because no initiators or catalysts were added to the resin. Instead the endothermic thermal event starting at about 200°C a result of the evaporation process of the NGDE was observed. For the NGDE/BA-a mixtures, the thermograms revealed three exothermic peaks of these resin mixtures. The two overlapping peaks at lower temperature were found to be in a range of $235\text{--}240^\circ\text{C}$ whereas the third peak at high temperature were observed at temperature about $275\text{--}285^\circ\text{C}$. Both peaks tended to shift to higher temperature with increasing epoxy content. The phenomenon is attributed to diluent effect of the liquid epoxy on benzoxazine curing [29]. Furthermore, the

Figure 1. DSC thermograms of NGDE/BA-a mixtures at various mole percents of BA-a: (●) NGDE, (■) 30 mol%, (◆) 40 mol%, (▲) 50 mol%, (▼) BA-a

reactions between the BA-a and the NGDE were found to comprise of at least two major reactions. The first reaction at the two overlapping exothermic peak at lower temperature is attributed to the polymerization reaction of the BA-a monomers, whereas the third exothermic peak at a higher temperature is the reaction between the phenolic hydroxyl group of the polybenzoxazine (PBA-a) and the epoxide group of the NGDE. This result is in good agreement with the curing behaviors of bisphenol-A based epoxy by the BA-a [29, 36].

Figure 2 illustrates DSC thermograms at a heating rate $10^\circ\text{C}/\text{min}$ of the NGDE/BA-a mixture at 50 mol% of the BA-a content at various curing conditions. The optimal curing conditions of the NGDE/BA-a mixtures were determined from the partial disappearance of the area under the curve of the exothermic peak in the DSC experiment. The heat of reaction of the uncured sample was measured to be 272.0 J/g . After a step curing at $130^\circ\text{C}/12\text{ h}$, $140^\circ\text{C}/4\text{ h}$, $150^\circ\text{C}/4\text{ h}$ and $160^\circ\text{C}/2\text{ h}$, the values decreased to 245.6 , 236.7 , 231.7 and 101.4 J/g , respectively, which corresponded to the degree of conversion of 9.7 , 12.9 , 14.8 and 62.7% . Liu *et al.* [37] suggested that the degree of conversion about 60% of shape memory epoxy provided samples with good balance properties between shape memory performance and thermomechanical properties. The fully cured samples, i.e. 100% conversion, were reported to give samples with too high crosslink density thus resulting in great reduction in molecular chain mobility and poorer shape memory perform-

Figure 2. DSC thermograms of NGDE/BA-a samples at 50 mol% BA-a at various curing conditions: (●) uncured, (■) 130°C/12 h, (◆) 130°C/12 h + 140°C/4 h, (▲) 130°C/12 h + 140°C/4 h + 150°C/4 h, (▼) 130°C/12 h + 140°C/4 h + 150°C/4 h + 160°C/2 h

ance. Therefore, the curing process under the above step cure conditions to achieve approximately 60% conversion was used in our work to cure all NGDE/BA-a mixtures preparing the NGDE/PBA-a shape memory samples for further characterizations.

3.2. Fourier transform infrared spectroscopy (FTIR) of BA-a/NGDE network formation

Chemical structures of benzoxazine resin (BA-a), aliphatic epoxy (NGDE) and their network formation were studied by FTIR spectroscopy. Figure 3 shows FTIR spectra taken from the BA-a, the NGDE and the NGDE/BA-a mixture at 50 mol% BA-a. The characteristic IR absorption bands of the BA-a were found at 1230 cm^{-1} assigned to C–O–C stretching mode of benzene ring and 1496 and 936 cm^{-1} assigned to tri-substituted benzene ring as shown in Figure 3 curve a [23, 38]. The IR absorption bands of the NGDE were observed at 1098 cm^{-1} assigned to C–O–C stretching mode of ethers as well as the peaks at 1254, 909 and 850 cm^{-1} assigned to epoxide ring mode [33] as depicted in Figure 3 curve b. In Figure 3 curve c, it was evidently confirmed by FTIR that the NGDE/BA-a mixture contained both BA-a and NGDE characteristic IR absorptions, such as those at 1496 and 936 cm^{-1} from the BA-a species and that of 1254, 909 and 850 cm^{-1} from epoxide ring of the NGDE.

The network formation between the BA-a and the NGDE after thermal cure were also monitored by

Figure 3. FTIR spectra of (a) BA-a, (b) NGDE, (c) NGDE/BA-a mixture at 50 mol% BA-a, (d) PBA-a, (e) NGDE/PBA-a copolymer at 50 mol% BA-a

FTIR. Figures 3a and 3d showed FTIR spectra taken from the BA-a and the polybenzoxazine (PBA-a). For BA-a polymerization process, the oxazine ring was opened by the breakage of a C–O bond of the ring. Then, the BA-a molecules were transformed from a ring structure to a network structure. During this process, the tri-substituted benzene ring, backbone of BA-a ring, became tetra-substituted benzene ring [23, 38]. The ring-opening polymerization of the BA-a was observed from the decrease of the absorption bands at 1496, and 936 cm^{-1} and the appearance of the new absorption band at 1477 cm^{-1} of the tetra-substituted benzene ring. In addition, a broad intensive IR absorption band appeared at 3400 cm^{-1} was assigned to O–H groups of the phenolic hydroxyl group that can react with epoxide group in the NGDE for ring opening polymerization. Moreover, the FTIR spectra of the NGDE/BA-a mixture at 50 mol% BA-a before and after polymerization were also shown in Figures 3c and 3e. After being step cured at 160°C for 2 h. The absorption band at 1477 cm^{-1} of the PBA-a was also found in the NGDE/PBA-a copolymers whereas the absorption bands at 1254 (vibration modes), 909 and 850 cm^{-1} (asymmetric stretching) assigned to the remained epoxide group appeared. Therefore, it can be suggested that epoxide groups can react with the phenolic hydroxyl group of the ring opened BA-a monomers to form new ether linkages and hydroxyl groups in epoxy moieties [39] as clearly seen the absorption bands at 1036 and 3400 cm^{-1} , respectively, in Figure 3 curve e. A possible chemical reaction

Figure 4. (a) Curing reaction of BA-a, (b) A possible chemical reaction between PBA-a and NGDE and (c) NGDE/PBA-a SMP at original shape, temporary shape and recovered shape at $T_g + 20^\circ\text{C}$

between the BA-a and the NGDE is shown in Figure 4. It was postulated that the BA-a ring was opened by heating at suitable temperature (Figure 4a). The phenolic hydroxyl groups of the ring opened the BA-a monomer then acted as an epoxy curing agent to open the epoxide ring to form the ether linkages in the copolymer networks as proposed in Figure 4b. These results are also in good agreement with the previous reports by our research group [30, 36] and Kimura *et al.* [31] using different types of epoxy resins.

3.3. Dynamic mechanical analysis of NGDE/PBA-a SMPs

Viscoelastic properties served as one key characterization for screening the series of NGDE/PBA-a shape memory polymers (SMPs) for good shape-

memory performance. Figure 5 and Figure 6 displays the temperature-dependence of storage modulus (E') and loss tangent ($\tan\delta$) of the aliphatic epoxy (NGDE)/polybenzoxazine (PBA-a) shape memory samples. From Figure 5, the storage moduli at a glassy state (35°C) of the NGDE/PBA-a SMPs at BA-a contents of 30, 35, 40, 45 and 50 mol% were measured to be 3.57, 3.79, 3.92, 4.29 and 4.50 GPa, respectively. From the results, the storage moduli of the samples tended to increase with increasing BA-a content. The phenomenon is attributed to the addition of the more rigid molecular segments of the PBA-a in the NGDE/PBA-a shape memory samples. Moreover, to obtain the optimum performance for a shape-memory polymer, the drop in modulus should not only be large and sharp but it should ideally be followed by an extended rubbery plateau

Figure 5. Storage modulus versus temperature of NGDE/PBA-a SMPs at various mole percents of BA-a: (●) 30 mol%, (■) 35 mol%, (◆) 40 mol%, (▲) 45 mol%, (▼) 50 mol%

Figure 6. Loss tangent versus temperature of NGDE/PBA-a SMPs at various mole percents of BA-a: (●) 30 mol%, (■) 35 mol%, (◆) 40 mol%, (▲) 45 mol%, (▼) 50 mol%

[40]. As seen in Figure 5, the addition of the BA-a also resulted in a systematic increase of the modulus in rubbery plateau region from 40 to 172 MPa. This characteristic suggested the BA-a to be an effective crosslinker for the aliphatic epoxy. In addition, we can see that a difference of two orders of magnitude of the high elasticity ratio between glassy state modulus (E_g) and rubbery modulus (E_r) was obtained in the SMPs. Therefore, the NGDE/PBA-a SMPs are easy shaping at $T > T_s$ (shape memory temperature) and they show great resistance to deformation at $T < T_s$ [41].

Loss tangent ($\tan \delta$) curves from a DMA experiment of the NGDE/PBA-a SMPs at various BA-a contents are depicted in Figure 6. The peak positions of the $\tan \delta$ were used to indicate T_g of the samples. We can see that, an increase of the BA-a content in the NGDE/PBA-a SMPs resulted in a systematic increase in the T_g of the samples. The T_g of the NGDE/PBA-a samples were 51°C for 30 mol% BA-a, 70°C for 35 mol% BA-a, 88°C for 40 mol% BA-a, 122°C for 45 mol% BA-a and 140°C for 50 mol% BA-a. As a consequence, a wide range of the T_g from 51 to 140°C allowing relatively wide range of service temperature was obtained in these NGDE/PBA-a SMPs. This behavior was attributed to the more rigid molecular structure of the polybenzoxazine compared to the epoxy [42]. Moreover, the peak height of the $\tan \delta$ corresponding to the strain energy dissipated by viscous friction was observed to decrease with increasing mole percent of the BA-a which suggested the elastic behavior of the NGDE/PBA-a

SMPs to be enhanced with the amount of the BA-a crosslinker. We also observed a broader width at half height of the curves which implied network heterogeneity to be more pronounced when the amount of the BA-a increased. However, the transparency and the single peak of $\tan \delta$ of each sample confirmed the single microscopic domain of the NGDE/PBA-a SMPs implying no phase separation in these copolymers. The single broad T_g or switching transition is desirable in some special cases of shape memory polymers such as in multiple shape memory polymers (MSMPs). Moreover, our samples also showed a relatively broad T_g range covering that of the commercially available epoxy-based shape memory polymer, i.e. Veriflex[®] E ($T_g = 62^\circ\text{C}$) and styrene-based shape memory polymer, i.e. Veriflex[®] ($T_g = 90^\circ\text{C}$) from Cornerstore Industries [43].

3.4. Mechanical properties of NGDE/PBA-a SMPs

Mechanical properties, i.e. flexural strength (σ_f) and modulus (E_f) at room temperature of the aliphatic epoxy (NGDE)/polybenzoxazine (PBA-a) SMPs as a function of BA-a content were examined as plotted in Figure 7. It can be seen that the flexural strength of the samples increased with an increase in the amount of the BA-a. The flexural strength of the samples were measured to be 52 MPa for 30 mol% BA-a, 78 MPa for 35 mol% BA-a, 108 MPa for 40 mol% BA-a, 124 MPa for 45 mol% BA-a, and 132 MPa for 50 mol% BA-a. This characteristic was due to the addition of high flexural strength PBA-a,

Figure 7. Flexural strength (●) and flexural modulus (■) at room temperature (25°C) of NGDE/PBA-a SMPs at various mole percents of BA-a

i.e. $\sigma_f \sim 126\text{--}139$ MPa [44] and chemical linkage formation between PBA-a with the epoxy network. The NGDE/PBA-a SMPs also rendered flexural strength higher than that of cyanate ester-epoxy shape memory samples, i.e. 14–100 MPa [45]. Moreover, an addition of the BA-a into the NGDE was expectedly found to improve flexural modulus of the NGDE/PBA-a SMPs, i.e. 1.6 GPa for BA-a = 30 mol% to 4.0 GPa for BA-a = 50 mol% as also seen in Figure 7. This is due to the addition of the more rigid PBA-a, i.e. $E_f \sim 4.5\text{--}5.8$ GPa [44] into the more flexible aliphatic epoxy as well as an enhanced crosslink density of the obtained polymer network described previously.

The potential applications in deployable structure of the NGDE/PBA-a SMPs were systematic investigated by flexural testing in the rubbery state ($T_g + 20^\circ\text{C}$). In this work, the flexural testing was carried out on the universal testing machine equipped with the environmental chamber at $T_g + 20^\circ\text{C}$. Figure 8 displayed a plot of flexural strength at $T_g + 20^\circ\text{C}$ of the NGDE/PBA-a SMPs at different BA-a contents. The flexural strength at a rubbery state of the samples with BA-a contents of 30, 35, 40, 45 and 50 mol% were measured to be 0.4, 0.6, 0.9, 1.5 and 2.3 MPa, respectively. From the results, the flexural strength at the rubbery state of the samples increased with increasing amount of BA-a similar to what observed in the strength at room temperature. The greater values of flexural strength at the rubbery state of the samples are attributed to the enhancement of crosslink density of the samples as discussed in DMA experiment. The flexural strength at the rubbery state of our NGDE/PBA-a SMPs at

Figure 8. Flexural strength (●) and flexural modulus (■) at $T_g + 20^\circ\text{C}$ of NGDE/PBA-a SMPs at various mole percents of BA-a

50 mol% BA-a is about 10 times higher than commercial SMPs based on styrene resin (Veriflex®), i.e. 0.23 ± 0.03 MPa [46]. Furthermore, the effects of BA-a contents on flexural modulus at $T_g + 20^\circ\text{C}$ of the shape memory samples are illustrated in Figure 8. The addition of the BA-a into the NGDE was found to increase flexural modulus at $T_g + 20^\circ\text{C}$ of the samples. The flexural modulus of the samples were ranging from 2.5 MPa for 30 mol% BA-a, up to 10.4 MPa for 50 mol% BA-a. The obtained values are in a same range as that of a commercial thermoset SMP epoxy system (DP7AR), i.e. E_f at $T_g + 20^\circ\text{C} = 8.51$ MPa [12] and a commercial SMPs based on styrene resin (Veriflex®), i.e. 6.48 ± 1.71 MPa [46].

3.5. Effect of BA-a contents on shape fixity of NGDE/PBA-a SMPs

Shape fixity (R_f) is one important shape memory performance indicating an ability to memorize temporary shape of shape memory polymers (SMPs). When SMPs is heated to a temperature above its glass transition temperature (T_g), the sample can develop relatively large deformation. Then, it can be fixed this temporary shape by cooling to a temperature below T_g or room temperature (25°C). Figure 9 showed shape fixity at various fixing temperatures of the NGDE/PBA-a shape memory samples. From the figure, R_f s of the samples were measured to be in a range of 83.1 to 84.5% at $T_g - 10^\circ\text{C}$, 96.5 to 97.4% at $T_g - 20^\circ\text{C}$ and 98.1 to 99.3% at 25°C . We can see that the R_f values of all samples at various fixing temperatures decreased slightly by an increase in the BA-a contents from 30 to 50 mol%. The decrease in the shape fixity values with an incorporation of the

Figure 9. Effect of BA-a contents on shape fixity at different fixing temperatures of NGDE/PBA-a SMPs: (●) room temperature (25°C), (■) $T_g - 20^\circ\text{C}$, (◆) $T_g - 10^\circ\text{C}$

hard rigid phase of the shape memory polymers had also been reported by Ji *et al.* [15]. In their studies, the shape fixity at fixing temperature of $T_g - 20^\circ\text{C}$ of polyurethanes (PUs) was reported to decrease from 96% to 84% with an increase of PU hard-segment content from 30% to 50%.

Moreover, it was also found that R_f of the NGDE/PBA-a SMPs comparing at the same BA-a content increased with lower fixing temperature, i.e. from $T_g - 10^\circ\text{C}$ to 25°C . This behavior is because some molecular chain segments were unfixed at $T_g - 10^\circ\text{C}$. Therefore, the samples can partially restore to permanent shape that made the samples less controllable of its temporary shape. The shape fixity values at $T_g - 20^\circ\text{C}$ and at 25°C are close to 100% because these fixing temperatures were sufficiently low to freeze the motion of the molecular segments. The shape fixities of our samples, i.e. about 83.1–84.5% at $T_g - 10^\circ\text{C}$ and 96.5–97.4% at $T_g - 20^\circ\text{C}$, are still higher than that of polyurethane SMPs (i.e. about 77% at $T_g - 10^\circ\text{C}$ and 95% at $T_g - 20^\circ\text{C}$) [47] suggesting a less chain mobility of our polymer network comparing at the same fixing temperature below their T_g above.

3.6. Effect of BA-a contents on shape recovery behaviors of NGDE/PBA-a SMPs

Shape recovery behaviors of the aliphatic epoxy (NGDE)/polybenzoxazine (PBA-a) SMPs were studied using a fold-deploy shape memory test. Bending deformation was widely employed for evaluating shape memory properties of polymer materials due to a large deflection being easily obtained in a

range of small strain through bending [48]. Figure 10 presents snapshots of the shape recovery sequence at $T_g + 20^\circ\text{C}$ of the sample at 40 mol% BA-a. It can be seen that the sample can fully recover its permanent shape with 100% shape recovery or with recovery angle of 180° . In addition, all of our SMPs, i.e. with benzoxazine resin (BA-a) contents from 30–50 mol%, also displayed shape recovery performance of about 100% at $T_g + 20^\circ\text{C}$. The photographs of NGDE/PBA-a SMP at original shape, temporary shape and recovered shape at $T_g + 20^\circ\text{C}$ was presented in Figure 4b. This characteristic suggests that the deformation of stable PBA-a network could be recovered completely if the NGDE/PBA-a SMPs were heated to sufficiently high temperature. In addition, it implies that the NGDE/PBA-a copolymers are covalently crosslinked to form three-dimensional network structures which become reversibly rubbery at above T_g [49].

The effect of BA-a contents on recovery angle as a function of time for the NGDE/PBA-a SMPs under a bending test at T_g and $T_g + 20^\circ\text{C}$, are depicted in Figure 11 and Figure 12, respectively. From the figures, all samples can completely recover to their permanent shape. The recovery time of the SMPs was found to increase with increasing BA-a from 30 to 50 mol%, i.e. from 75 to 145 s at T_g and from 60 to 120 s at $T_g + 20^\circ\text{C}$. Its recovery time is about the same as that of shape memory materials based on epoxy and activity polyurethane (APU) [50] showing recovery time of about 120 s at their T_g . In addition, the curve in Figures 11 and 12 can be divided into three zones. The start stage (at a recovery angle of 0 to 50°), transition stage (a recovery angle of 50 to 150°) and terminal stage (a recovery angle of 150 to 180°). This behavior suggests that the NGDE/PBA-a SMPs have a relative low recovery rate at the start and terminal stage. At the start stage, the release of constrained force was followed by heavy friction among molecules, thus the recovery angle slowly increased. After that, fraction force reduced under the gradual adjustment of segments results in the slopes of recovery angle is sharply as named the transition stage. At the terminal stage, the shape recovery rate becomes slower than the transition stage because the constrained force of the sample had been released due to a little of it remaining [7, 37, 51].

In addition, the shape recovery time of the samples tended to decrease with increasing the active temperature from T_g to $T_g + 20^\circ\text{C}$. This phenomenon is

Figure 10. Series of images showed shape recovery of NGDE/PBA-a SMP with 40 mol% BA-a at a $T_g + 20^\circ\text{C}$ (108°C). The permanent and temporary shapes are rectangular and U-shape, respectively.

Figure 11. Recovery angle as a function of recovery time during the shape recovery process at a T_g of NGDE/PBA-a SMPs at various mole percents of BA-a: (●) 30 mol%, (■) 35 mol%, (◆) 40 mol%, (▲) 45 mol%, (▼) 50 mol%

Figure 12. Recovery angle as a function of recovery time during the shape recovery process at a $T_g + 20^\circ\text{C}$ of NGDE/PBA-a SMPs at various mole percents of BA-a: (●) 30 mol%, (■) 35 mol%, (◆) 40 mol%, (▲) 45 mol%, (▼) 50 mol%

due to the fact that, at higher temperature, the activated molecular chain segments can move more intensely. Moreover, the shape recovery time of the samples increased with an increasing amount of BA-a content. This implied that the movement of the molecular chain segment of the NGDE/PBA-a shape

memory samples could be more restricted with increasing BA-a content since an increasing of storage modulus at rubbery plateau was observed in the DMA results. The recovery times of our SMPs were in the same range as that of epoxy resin E-51 (WSR 618) cured by aromatic amine curing agent [37].

Therefore, the incorporation of the BA-a into the NGDE/PBA-a SMPs can prolong the shape recovery time thus broadening the range of application of these SMPs.

Furthermore, in order to observe the performance of the shape memory behavior over period of time for fixed temporary shape. The NGDE/PBA-a SMP at 40 mol% BA-a was used as a representative sample to demonstrate the shape memory behavior after the time period of 20 min, 7 days, 15 days and 30 days used to fix its temporary shape. The samples showed negligible change in its temporary shape after all time periods. In addition, the time for complete recovery to their permanent shape of these samples after heated up to $T_g + 20^\circ\text{C}$ was 84, 85, 85 and 86 s, respectively. This result implied that the performance of the SMPs based on the NGDE/PBA-a copolymers indicates a relatively good shape memory as they can be maintained over a long period of time.

3.7. Effect of BA-a contents on recovery stress of NGDE/PBA-a SMPs

The experimental procedure of the recovery stress test of the aliphatic epoxy (NGDE)/polybenzoxazine (PBA-a) SMPs is depicted in Figure 13. Firstly, the

sample at its permanent state was heated to 20°C above T_g ($T_g + 20^\circ\text{C}$) as seen in Figure 13a. After that it was applied by flexural load during heating at $T_g + 20^\circ\text{C}$ until its maximum deflection ($y_{\text{max}} = 10\text{ mm}$) as shown in Figure 13b. The deformed state of $y_{\text{max}} = 10\text{ mm}$ at $T_g + 20^\circ\text{C}$ is almost maintained after cooling down to room temperature. Then, the sample was held at room temperature under unloaded condition for 20 min as presented in Figure 13c. Finally, the sample was heated to $T_g + 20^\circ\text{C}$ by maintaining the fixed deflection constant as can be seen in Figure 13d. Recovery stress during heating was measured from the transition stage of the shape-fixed stage to the recovery shape stage.

The recovery stress versus time of the SMPs is shown in Figure 14. The maximum recovery stress of the samples were observed to be 0.25, 0.39, 0.62, 0.98 and 1.59 MPa at BA-a contents ranging from 30, 35, 40, 45 and 50 mol%, respectively. As a result, it could be seen that content of the BA-a is an efficient way to increase recovery stress of the SMPs. Recently, the recovery stress obtained from the thermomechanical analysis (TMA) experiments of shape memory polymer based on styrene cured with benzoyl peroxide has been studied [17, 52–54]. It

Figure 13. Photographs showing various states of bending in recovery stress process for NGDE/PBA-a SMPs: (a) permanent state of the sample at room temperature, (b) deformed state with $y_{\text{max}} = 10\text{ mm}$ at $T_g + 20^\circ\text{C}$, (c) shape-fixed state after cooling followed by unloading at room temperature for 20 min and (d) shape-recovered state after heating up to $T_g + 20^\circ\text{C}$ and stress during reheating was measured

Figure 14. Recovery stress versus time of NGDE/PBA-a SMPs at various mole percents of BA-a: (●) 30 mol%, (■) 35 mol%, (◆) 40 mol%, (▲) 45 mol%, (▼) 50 mol%

has been reported that the recovery stress obtained from the TMA experiments of the commercial styrene cured with benzoyl peroxide based shape memory polymer (Veriflex VF62 of CRG Industries in Dayton, OH) was reported to be about 0.05 MPa [17]. Therefore, some of our SMPs showed a significantly high shape recovery stress that could result in complete expansive shape recovery within a spatially constraint environment such as narrowed or middle-sized vessel. In addition, the increase of the recovery stress was observed in shape memory epoxy nanocomposites [12]. It was found that at maximum SiC nano powder filler loading (20 wt%), the recovery stress of the nanocomposite was observed to be 1.5 MPa, i.e. 1 time greater than that of the neat epoxy SMP, having the recovery stress of about 0.8 MPa. Interestingly, NGDE/PBA-a SMPs can provide recovery stress about 6 times from 0.25 MPa at 30 mol% BA-a to 1.59 MPa at 50 mol% BA-a, which is substantially more than that of the epoxy SMPs nanocomposites. This is to say that the increasing of the recovery stress of the NGDE/PBA-a SMPs was due to the presence of the BA-a in the copolymers, resulting in increasing crosslink density that can enhance storage modulus at rubbery state of the copolymers [49]. Thus, the SMPs based on the polybenzoxazine is a good candidate to use for deployable structures, such as hinge [55].

4. Conclusions

Polybenzoxazine blending with aliphatic epoxy based shape memory polymer (SMP) is developed. The effect of benzoxazine resin content in aliphatic epoxy

based SMPs on thermal stability, mechanical properties and shape memory properties were characterized. An incorporation of the benzoxazine resin in the aliphatic epoxy based SMP resulted in an increase of glass transition temperature, storage modulus, crosslink density and recovery stress of the SMPs. The same trend was also observed in their flexural strength and modulus at room temperature as well as in the rubbery state. Interestingly, the obtained SMPs provided an outstanding shape fixity value up to 99% at room temperature. At different active temperatures, i.e. T_g and $T_g + 20^\circ\text{C}$, all SMPs needed only 1–3 minutes to fully recover to their permanent shape. Moreover, the addition of the benzoxazine fraction can prolong the shape recovery time of the resulting SMPs. Therefore, the obtained aliphatic epoxy/polybenzoxazine SMPs are attractive as shape memory materials to be used in a broad range of applications such as hinge or deployable structure.

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References

- [1] Liu Y., Du H., Liu L., Leng J.: Shape memory polymers and their composites in aerospace applications: A review. *Smart Materials and Structures*, **23**, 023001/1–023001/22 (2014). DOI: [10.1088/0964-1726/23/2/023001](https://doi.org/10.1088/0964-1726/23/2/023001)
- [2] Kolesov I. S., Radusch H.-J.: Multiple shape-memory behavior and thermal-mechanical properties of peroxide cross-linked blends of linear and short-chain branched polyethylenes. *Express Polymer Letters*, **2**, 461–473 (2008). DOI: [10.3144/expresspolymlett.2008.56](https://doi.org/10.3144/expresspolymlett.2008.56)
- [3] Kang S. M., Lee S. J., Kim B. K.: Shape memory polyurethane foams. *Express Polymer Letters*, **6**, 63–69 (2012). DOI: [10.3144/expresspolymlett.2012.7](https://doi.org/10.3144/expresspolymlett.2012.7)
- [4] Ehrenstein G. W.: *Polymeric materials: Structure, properties, applications*. Hanser, Munich (2001).
- [5] Liu L., Cai W.: Novel copolyester for a shape-memory biodegradable material *in vivo*. *Materials Letters*, **63**, 1656–1658 (2009). DOI: [10.1016/j.matlet.2009.04.037](https://doi.org/10.1016/j.matlet.2009.04.037)
- [6] Fan K., Huang W. M., Wang C. C., Ding Z., Zhao Y., Purnawali H., Liew K. C., Zheng L. X.: Water-responsive shape memory hybrid: Design concept and demonstration. *Express Polymer Letters*, **5**, 409–416 (2011). DOI: [10.3144/expresspolymlett.2011.40](https://doi.org/10.3144/expresspolymlett.2011.40)

- [7] Rimdusit S., Lohwerathama M., Hemvichian K., Kasemsiri P., Dueramae I.: Shape memory polymers from benzoxazine-modified epoxy. *Smart Materials and Structures*, **22**, 075033/1–075033/12 (2013). DOI: [10.1088/0964-1726/22/7/075033](https://doi.org/10.1088/0964-1726/22/7/075033)
- [8] Leng J., Lan X., Liu Y., Du S.: Shape-memory polymers and their composites: Stimulus methods and applications. *Progress in Materials Science*, **56**, 1077–1135 (2011). DOI: [10.1016/j.pmatsci.2011.03.001](https://doi.org/10.1016/j.pmatsci.2011.03.001)
- [9] Karger-Kocsis J., Kéki S.: Biodegradable polyester-based shape memory polymers: Concepts of (supra) molecular architecture. *Express Polymer Letters*, **8**, 397–412 (2014). DOI: [10.3144/expresspolymlett.2014.44](https://doi.org/10.3144/expresspolymlett.2014.44)
- [10] Hu J., Zhu Y., Huang H., Lu J.: Recent advances in shape-memory polymers: Structure, mechanism, functionality, modeling and applications. *Progress in Polymer Science*, **37**, 1720–1763 (2012). DOI: [10.1016/j.progpolymsci.2012.06.001](https://doi.org/10.1016/j.progpolymsci.2012.06.001)
- [11] Meng Q., Hu J.: A review of shape memory polymer composites and blends. *Composites Part A: Applied Science and Manufacturing*, **40**, 1661–1672 (2009). DOI: [10.1016/j.compositesa.2009.08.011](https://doi.org/10.1016/j.compositesa.2009.08.011)
- [12] Liu Y., Gall K., Dunn M. L., McCluskey P.: Thermo-mechanics of shape memory polymer nanocomposites. *Mechanics of Materials*, **36**, 929–940 (2004). DOI: [10.1016/j.mechmat.2003.08.012](https://doi.org/10.1016/j.mechmat.2003.08.012)
- [13] Santhosh Kumar K. S., Biju R., Reghunadhan Nair C. P.: Progress in shape memory epoxy resins. *Reactive and Functional Polymers*, **73**, 421–430 (2013). DOI: [10.1016/j.reactfunctpolym.2012.06.009](https://doi.org/10.1016/j.reactfunctpolym.2012.06.009)
- [14] Meng H., Li G.: A review of stimuli-responsive shape memory polymer composites. *Polymer*, **54**, 2199–2221 (2013). DOI: [10.1016/j.polymer.2013.02.023](https://doi.org/10.1016/j.polymer.2013.02.023)
- [15] Ji F. L., Hu J. L., Li T. C., Wong Y. W.: Morphology and shape memory effect of segmented polyurethanes. Part I: With crystalline reversible phase. *Polymer*, **48**, 5133–5145 (2007). DOI: [10.1016/j.polymer.2007.06.032](https://doi.org/10.1016/j.polymer.2007.06.032)
- [16] Havens E., Snyder E. A., Tong T. H.: Light activated shapem polymers and associated applications. *Proceeding of SPIE, Smart Structures and Materials*, **5762**, 48–55 (2005). DOI: [10.1117/12.606109](https://doi.org/10.1117/12.606109)
- [17] Ivens J., Urbanus M., De Smet C.: Shape recovery in a thermoset shape memory polymer and its fabric-reinforced composites. *Express Polymer Letters*, **5**, 254–261 (2011). DOI: [10.3144/expresspolymlett.2011.25](https://doi.org/10.3144/expresspolymlett.2011.25)
- [18] Dorigato A., Giusti G., Bondioli F., Pegoretti A.: Electrically conductive epoxy nanocomposites containing carbonaceous fillers and *in-situ* generated silver nanoparticles. *Express Polymer Letters*, **7**, 673–682 (2013). DOI: [10.3144/expresspolymlett.2013.64](https://doi.org/10.3144/expresspolymlett.2013.64)
- [19] Fejös M., Karger-Kocsis J.: Shape memory performance of asymmetrically reinforced epoxy/carbon fibre fabric composites in flexure. *Express Polymer Letters*, **7**, 528–534 (2013). DOI: [10.3144/expresspolymlett.2013.49](https://doi.org/10.3144/expresspolymlett.2013.49)
- [20] Xie T., Rousseau I. A.: Facile tailoring of thermal transition temperatures of epoxy shape memory polymers. *Polymer*, **50**, 1852–1856 (2009). DOI: [10.1016/j.polymer.2009.02.035](https://doi.org/10.1016/j.polymer.2009.02.035)
- [21] Zheng N., Fang G., Cao Z., Zhao Q., Xie T.: High strain epoxy shape memory polymer. *Polymer Chemistry*, **6**, 3046–3053 (2015). DOI: [10.1039/C5PY00172B](https://doi.org/10.1039/C5PY00172B)
- [22] Wright W. W.: High performance polymers and composites. Wiley, New York (1991).
- [23] Ishida H., Agag T.: Handbook of benzoxazine resins. Elsevier, New York (2011).
- [24] Ishida H., Rimdusit S.: Very high thermal conductivity obtained by boron nitride-filled polybenzoxazine. *Thermochimica Acta*, **320**, 177–186 (1998). DOI: [10.1016/S0040-6031\(98\)00463-8](https://doi.org/10.1016/S0040-6031(98)00463-8)
- [25] Rimdusit S., Tanthapanichakoon W., Jubsilp C.: High performance wood composites from highly filled polybenzoxazine. *Journal of Applied Polymer Science*, **99**, 1240–1253 (2006). DOI: [10.1002/app.22607](https://doi.org/10.1002/app.22607)
- [26] Jubsilp C., Takeichi T., Hiziroglu S., Rimdusit S.: High performance wood composites based on benzoxazine-epoxy alloys. *Bioresource Technology*, **99**, 8880–8886 (2008). DOI: [10.1016/j.biortech.2008.04.057](https://doi.org/10.1016/j.biortech.2008.04.057)
- [27] Rimdusit S., Jubsilp C., Tiptipakorn S.: Alloys and composites of polybenzoxazines: Properties and applications. Springer, Singapore (2013).
- [28] Jubsilp C., Rimdusit S., Takeichi T.: Aniline-based polybenzoxazine and their copolymers or composites: Molecular design and potential applications. in ‘Aniline: structure/physical properties, reactions and environmental effects’ (eds.: Hernandez K., Holloway M.) Nova Science Publishers, New York, 55–90 (2013).
- [29] Jubsilp C., Punson K., Takeichi T., Rimdusit S.: Curing kinetics of benzoxazine–epoxy copolymer investigated by non-isothermal differential scanning calorimetry. *Polymer Degradation and Stability*, **95**, 918–924 (2010). DOI: [10.1016/j.polymdegradstab.2010.03.029](https://doi.org/10.1016/j.polymdegradstab.2010.03.029)
- [30] Rimdusit S., Kunopast P., Dueramae I.: Thermomechanical properties of arylamine-based benzoxazine resins alloyed with epoxy resin. *Polymer Engineering and Science*, **51**, 1797–1807 (2011). DOI: [10.1002/pen.21969](https://doi.org/10.1002/pen.21969)
- [31] Kimura H., Matsumoto A., Hasegawa K., Ohtsuka K., Fukuda A.: Epoxy resin cured by bisphenol A based benzoxazine. *Journal of Applied Polymer Science*, **68**, 1903–1910 (1998). DOI: [10.1002/\(SICI\)1097-4628\(19980620\)68:12<1903::AID-APP2>3.0.CO;2-P](https://doi.org/10.1002/(SICI)1097-4628(19980620)68:12<1903::AID-APP2>3.0.CO;2-P)

- [32] Erden N., Jana S. C.: Synthesis and characterization of shape-memory polyurethane–polybenzoxazine compounds. *Macromolecular Chemistry and Physics*, **214**, 1225–1237 (2013). DOI: [10.1002/macp.201200315](https://doi.org/10.1002/macp.201200315)
- [33] Ishida H.: Process for preparation of benzoxazine compounds in solventless systems. U.S. Patent 5543516, USA (1996).
- [34] Lan X., Liu Y., Lv H., Wang X., Leng J., Du S.: Fiber reinforced shape-memory polymer composite and its application in a deployable hinge. *Smart Materials and Structures*, **18**, 024002/1–024002/6 (2009). DOI: [10.1088/0964-1726/18/2/024002](https://doi.org/10.1088/0964-1726/18/2/024002)
- [35] Tobushi H., Hayashi S., Hoshio K., Makino Y., Miwa N.: Bending actuation characteristics of shape memory composite with SMA and SMP. *Journal of Intelligent Material Systems and Structures*, **17**, 1075–1081 (2006). DOI: [10.1177/1045389X06064885](https://doi.org/10.1177/1045389X06064885)
- [36] Rimdusit S., Ishida H.: Development of new class of electronic packaging materials based on ternary systems of benzoxazine, epoxy, and phenolic resins. *Polymer*, **41**, 7941–7949 (2000). DOI: [10.1016/S0032-3861\(00\)00164-6](https://doi.org/10.1016/S0032-3861(00)00164-6)
- [37] Liu Y., Han C., Tan H., Du X.: Thermal, mechanical and shape memory properties of shape memory epoxy resin. *Materials Science and Engineering: A*, **527**, 2510–2514 (2010). DOI: [10.1016/j.msea.2009.12.014](https://doi.org/10.1016/j.msea.2009.12.014)
- [38] Jubsilp C., Ramsiri B., Rimdusit S.: Effects of aromatic carboxylic dianhydrides on thermomechanical properties of polybenzoxazine-dianhydride copolymers. *Polymer Engineering and Science*, **52**, 1640–1648 (2012). DOI: [10.1002/pen.23107](https://doi.org/10.1002/pen.23107)
- [39] Silverstein R. M., Bassler G. C., Morrill T. C.: Spectrometric identification of organic compounds. Wiley, New York (1981).
- [40] Schuh C., Schuh K., Lechmann M. C., Garnier L., Kraft A.: Shape-memory properties of segmented polymers containing aramid hard segments and polycaprolactone soft segments. *Polymers*, **2**, 71–85 (2010). DOI: [10.3390/polym2020071](https://doi.org/10.3390/polym2020071)
- [41] Cao Y-P., Guan Y., Du J., Peng Y-X., Yip C. W., Chan A. S. C.: Polymer network-poly(ethylene glycol) complexes with shape memory effect. *Chinese Journal of Polymer Science*, **21**, 29–33 (2003).
- [42] Rimdusit S., Pirstpindvong S., Tanthapanichakoon W., Damrongsakkul S.: Toughening of polybenzoxazine by alloying with urethane prepolymer and flexible epoxy: A comparative study. *Polymer Engineering and Science*, **45**, 288–296 (2005). DOI: [10.1002/pen.20273](https://doi.org/10.1002/pen.20273)
- [43] Barnell T., Margraf T. W.: Healable, shape memory polymer for reflexive composites. in ‘SAMPE 2008 - 52nd International SAMPE Symposium, Baltimore, USA’ p.10 (2008).
- [44] Rimdusit S., Tiptipakorn S., Jubsilp C., Takeichi T.: Polybenzoxazine alloys and blends: Some unique properties and applications. *Reactive and Functional Polymers*, **73**, 369–380 (2013). DOI: [10.1016/j.reactfunctpolym.2012.04.022](https://doi.org/10.1016/j.reactfunctpolym.2012.04.022)
- [45] Biju R., Gouri C., Reghunadhan Nair C. P.: Shape memory polymers based on cyanate ester-epoxy-poly (tetramethyleneoxide) co-reacted system. *European Polymer Journal*, **48**, 499–511 (2012). DOI: [10.1016/j.eurpolymj.2011.11.019](https://doi.org/10.1016/j.eurpolymj.2011.11.019)
- [46] Beblo R., Gross K., Mauck Weiland L.: Mechanical and curing properties of a styrene-based shape memory polymer. *Journal of Intelligent Material Systems and Structures*, **21**, 677–683 (2010). DOI: [10.1177/1045389X10364860](https://doi.org/10.1177/1045389X10364860)
- [47] Hu J. L., Ji F. L., Wong Y. W.: Dependency of the shape memory properties of a polyurethane upon thermomechanical cyclic conditions. *Polymer International*, **54**, 600–605 (2005). DOI: [10.1002/pi.1745](https://doi.org/10.1002/pi.1745)
- [48] Ratna D., Karger-Kocsis J.: Shape memory polymer system of semi-interpenetrating network structure composed of crosslinked poly (methyl methacrylate) and poly (ethylene oxide). *Polymer*, **52**, 1063–1070 (2011). DOI: [10.1016/j.polymer.2010.12.054](https://doi.org/10.1016/j.polymer.2010.12.054)
- [49] Rousseau I. A.: Challenges of shape memory polymers: A review of the progress toward overcoming SMP’s limitations. *Polymer Engineering and Science*, **48**, 2075–2089 (2008). DOI: [10.1002/pen.21213](https://doi.org/10.1002/pen.21213)
- [50] Liu Y., Sun H., Tan H., Du X.: Modified shape memory epoxy resin composites by blending activity polyurethane. *Journal of Applied Polymer Science*, **127**, 3152–3158 (2013). DOI: [10.1002/app.37688](https://doi.org/10.1002/app.37688)
- [51] Fan M., Yu H., Li X., Cheng J., Zhang J.: Thermomechanical and shape-memory properties of epoxy-based shape-memory polymer using diglycidyl ether of ethoxylated bisphenol-A. *Smart Materials and Structures*, **22**, 055034/1–055034/7 (2013). DOI: [10.1088/0964-1726/22/5/055034](https://doi.org/10.1088/0964-1726/22/5/055034)
- [52] Nji J., Li G.: A biomimic shape memory polymer based self-healing particulate composite. *Polymer*, **51**, 6021–6029 (2010). DOI: [10.1016/j.polymer.2010.10.021](https://doi.org/10.1016/j.polymer.2010.10.021)
- [53] Li G., Uppu N.: Shape memory polymer based self-healing syntactic foam: 3-D confined thermomechanical characterization. *Composites Science and Technology*, **70**, 1419–1427 (2010). DOI: [10.1016/j.compscitech.2010.04.026](https://doi.org/10.1016/j.compscitech.2010.04.026)
- [54] Li G., Nettles D.: Thermomechanical characterization of a shape memory polymer based self-repairing syntactic foam. *Polymer*, **51**, 755–762 (2010). DOI: [10.1016/j.polymer.2009.12.002](https://doi.org/10.1016/j.polymer.2009.12.002)
- [55] Tandon G. P., Goecke K., Cable K., Baur J.: Environmental durability of fabric-reinforced shape-memory polymer composites. *Journal of Intelligent Material Systems and Structures*, **21**, 1365–1381 (2010). DOI: [10.1177/1045389X10386265](https://doi.org/10.1177/1045389X10386265)