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SHAPE MEMORY POLYMERS FROM BENZOXAZINE-MODIFIED EPOXY

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Thesis Title	SHAPE MEMORY POLYMERS FROM BENZOXAZINE-MODIFIED EPOXY
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มณฑา หล่อวีระธรรม : พอลิเมอร์ที่จำรูปร่างได้จากอีพอกซีที่ดัดแปรด้วยเบนซอกซาซีน (Shape Memory Polymers from Benzoxazine-Modified Epoxy) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. ศราวุธ ริมดุสิต, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: ดร. เกศินี เหมวิเชียร, 104 หน้า.

งานวิจัยนี้ได้ศึกษาสมบัติการจำรูปร่างได้ของระบบพอลิเมอร์ที่มีองค์ประกอบคืออีพอกซีชนิดอะโรมาติก (E), อีพอกซีชนิดแอลิฟาติก (N), สารบ่มชนิด Jeffamine D230 (D) ผสมกับเบนซอกซาซีนมอนอเมอร์(B) โดยสัดส่วนโดยโมลระหว่างสาร D ต่อ สาร B ที่ 1/0, 0.8/0.2, 0.6/0.4, 0.4/0.6, 0.2/0.8 และ 0/1 ได้ถูกนำมาใช้เป็นสารบ่มสำหรับระบบอีพอกซีที่ประกอบไปด้วยอีพวกซีชนิด E และชนิด N ในสัดส่วนโดยโมลคงที่ เท่ากับ 1/1 ซึ่งในงานวิจัยนี้ได้ศึกษาผลของปริมาณเบนซอกซาซีนเรซินในระบบสารบ่มลูกผสมข้างต้น ต่อสมบัติทางความร้อน สมบัติทางกล และสมบัติการจำรูปร่างได้ของระบบพอลิเมอร์ที่จำรูปร่างได้จากอีพอกซี โดยทำการวิเคราะห์ด้วยเทคนิค Differential scanning calorimetry (DSC), Dynamic mechanical analysis (DMA), การทดสอบสมบัติทางกลภายใต้แรงดัดโค้ง และการทดสอบการคืนรูปร่าง จากการศึกษาพบว่า พอลิเมอร์ที่จำรูปร่างได้จากอีพอกซีที่ได้รับการดัดแปรด้วยเบนซอกซาซีนเรซินมีค่าความแข็งแรงและค่าความแข็งเกร็งภายใต้แรงดัดโค้งมากกว่าพอลิเมอร์ที่จำรูปร่างได้จากอีพอกซีดั้งเดิมทั้งที่อุณหภูมิห้องและที่อุณหภูมิสูงกว่าอุณหภูมิการเปลี่ยนสถานะคล้ายแก้ว 20 องศาเซลเซียส จากการเติมเบนซอกซาซีนเรซินสูงสุดที่ปริมาณ 1 โมล เพื่อทำหน้าที่เป็นสารบ่มอีพอกซี ทำให้อุณหภูมิการเปลี่ยนสถานะคล้ายแก้วมีค่าสูงที่สุดซึ่งสูงกว่าค่าที่ได้จากอีพอกซีที่ใช้ Jeffamine D230 เป็นสารบ่มเพียงอย่างเดียวถึง 72 องศาเซลเซียส ผลจากการทดสอบสมบัติการจำรูปร่างได้ แสดงให้เห็นว่าสมรรถนะการคืนรูปร่างและการคงรูปร่างของพอลิเมอร์มีค่าดีขึ้นเมื่อเติมเบนซอกซาซีน โดยพบว่าพอลิเมอร์ที่จำรูปร่างได้จากอีพอกซีที่ดัดแปรด้วยเบนซอกซาซีนที่สัดส่วนต่างๆใช้เวลาในการคืนรูปร่างสู่รูปร่างเดิมอย่างสมบูรณ์เพียง 2-3 นาที และให้ค่าการคงรูปร่างสูงถึง 98-99% รวมทั้งมีอัตราการคืนรูปร่างสูงถึง 90-100% ซึ่งสมบัติเหล่านี้จะเพิ่มขึ้นตามการเพิ่มอุณหภูมิที่ใช้ในการคืนรูปร่าง นอกจากนี้ค่าความเค้นของการคืนรูปร่างจะเพิ่มขึ้นเมื่อปริมาณเบนซอกซาซีนเพิ่มขึ้น โดยเพิ่มขึ้นจาก 20 กิโลปาสคาลเป็น 38 กิโลปาสคาล เมื่อเติมสารบ่มเบนซอกซาซีนที่ปริมาณ 1 โมล เมื่อทำการทดสอบสมบัติทางกลภายใต้แรงดัดโค้งซ้ำ 100 รอบ พบว่าพอลิเมอร์ที่ได้สามารถคืนกลับสู่รูปร่างเดิมได้อย่างสมบูรณ์ โดยที่ความแข็งแรงภายใต้แรงดัดโค้งมีการเปลี่ยนแปลงเพียงเล็กน้อยเท่านั้น

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต
สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก
ปีการศึกษา 2554 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม

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MONTHA LOHWERATHAM: SHAPE MEMORY POLYMERS FROM BENZOXAZINE-MODIFIED EPOXY. ADVISOR: ASSOC. PROF. SARAWUT RIMDUSIT, Ph.D., CO-ADVISOR: KASINEE HEMVICHIAN, Ph.D., 104 pp.

Shape memory properties of specimens consisted of aromatic epoxy (E), aliphatic epoxy (N), Jeffamine D230 (D) and BA-a benzoxazine monomer (B) were evaluated. The mole ratio of D/B = 1/0, 0.8/0.2, 0.6/0.4, 0.4/0.6, 0.2/0.8 and 0/1 were used as a mixed curing agent for epoxy system with a fixed E/N mole ratio of 1/1. Effects of BA-a content on 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 (T_g). The presence of 1 mole BA-a as a curing agent provided the specimen with the highest T_g, i.e. about 72°C higher than that of epoxy-based SMP cured by Jeffamine D230. The results of the shape-memory tests suggested that the obtained SMPs showed outstanding shape recovery and shape fixity performances with an addition of the BA-a. 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%) which increased with increasing recovery temperature. In addition, recovery stress values increased with increasing BA-a mole ratio from 20 kPa to 38 kPa, when BA-a up to 1 mole ratio was added. All of the SMP samples fully recovered to their original shape at the end of 100 cycles with minimum change on their flexural strength.

Department : Chemical Engineering	Student's Signature
Field of Study : Chemical Engineering	Advisor's Signature
Academic Year : 2011	Co-advisor's Signature

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CHAPTER 1

INTRODUCTION

1.1 Overview

Shape memory polymers (SMPs) have gained a great deal of attention in the field of smart materials research during the last two decades. In some applications, SMPs have been used to substitute shape memory alloys (SMA) because they possess more advantage including excellent processing, light weight, low cost, easy control of activation temperature and great flexibility (Atli et al., 2009). It evinces great interest due to the adaptability for shape change when temperature switches from below to above the transition temperature. They provide great potential for application in self-deployable structures for space applications (Leng et al., 2011), micron-sized actuators, orthodontic applications, medical treatment etc (Biju et al., 2012).

Generally, thermosets are widely used as SMP materials because thermoset SMPs have chemical crosslinks, and can be softened but do not melt at elevated temperatures (Ehrenstein, 2001). Thermoset resins are preferred to thermoplastics in some applications i.e. spacecraft, due to their better mechanical performance and environmental endurance (Lake and Beavers, 2002). Epoxy resin is one of the most popular thermoset that have been used as structure and can apply for extreme applications. Shape memory epoxies have attracted much attention from academic and industrial researchers because they possess excellent shape memory performance. Recently (Atli et al., 2009), they are commercially available which reported properties are comprised in the range of large deformations, low recovery stresses and low glass transition temperature.

Recently, Xie et al., (2009) developed methods to tailor epoxy SMP's T_g. 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 $89^{o}C$. 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 (Lu et al., 2010). The ability to fine tune glass transition temperature and mechanical property of the SMPs is thus important requirement to suit their particular applications. There are two major methods use to meet the requirement, structure modification and blending with the other. The latter one is preferable due to ease of processing and tailored properties.

Benzoxazine resins are a novel kind of thermosetting phenolic resin that can be synthesized from phenol, formaldehyde and amine group. The curing of the resins involves ring-opening polymerization without a catalyst or a curing agent and does not produce by-products upon curing which results in void-free products. Polybenzoxazines have some reported outstanding properties such as high glass-transition temperature, high thermal stability, near-zero volumetric shrinkage or expansion upon polymerization, low melt viscosity before cure resulting in its high process ability, low water absorption. Furthermore, polybenzoxazines possess high electrical properties, excellent mechanical performance and wide molecular design flexibility (Ning and Ishida, 1994 and Wang and Ishida, 2002).

In recent years, epoxy-benzoxazine alloys have gained much interest from researchers to enhance the alloys properties (Rimdusit et al., 2011). Ishida and Allen (1996) have studied benzoxazine-epoxy copolymers system. It was revealed that the significant increase in crosslink density of the thermosetting matrix strongly influences to its mechanical properties that leads to significant increases in the glass transition temperature, flexural stress, and flexural strain at break over those of the polybenzoxazine homopolymer, with only a minimal loss of stiffness.

Therefore, the first aim of this study is to develop benzoxazine-epoxy based SMPs using EPON 826, NGDE and Jeffamine D230 as aromatic epoxy, aliphatic epoxy and curing agent, respectively. The thermal and mechanical properties are characterized. The second one is to investigate properties on shape memory such as shape fixity and shape recovery.

1.2 Objectives

1. To develop shape memory epoxy modified with benzoxazine resin for mechanical properties, shape memory properties and thermal stability enhancement.
2. To study the effects of benzoxazine resin and curing agent contents on properties of benzoxazine-modified epoxy based shape memory polymer.

1.3 Scopes of the Study

1. Synthesis of BA-a typed benzoxazine resin by solventless synthesis technology.
2. Preparation of polymeric alloys using EPON 826 as aromatic epoxy and NGDE as aliphatic epoxy and using Jeffamine D230 as curing agent. Parameters to be investigated is Jeffamind D230/BA-a contents: 1/0, 0.8/0.2, 0.6/0.4, 0.4/0.6, 0.2/0.8 and 0/1 mole ratio.
3. Characterization.
    - 3.1. Thermal and mechanical properties of epoxy-benzoxazine alloys
        - Differential Scanning Calorimeter (DSC)
        - Dynamic Mechanical Analysis (DMA): three point bending mode
        - Universal Testing Machine: flexural mode
    - 3.2 Shape memory properties (shape fixity and shape recovery)

CHAPTER 2

THEORY

2.1 Shape Memory Polymers (SMPs)

Shape memory polymers (SMPs) represent responsive polymers which can fix deformed temporary shape and recover their original shape depend on external stimulus. They can be stimulated by temperature, pH, chemicals, and light upon application of an external stimulus, they also have the ability to change their shape. The shape of thermally responsive shape memory polymers can be readily changed above the shape memory transition temperature (T_{trans}) and the deformation can be fixed below this temperature. As a result, when they are heated above T_{trans} their original shape can be recovered automatically.

The permanent shape can be recovered when the material is heated back above a critical temperature. This phenomenon is the shape memory effect. The critical temperature at which the polymer stiffness changes drastically with heating or cooling is called the glass transition temperature (T_g). The low temperature region where the material has high stiffness is referred to as the glassy state, and the region with low stiffness at high temperature is called the rubbery state.

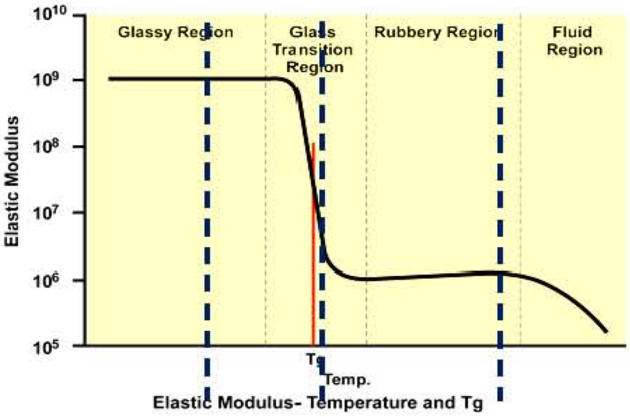


Figure 2.1 Elasticity versus temperature of amorphous polymers (Feninat et al., 2002).

For a polymer to possess shape memory properties, it has to have a permanent network and a reversible phase. Permanent shape can be achieved via chemical crosslinking or physical crosslinking (e.g. chain entanglement and crystallization). The fixing of temporary shapes is due to the reversible phase, which corresponds to either a glass transition or a melting transition. When a reversible thermal phase transition is utilized to fix temporary shapes, the corresponding temperature is typically called the shape memory transition temperature (T_{trans}). Since most polymers possess at least one reversible thermal transition, they can be converted into SMP by introducing a permanent network (e.g. chemical crosslinking).

Most of the shape memory effects are based on the existence of separated phases related to the coiled polymer structure, cross-links, hydrogen bonding, etc. Chains tend to go back to the random coiled configuration, unless they are constrained by permanent or temporary cross-links and partial bonding. The shape memory transformation depends on the mechanism by which polymer molecules transpose between the constrained and random entangled conformations. Shape memory polymers are processed by conventional methods to have a permanent shape. This permanent shape is stored in the system while the polymer assumes different temporary shapes, and by heating the polymer higher than the transition temperature, the permanent shape can be restored. The phase corresponding to the higher transition polymer component acts as the physical crosslink responsible for the permanent shape. The second component acts as a molecular switch and helps to freeze temporary shapes below the transition temperature.

Chemical crosslinks can also be used in elastomeric shape memory polymers, instead of physical crosslinks. Temporary shapes can thus be formed above the transition temperature and can be frozen by keeping the material below the transition temperature, while the permanent shape can be obtained again by heating above the s transition temperature. This is the reason why most of the thermally induced SMPs have a one-way shape memory effect: they remember one permanent shape formed at the higher temperature, while many temporary shapes are possible at lower temperatures for which the systems do not have any memory.

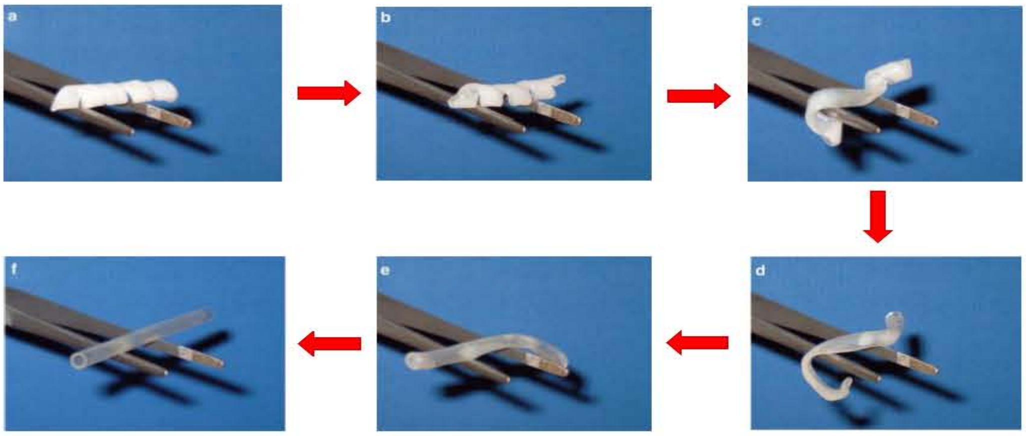


Figure 2.2 Time series photographs that show the recovery of a shape memory tube. (a)–(f) Start to finish of the process takes a total of 10 s at 50°C (Behl and Lendlein, 2007).

In terms of chemical structure, SMPs can be considered as phase-segregated linear block copolymers having a hard segment and a soft segment. The hard segment acts as the frozen phase and the soft segment acts as the reversible phase. The reversible phase transformation of the soft segment is responsible for the shape memory effect. Researcher found that the shape memory effect could be controlled by a thermo-mechanical cycle. When the SMP is heated above the glass transition temperature of the hard segment, the material can be processed. This original shape can be memorized by cooling the SMP below the glass transition temperature of the hard segment. When the shaped SMP is cooled below the glass transition temperature of the soft segment at which the shape is deformed, the temporary shape is fixed. The original shape is recovered by heating the material above the glass transition temperature of the soft segment. Another method for setting a temporary shape involves the material being deformed at a temperature lower than the glass transition temperature of the soft segment, resulting in stress and strain being absorbed by the soft segment. When the material is heated above the glass transition temperature of the soft segment, the stresses and strains are relieved and the material returns to its original shape. Examples of polymers used to prepare hard and soft segments of SMPs include various polyether, polyacrylate, polyamide, polysiloxane, polyurethane, polyether amide, polyvinyl ether, polyurethane-urea, polyether ester, and urethane/butadiene copolymers. The shape-fixing process, deformation, and shape recovery are schematically illustrated in Figure 2.3. It describes the thermo-mechanical cycle:

- Process 1 The polymer pellets are heated above the melting temperature of the hard segment, T_m, then the polymer melts and is cross-linked. This is denoted as the first synthetic form.
- Process 2 The polymer is cooled and crystallization occurs, having the primary shape (predetermined shape). This is the fixed shape into which the polymer returns upon triggered by the temperature change.
- Process 3 The polymer is heated to the T_g, together with the application of an external force, the polymer is left in a secondary shape.
- Process 4 The external force in process 3 is still applied on the copolymer but the temperature is lowered until it reaches a temporary shape.
- Process 5 Once the copolymer is heated above the T_g, it returns to the primary shape. A thermal-mechanical cycle of the shape memory effect is complete.

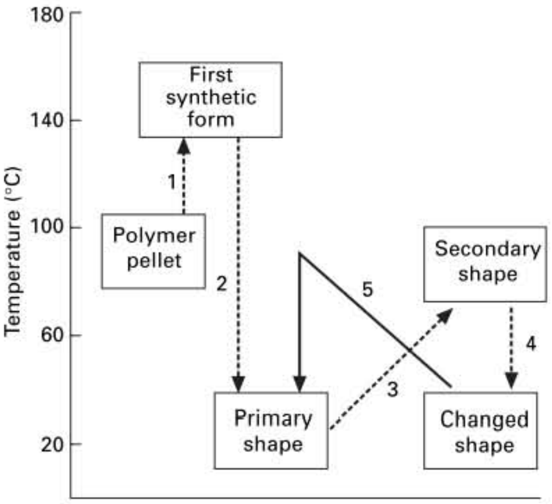


Figure 2.3 Shape fixing and recovering processes of a shape memory polymer (Rousseau, 2008).

The four classes of SMPs are defined later. Typical examples of SMP compositions for each SMP class as well as a summary of their resulting SMP properties as reported in the literature are included (Rousseau, 2008).

Class I: Chemically Cross-linked Glassy Thermosets. In such a system, the macromolecules are covalently linked and the resulting three-dimensional network exhibits a T_g below or above which the thermoset becomes reversibly glassy or rubbery, respectively. T_g governs the shape memory behavior in this case and the temporary shape is commonly formed at T_g and fixed by cooling below T_g. The permanent shape is set by the covalent bonds of the three-dimensional network during processing. For this class of materials, usually excellent shape fixity and recovery are observed due to the high modulus below T_g and excellent rubber elasticity above T_g. Indeed, the most common examples for this class of materials are epoxy-based SMPs that have been reported in the literature to show fixing and recovery of 95–100% when explicitly quantified. Typically, such epoxy systems are commercially available thermoset epoxy systems with proprietary formulation.

Class II: Chemically Cross-linked Semi-crystalline Rubbers. Here, the permanent shape is again set by the chemical crosslinks formed during processing; however, a temporary shape is formed and fixed when the sample is deformed above the T_m of the crystalline regions and subsequently cooled below their crystallization temperature. For this class of materials, there exists a wider range of shape fixity and recovery attainable that depends on the composition of the network compared to class I SMPs. Examples of such SMPs include cross-linked ethylene-vinyl acetate rubbers with 30–95% recovery depending on their composition. Cross-linked polyethylene systems commonly used as heat shrink materials with fixing and recovery of up to 96 and 94%, respectively, and cross-linked poly-cyclooctene with almost complete (≈100%) shape fixity and recovery have also been reported.

Therefore, class II SMPs can be tailored to optimize performance and reach shape fixity and recovery values of up to 95%. However, because the temporary shape is fixed through crystallization, the modulus in the fixed state is relatively low, in the order of 10^8 Pa, one order of magnitude lower than that for class I SMPs. Moreover, because intrinsically polymers show large thermal hysteresis between melting and crystallization transition temperatures, it is expected that class II SMPs would have to be cooled to lower temperatures relative to T_g compared to class I SMPs to allow full crystallization for good shape fixity, potentially extending the SM cycle time.

Class III: Physically Cross-linked Amorphous Thermoplastics. For physically cross-linked amorphous thermoplastics, the SM behavior is attributed to the T_g of the soft segment regions and, therefore, a deformed shape obtained at $T > T_g$ is maintained by cooling below the glass transition. In contrast, the permanent shape of the network is provided by physical crosslinking of the hard segments through molecular interactions such as van der Waals, dipole–dipole interactions, or hydrogen bonding. Physically cross-linked amorphous PUs represents the majority of this class of SMPs. Again, they are generally synthesized following common synthetic routes such as reacting diisocyanates and polyols with a diol or a triol as a cross-linker. Their shape fixity and recovery abilities have been reported to vary from 80 to 90% and 75 to 100%, respectively. Researchers have reported how the length and/or molecular weight distribution of soft segment and the hard segment content affect SM performance, especially with respect to recovery rate and to a lesser extent shape fixity and recovery speed. For example, as noted earlier, an MDI-PTMG-based PU showed increased shape retention and a higher rate of recovery if a bimodal molecular weight distribution of soft segment and a copolymer block-type arrangement were used. Again, this emphasizes the need for optimizing material/structure/properties of SMPs in order to increase SM performance. With regards to cycle life, Ohki et al. reported on the SM behavior of a glass fiber reinforced PU, which underwent 60 consecutive mechanical cycles without failure and only a slight accumulation of residual strain as the cycle number increased; however, they tested only five consecutive thermo-mechanical cycles. In addition, Lin and Chen tested their polyether-based PU SMP through 200 consecutive SM cycles. They observed an improvement in shape fixity and shape recovery for subsequent cycles with increasing cycle number although with a slight decrease in these properties relative to the initial, starting strain of the first cycle. In conclusion, class III SMPs generally exhibit slightly lower SM performances compared to class I and II SMPs, specifically shape recovery and fixity. This is mainly explained by a loss in physical crosslinks integrity caused by mechanical deformation. However, class III-SMPs exhibit a relatively high modulus below T_g, comparable to that of class I SMPs, in the order of 10^9 Pa.

Class IV: Physically Cross-linked Semi-crystalline Block Copolymers. Very similar in their structure to class III SMPs described earlier, the physically cross-linked semi-crystalline block copolymers exhibit SM behavior about the soft segment T_m, whereas retention of their permanent shape is achieved by physical crosslinking between hard segments through molecular interactions in crystalline regions. Again, for this class of SMPs, the most commonly reported systems are PU-based with common chemistries involving for instance the use of polycaprolactone diol (PCL) as a soft segment, methylene diisocyanate (MDI) as a hard segment, and butandiol (BD) as the cross-linker. Commercially available PU formulations have also been used. For this class of SMPs, shape fixity and recovery have been stated to range anywhere from 65 to 96% and 56 to 100% depending on the composition (soft segments length and/or molecular weight distribution and hard segment content). For instance, hard segment contents varying from 10 to 33% have been reported as optimum values for increased SM behavior in the PU systems described by Li et al. and Park et al., respectively. In addition, Li et al. also stated that their PCL/MDI/BD-based PU exhibited a lower limit of soft segment molecular weight, of 2000 to 3000 g/mol.

Although shape memory behavior of class III and IV SMPs can be tailored to reach relatively high performance levels comparable to those of class I and II SMPs, they require SM training through a minimum of 2–3 cycles. Indeed, in contrast to covalently cross-linked SMPs, a significant irrecoverable strain generally results from the first completed SM cycle which persists through subsequent thermo-mechanical cycles. Therefore, an optimized behavior for a specific class IV SMP is achieved after the sample has been trained, that is, it has been cycled thermo-mechanically several times according to the application requirements prior to utilization.

2.1.1 Shape Memory Properties

For a polymer to possess shape memory properties, it has to have a permanent network and a reversible phase. The phase showing the highest thermal transition acts as the physical cross-link and is responsible for the permanent shape. Above this temperature the polymer melts and can be processed. A second phase serves as a molecular switch and enables the fixation of the temporary shape. The transition temperature for the fixation of the switching segments can be a glass transition (T_g). After forming the material above the switching temperature, but below T_g, the temporary shape can be fixed by cooling the polymer below the switching temperature. Heating up the material above T_g again cleaves the physical cross-links in the switching phase as a result of its entropy elasticity (Lendlein and Kelch, 2002).

Entropy elasticity which described flow of the polymer chains under stress can be stopped by cross-linking the chains. The cross-linkage points act as permanent entanglements and prevent the chains from slipping from each other. The cross-links can either be chemical and/or physical.

Chemically cross-linked polymers form insoluble materials. Their shape is fixed during the cross-linking and cannot be changed afterwards. Thermoplastic elastomers contain physical net-points. A requisite for the formation of the net-points is the existence of certain morphology of a phase-separated material, as found for block copolymers containing thermodynamically immiscible components. The highest thermal transition is related to the hard-segment-forming phase. If this thermal transition is not exceeded, these domains will stabilize the permanent shape by acting as physical net-points in the material. Besides the net-points, networks contain flexible components in the form of amorphous chain segments. If the glass transition temperature of these segments is below the working temperature, the networks will be elastic. They show entropy elasticity and can be stretched with a loss of entropy. The distances between net-points increase during stretching and they become oriented. As soon as the external force is released, the material returns to its original shape and gains back the entropy lost before. As a result, the polymer network is able to maintain the mechanical stress in equilibrium.

The elastic modulus increases upon heating; the coefficient of thermal expansions for a stretched elastomer is negative above the glass transition temperature; below the T_g value the sample behaves like a glass and contracts if it is further cooled down (Figure 2.4).

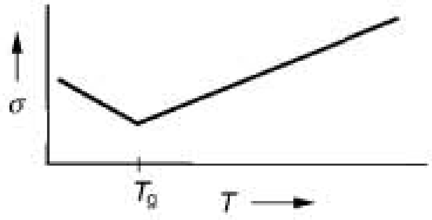


Figure 2.4 Plot of the stress σ in an elastomer which is stretched and then kept under constant strain over a temperature range above and below the T_g value (Lendlein and Kelch, 2002).

2.1.2 Shape Memory Effect (SME)

Shape memory behavior can be observed in various polymer systems which are significantly different in molecular structure, morphology and processing method. Figure 2.5 shows a general approach for producing a shape memory effect. A temporary shape can be fixed after processing and the permanent shape subsequently can be recovered from the temporary shape when triggered by the external stimulus such as heating to a certain temperature.

In its molecular mechanism, the polymer will exhibit shape memory functionality if the material can be stabilized in the deformed state in a temperature range that is relevant for the particular application. This can be reached by using the network chains as a kind of molecular switch. For this purpose the flexibility of the segments should be a function of the temperature. One possibility for a switch function is a thermal transition (T_g) of the network chains in the temperature range of interest for the particular application. At temperatures above T_g the chain segments are flexible, whereas the flexibility of the chains below this thermal transition is at least partly limited. In the case of a transition from the rubber-elastic or viscous state to the glassy state, the flexibility of the entire segment is limited. If the thermal transition chosen for the fixation of the temporary shape is a melting point, strain-induced crystallization of the switching segment can be initiated by cooling the material which has been stretched above the T_g value. The crystallization achieved is always incomplete, which means that a certain amount of the chains remains amorphous. The crystallites formed prevent the segments from immediately reforming the coil-like structure and from spontaneously recovering the permanent shape that is defined by the net-points. The permanent shape of shape-memory networks is stabilized by covalent net-points, whereas the permanent shape is fixed by the phase with the highest thermal transition at T_g.

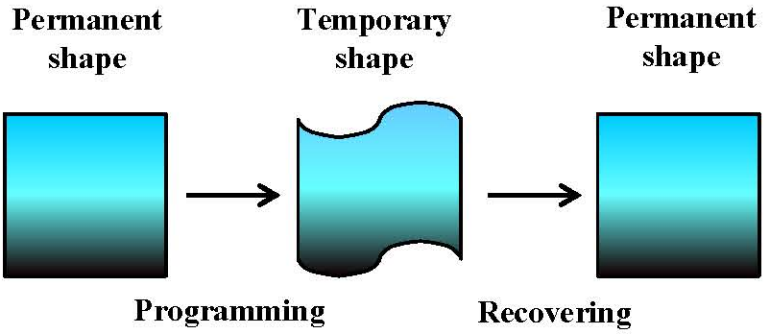


Figure 2.5 Schematic representation of processing of shape memory effect.

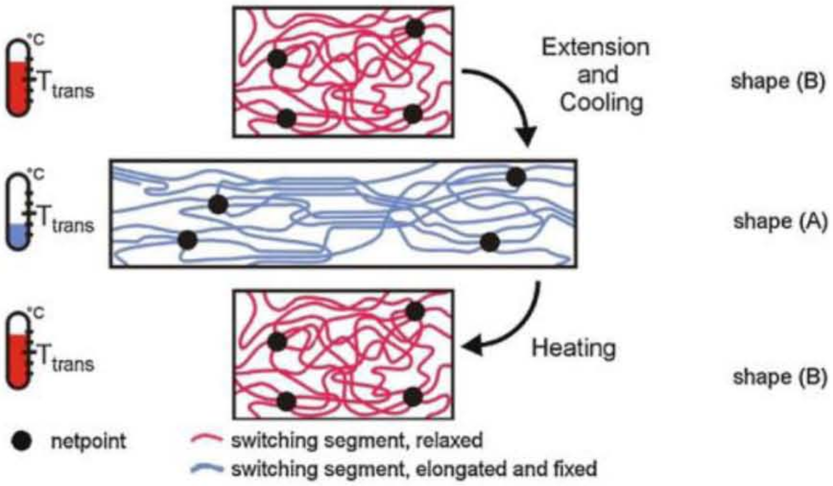


Figure 2.6 Molecular mechanism of the thermally-induced SME. T_g is the thermal transition temperature of the switching phase (Behl and Lendlein, 2007).

The molecular mechanism of programming the temporary form and recovering the permanent shape is demonstrated schematically in Figure 2.6. A quick deformation of the amorphous material by a sudden subsequent decrease or reduction of the external force, the polymer reforms its original shape. Such polymers will also exhibit a shape memory effect if a suitable programming technique is applied. The temporary entanglements of the polymer chains which act as physically net-points can be used for the fixation of the permanent shape. This thermal transition can be used as a switching transition if the glass transition is in the temperature range that is relevant for a specific application.

2.1.3 Parameters for Characterization of SMPs (Hu, 2007)

To characterize the shape memory properties of polymers, a set of parameters is needed. First, the parameters should be able to reflect the nature of polymers. Second, to distinguish them from other properties of materials, shape memory properties are shown through a series of thermo-mechanical cyclic processes. Therefore the parameters should be able to define the whole shape memory processes as well. At last, the design of the parameters should consider the potential applications. The parameters are introduced in the following.

1) Shape fixity (R_f)

The parameter which described when a shape memory polymer is heated to a temperature above the transition temperature for triggering shape memory behaviors (T_g), it can develop large deformations which can be mostly fixed by cooling to a temperature below T_g. This parameter was proposed to describe the extent of a temporary shape being fixed in one cycle of shape memorization. Shape fixity is equal to the amplitude ratio of the fixed deformation to the total deformation. Shape fixity related to both structures of polymers and the thermo-mechanical conditions of shape memorization. As compared with the structures of SMPs, the thermo-mechanical conditions play equally or even more important roles in determining the shape fixity and other shape memory properties.

2) Shape recovery (R_r)

A given SMP holding a deformation by low temperature can restore its original shape by being heated up above T_g. Shape recovery is used to reflect how well an original shape has been memorized. Compared with the case of shape fixity, the diverse and confused usages take place not only to notation but also to mathematical expressions for this parameter.

Like shape fixity, shape recovery depends on both the structures of polymers and the thermo-mechanical conditions of shape memorization.

3) Recovery stress

Recovery stress stems from the elastic recovery stress generated in the deformation process. When SMPs are heated and deformed, the elastic stress is generated and the elastic stress is stored when SMPs are cooled below T_g. If the deformed and fixed SMPs are reheated above T_g, the stress stored in SMPs is released as shape recovery stress. In this sense, one cycle of shape memorization can be looked on as a thermo-mechanical cycle consisting of stress generation, stress storage, and stress release. SMPs are considered promising in development of smart actuators. The characterization of shape recovery stress is therefore essential.

The dilemma for the characterization of recovery stress of SMPs is chiefly caused by viscoelasticity of polymers, especially for the thermoplastic SMPs. Owing to the limitations of equipment and efficiency of heat transfer, it is practically impossible to heat or cool an SMP to a certain temperature in a sufficiently short time in experiments. Therefore the stress relaxation is inevitable by all means if only the SMP is in a constrained state. As a consequent, the stress generated in deformation must be lost more or less in the shape fixing and shape recovery processes. Additionally, the rate of stress relaxation alters with the temperature change in the whole shape memory process, which means that its influence on the recovery stress is unknown. In the other words, the recovery stress may change all the time with the stress relaxation, but the exact nature of the change is uncertain. Therefore it is difficult to calculate the recovery stress in quantitative terms.

4) Recovery rate

This parameter is a dimension for describing the speed when a given SMP recovered from a temporary shape to its original shape by being heated. The parameter has no uniform name, which called were as speed of recovery process, deformation recovery speed or shape recovery speed. The parameter can be measured qualitatively and quantitatively.

Liu et al. investigated the shape recovery process of some SMPs and qualitatively studied the shape recovery speed using a video camera at a rate of 20 frames/s. It was evident that the SMP was restored to its original shape in 0.7 s. Li et al. and Luo et al. investigated the shape recovery of SMPs with a constant heating rate. Through the curve of shape recovery as a function of temperature, the shape recovery speed was calculated.

2.1.4 Applications of Shape Memory Polymer (Leng et al., 2011)

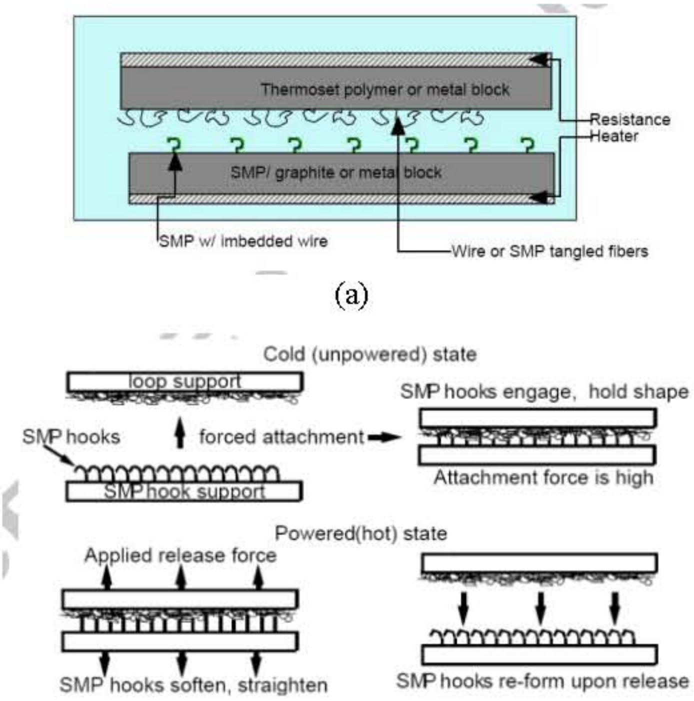
The potential applications for SMPs that include smart clothing, space and medical applications, smart structural repair, reconfigurable tooling, micro-electromechanical systems, actuators, self-healing, health monitoring, biomedical devices, self-repairing auto bodies, kitchen utensils, switches, sensors, intelligent packing, heat-shrinkable tubes, and biosensors. Specific examples from recent works are detailed from now on.

1) Deployable structures

For the traditional aerospace deployable devices, the change of structural configuration in-orbit is accomplished through the use of a mechanical hinge, stored energy devices or motor driven tools. There are some intrinsic drawbacks for the traditional deployment devices, such as complex assembling process, massive mechanisms, large volumes and undesired effects during deployment. In contrast, the deployment devices fabricated using SMPs and their composites may overcome certain inherent disadvantages.

2) Automobile

SMPs have been used in automobile engineering, and many interesting products have been developed. Some interesting applications of SMPs include seat assemblies, reconfigurable storage bins, energy-absorbing assemblies, tunable vehicle structures, hood assemblies, releasable fastener systems, airflow control devices, adaptive lens assemblies and automotive body molding. The reasons for using SMPs are due to their excellent advantages such as shape memory behavior, easy manufacturing, high deformed strain and low cost. That is why they have attracted a lot of attention in automobile engineering and have even been used to replace the traditional structural materials, actuators or sensors.



(a)

(b)

Figure 2.7 A reversible attachment based on SMPs: (a) an alternative SMP based smart hook and loop attachment embodiment; (b) schematics of working process of the active hook-and-loop fastener (Leng et al., 2011).

As a typical example, SMPs are proposed to be used for the reversible attachments, as shown in Figure 2.7. In this embodiment (see Figure 2.7a), one of the two surfaces to be engaged contains smart hooks, at least one portion of which is made from SMPs materials. By actuating the hook and/or the loop, the on-demand remote engagement and disengagement of joints/attachments can be realized (see Figure 2.7b). With a memorized hook shape, the release is effective and the pull-off force can be dramatically reduced by heating above the T_g. It can be used for a reversible lockdown system in the lockdown regions between the vehicle body and closure.

SMPs can also be used in an airflow control system to solve a long-time problem for automobiles. As we know, airflow over, under, around, and/or through a vehicle can affect many aspects of vehicle performance, including vehicle drag, vehicle lift and down force, and cooling/heating exchange. Reduction to vehicle drag reduces the consumption of fuel. A vehicle airflow control system, which comprises an activation device made of SMP material, actively responses to the external activation signal and alters the deflection angle accordingly. Thus, the airflow is under control based on the environmental changes.

3) Self-healing composite system

A healable composite system for use as primary load-bearing aircraft components has been developed by Cornerstone Research Group (CRG), Inc. The composite system consists of piezoelectric structural health monitoring system and thermal activation systems based on SMPs (see Figure 2.8). Upon damaging, the monitoring system will sense the location and magnitude of damage, send the corresponding signals to the controlling system, resistively heat the SMPs at the location of damage, and finally the induced shape-recovery of SMPs will heal the damage. As shown in Figure 2.9, the SMP composite system can recover 75-85 % of flexural strength upon bending test.

Figure 2.8 Self-healing system based on SMP (Leng et al., 2011).

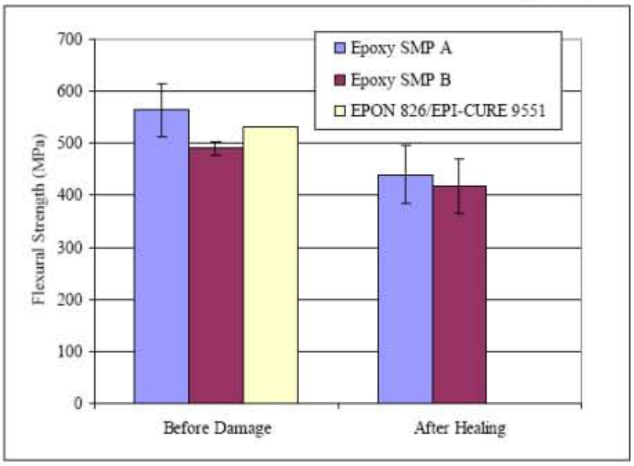


Figure 2.9 Flexural strength of epoxy-based composites before damage and after healing (Leng et al., 2011).

4) Morphing structures

Flight vehicles are envisioned to be multi-functional so that they can perform more missions during a single flight, such as an efficient cruising and a high maneuverability mode. When the airplane moves towards other portions of the flight envelope, its performance and efficiency may deteriorate rapidly. To solve this problem, researchers have proposed to radically change the shape of the aircraft during flight. By applying this kind of technology, both the efficiency and flight envelope can be improved. This is because different shapes correspond to different trade-offs between beneficial characteristics, such as speed, low energy consumption and maneuverability. For instance, the Defense Advanced Research Projects Agency (DARPA) is also developing morphing technology to demonstrate such radical shape changes. As illustrated in Figure 2.10, Lockheed Martin is addressing technologies to achieve a z-shaped morphing change under the DARPA's program fund.

During the development of morphing aircraft, finding a proper skin under certain criteria is crucial. Generally, a wing skin is necessary, especially for the wing of a morphing aircraft. Researchers focus their works on investigating proper types of materials that are currently available to be used as a skin material for a morphing wing. In this case, the SMPs show more advantages for this application. It becomes flexible when heated to a certain degree, and then returns to a solid state when the stimulus is terminated. Since SMPs holds the ability to change its elastic modulus, they could potentially be used in the mentioned concept designs.

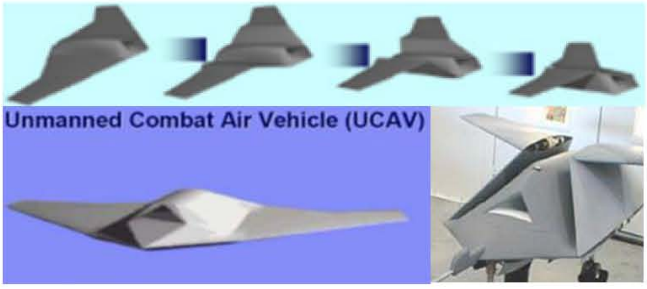


Figure 2.10 Z-shaped morphing wings produced by Lockheed Martin (Leng et al., 2011).

5) Reflector

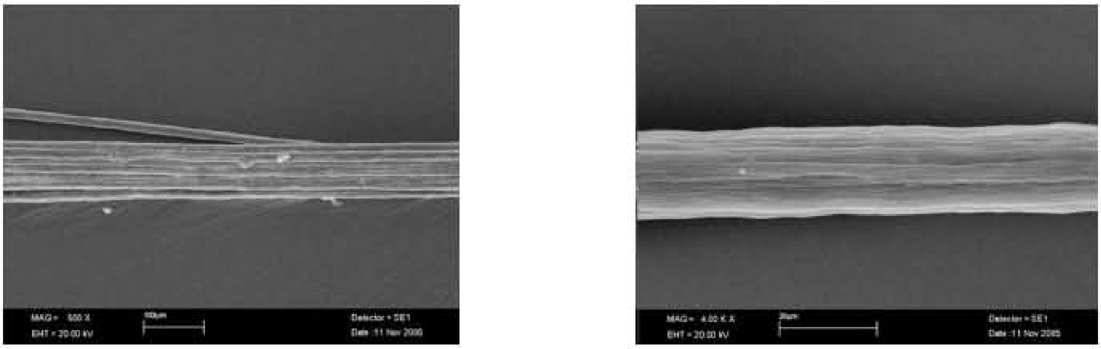
Stiffness for a flexible reflector, a new kind of solid surface deployable reflector was developed by Harris Corporation, which is similar to a spring back reflector. By enabling large aperture antennas to be stowed within an existing launch vehicle, the reflector is envisioned to significantly promote the ability of satellite communication systems. In addition, Harris Corporation is now considering the use of elastic memory composite (EMC) materials for the system (see Figure 2.11) to realize the full potential. The stiffener around the edge of the antenna can be made by EMC materials. The antenna can be stowed in the spacecraft and then its deployment can be triggered by the shape memory effect to finally hold the surface of the antenna in a precision micro-system.


(a) (b)

Figure 2.11 Shape memory polymer composite reflectors: (a) pre-deformed shape and (b) recovered shape (Leng et al., 2011).

6) Shape memory polymer textiles and applications

Shape memory fibers based on SMPs can be implemented to develop smart textiles that respond to thermal stimulus. SMPs can be used for textiles, clothing and related products in the form of shape memory fibers, shape memory yarns and shape memory fabrics. Hu et al. at Hong Kong Polytechnic University have comprehensively investigated shape memory finishing chemicals and technologies for cotton fabrics, wool fabrics and garment finishing. Figure 2.12 shows morphology of a shape memory fiber detected by SEM. On the surface of a single filament of this shape memory fiber, the grooves can be observed which are due to the traces after the solution is extruded from the pinholes of the spinneret. The diameter of the single filament is measured as about 16 μm. Furthermore, shape memory finishing fabrics can be produced with coating shape memory emulsion or combining shape memory films. When washed in hot water or dried at temperatures higher than T_g, their wrinkles will disappear and they can recover the original flat shape. It is also expected that the smart fibers may be used for novel fiber sensors or advanced medical usage.



(a) (b)

Figure 2.12 Scanning electron microscopy of shape memory fiber: (a) View of multi-filament (500×) (b) view of an isolated single filament (4000×) (Leng et al., 2011).

2.1.5 Shape Memory Epoxy (Feldkamp and Rousseau, 2010)

Epoxies are an important family of shape memory polymers (SMPs) due to their excellent stability and thermo-mechanical endurance and the high values of shape fixity and shape recovery. Actuators based on these materials can be designed for large tensile elongations (e.g., 75% or higher) or large recovered stresses (e.g., 3 MPa or higher). We show that an SMP based on an epoxy network with both chemical and physical crosslinks could be strained up to 75% in 4 repeated shape memory cycles with tensile stresses close to 3 MPa. Shape fixity and shape recovery values were close to 98% and 96%, respectively, without any significant change between the first and subsequent cycles.

In previous reports, we showed that epoxy resins exhibit excellent instantaneous shape memory effect with nearly complete shape fixity and shape recovery at deformation strains above 6–7%. Adequate material design enabled for maintaining these excellent characteristics even under more drastic conditions, which included increased times spent under load in the hot stage, increased times in the temporarily fixed state, or even extensive cycle repetitions.

2.1.6 Shape Memory Polymer Composites (Leng et al., 2011)

1) Particle-filled shape memory polymers

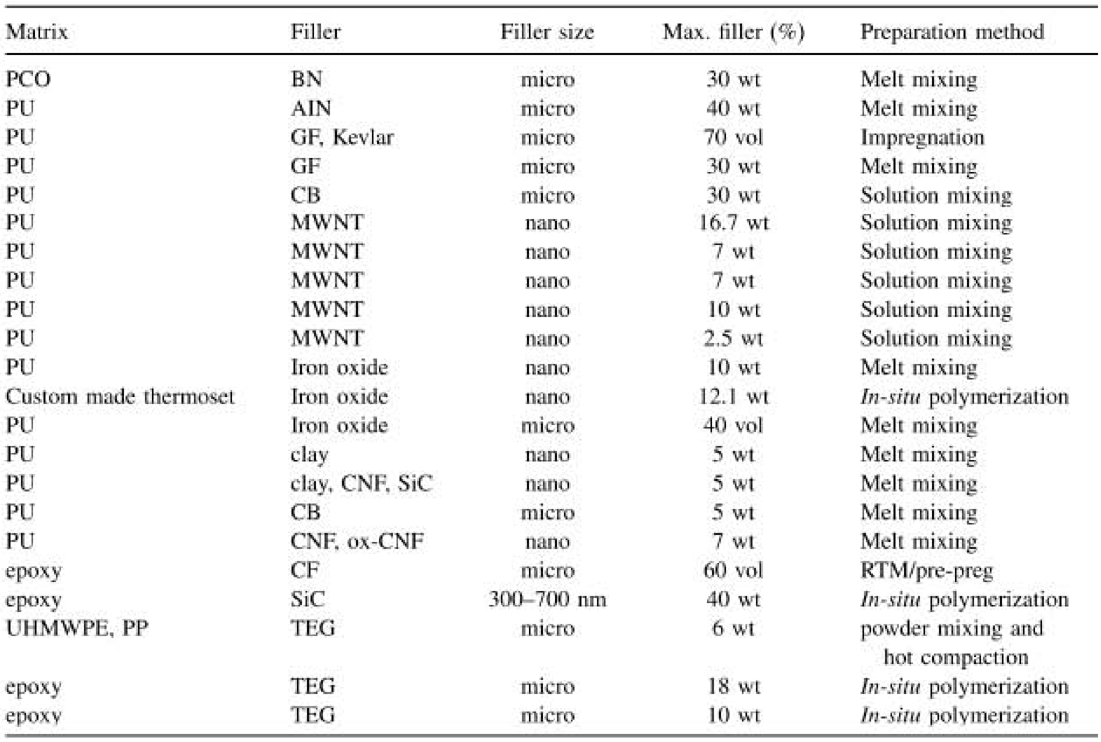
The thermo mechanical behavior of SMPs can be designed either through modification of the molecular structure of the polymer or through the addition of functional fillers into the polymer as a matrix for multi-phase composites. The SMP composites can be classified as particle- or fiber- reinforced depending on the type of filler they employ. SMP composites filled with particles (e.g., carbon black, carbon nanotubes, carbon nano-fibers, SiC, Ni, Fe_3O_4, clay, and short or continuous fibers may meet various requirements in practical applications. In general, the SMP composites filled with particles or short fiber develop some particular function, such as high electrical conductivity, magnetic-responsive performance, or high stiffness on the micro scale. Hence, this type of SMP composites is studied as a multifunctional material. Yang and Huang investigated the thermo mechanical properties of polyurethane SMP filled with carbon powders. Their results demonstrate that the incorporation of carbon powders is an efficient means of increasing the recovery stress. In addition, Gall et al., (2002) comprehensively investigated the thermo mechanics of SMPs and their composites, including a SiC reinforced epoxy SMP. The

SiC/SMP nano-composites were found to have a higher elastic modulus and were capable of generating higher recovery forces in comparison with pure SMP specimen carbon nano-fibers have the potential to be used in nano-electronic devices, such as artificial muscles, as well as in electrochemical energy storage matrices. Carbon nano-fibers usually vary from 5 to 1000 microns in length and are between 50 to 300 nm in diameter. The Young's modulus of these nano-fibers can reach as high as 1.2 TPa and some samples have been reported to have tensile strengths up to 64 GPa, compared to conventional carbon fibers that have strengths equal to about 4.0-5.0 GPa. Thus, it is expected that composites filled with carbon nano-fibers may present better performances when compared to the conventional carbon fiber reinforced materials. Consequently, carbon nano-fibers with diameters of 24 nm and lengths 300 nm were used for reinforcement of SMPs by Manpreet. They demonstrated that the presence of nano-fibers in SMP leaded to significant reinforcement for SMPs. Pure SMPs or particle-reinforced SMPs are not suitable for use as structural materials; however, they are generally used as functional materials through the addition of some particular particle fillers. For instance, electrically conductive carbon black, carbon nanotubes, nickel powders and chopped carbon fibers are incorporated into SMPs to develop electro active SMPs. Ferromagnetic Fe_3O_4-filled SMPs can lead to magnetism induced SMPs. Moreover, infrared optical fiber could be embedded into SMPs to develop light-induced SMPs by transmitting the infrared light through the fiber to heat the SMP.

2) Fiber-reinforced shape memory polymers

In general, since the improvement in their mechanical properties is quite limited and their strength and stiffness remain low, SMP composite’s reinforced with particles or short fibers cannot be used as structural materials. In contrast, continuous fiber-reinforced SMPs offer a significant improved in strength, stiffness and resistance against relaxation and creep, thereby providing better mechanical properties. As both a functional and structural material, these SMPs show good potential for many advanced applications. When used as actuator materials, they require no moving parts. Substantial interest has therefore been generated for the use of fiber-reinforced SMPs in deployable structures including antennas, trusses and solar arrays. In addition, most studies regarding SMP composites are focused on thermoplastic SMP resins such as polyurethane SMP. However, the relatively poor thermal and mechanical properties (e.g., temperature, moisture and chemical resistance) of thermoplastic SMPs cannot fully meet practical requirements. Thermosetting SMPs, however, show an improvement in the aforementioned properties and can be widely used as functional or structural materials. A carbon fiber fabric reinforced polyurethane SMP was developed for industrial applications. The bending recovery ratio of this SMP based laminates was larger than that of pure SMP sheet for any given recovery time. Epoxy SMP composites (Elastic Memory Composite, EMC) show great potential for light weight deployable spacecraft structures applications. Composite Technology Development (CTD), Inc. firstly started to comprehensively researched the EMC and the relevant applications in deployable structures since the 1990s. A study of the micro-mechanisms of deformation in EMC materials has been conducted by CTD and Gall et al. Their studies have investigated several interaction phenomena between the reinforcement fibers and the SMP resin in an epoxy EMC laminate. Due to the effects of micro buckling and the shift in the neutral-strain surface, the fiber-reinforced SMP composites laminate can achieve much larger compressive strains than traditional hard-resin composite. In addition, Leng et al. developed a fiber-reinforced thermosetting styrene-based SMP composite. Based on the high strain capability and relatively good mechanical properties, the fiber reinforced SMP composites show potential for deployable structures applications. The aforementioned carbon-fiber reinforced SMP composites exhibit better mechanical and thermo mechanical properties than pure SMPs, and they can also be activated by loading a voltage on the carbon fibers embedded in the SMP matrix. Hence, they could be somewhat described as a multi-functional materials. In addition to carbon-fiber reinforced SMPs, glass-fiber or Kevlar-fiber reinforced SMPs are also an important type of shape memory composite. Liang et al. previously investigated glass and Kevlar fiber reinforced thermoplastic SMP composites. They found an improvement in stiffness but a decrease in recoverable strain as a result of the incorporation of the reinforcement. Ohki et al. investigated the mechanical and shape recovery properties of thermoplastic SMP composites reinforced by chopped strand glass fiber, especially for the relationship between fiber weight fraction and recoverability. With the incorporation of 50 wt% of glass fiber, they found that the failure stress increased by 140% while the recovery rate decreased by 62%.

Table 2.1 Summary for the filled SMP systems.



Matrix	Filler	Filler size	Max. filler (%)	Preparation method
PCO	BN	micro	30 wt	Melt mixing
PU	AIN	micro	40 wt	Melt mixing
PU	GF, Kevlar	micro	70 vol	Impregnation
PU	GF	micro	30 wt	Melt mixing
PU	CB	micro	30 wt	Solution mixing
PU	MWNT	nano	16.7 wt	Solution mixing
PU	MWNT	nano	7 wt	Solution mixing
PU	MWNT	nano	7 wt	Solution mixing
PU	MWNT	nano	10 wt	Solution mixing
PU	MWNT	nano	2.5 wt	Solution mixing
PU	Iron oxide	nano	10 wt	Melt mixing
Custom made thermoset	Iron oxide	nano	12.1 wt	*In-situ* polymerization
PU	Iron oxide	micro	40 vol	Melt mixing
PU	clay	nano	5 wt	Melt mixing
PU	clay, CNF, SiC	nano	5 wt	Melt mixing
PU	CB	micro	5 wt	Melt mixing
PU	CNF, ox-CNF	nano	7 wt	Melt mixing
epoxy	CF	micro	60 vol	RTM/pre-preg
epoxy	SiC	300–700 nm	40 wt	*In-situ* polymerization
UHMWPE, PP	TEG	micro	6 wt	powder mixing and hot compaction
epoxy	TEG	micro	18 wt	*In-situ* polymerization
epoxy	TEG	micro	10 wt	*In-situ* polymerization

Notes: PCO: poly-cyclooctene, PU: polyurethane, UHMWPE: ultra-high molecular weight polyethylene, PP: polypropylene, BN: boron nitride, AIN: aluminum nitride, GF: glass fiber, CB: carbon black, MWNT: multi wall carbon nanotube, clay: organoclay, CNF: carbon nano-fiber, oxygen rich, surface modified carbon nano-fiber, SiC: silicon carbide, CF: carbon fiber, TEG: thermo-expanded graphite, RTM: resin transfer molding (Gunes and Jana, 2008).

2.2 Epoxy Resin

The generic term epoxy (epoxide in Europe) is now understood to mean the base (thermoplastic, uncured) resins as well as the resultant cross-linked (thermoset, cured) plastic. The epoxy, epoxide or oxirane group is a three-membered ring consisting of two carbon atoms and one oxygen atom. The nature of this three-membered ring makes it highly reactive. The structure for an epoxy resin is given in Figure 2.13. Chemically, an epoxy resin contain one or more epoxy (oxirane) groups per molecule which can be situated terminally, cyclicly, or internally in a molecule and can be converted to a solid through a thermosetting reaction.

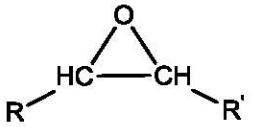


Figure 2.13 General structure of an epoxy resin.

Three major types of epoxy resin:

1. Cycloaliphatic epoxy resins (R and R′ are part of a six-membered ring).
2. Epoxidized oils (R and R′ are fragments of an unsaturated fatty acid, such as oleic acid in soybean oil).
3. Glycidated resins (R is hydrogen and R′ can be a polyhydroxyphenol, polybasic acid, or polyamine). There are the epoxides used in most commercial application.

Diglycidyl Ether of Bisphenol (Standard Epoxy)

Most widely used epoxy resins are made from diglycidyl ether of bisphenol A. The chemical structure of bisphenol A is illustrated in Figure 2.14.

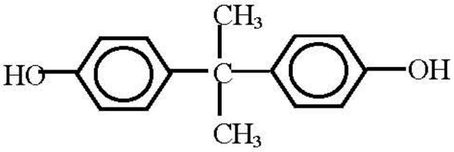


Figure 2.14 Chemical structure of bisphenol A.

Bisphenol A epoxy resins find large volume application in protective coating, and significant uses as adhesive, sealants impregnate, bonding, and laminating materials. In addition epoxy resin used in this study is diglycydyl ether of bisphenol A (DGEBA). The formation of DGEBA from bisphenol A and epichlorohydrin is shown in Figure 2.15. From the reaction, DGEBA is obtained by reacting epichlorohydrin with bisphenol A in the presence of sodium hydroxide. The reaction takes place in two steps; they are the formation of a chlorohydrin intermediate and the dehydrohalogenation of the intermediate to the diglycydyl ether, respectively. Each molecule of the diglycydyl ether will react with that of the bisphenol A at the epoxide group, forming eventually the higher molecular weight DGEBA at last.

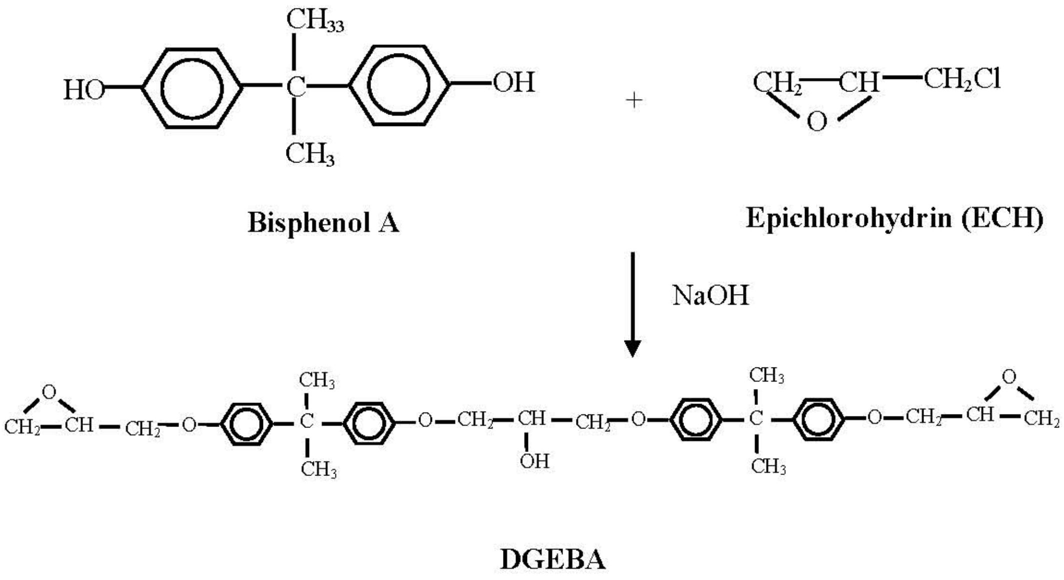


Figure 2.15 Formation of diglycydyl ether of bisphenol A (DGEBA).

The choice of resin and curing agent depends on the application and on handling characteristic (viscosity, pot life, gel time); curing temperature and time; use properties (mechanical, chemical, thermal and electrical); toxicological and environmental limit; and cost. A description of curing agents is given in Table 2.2.

Basic Characteristics of Epoxy Resins

The epoxy resins possess a preferably unique combination of properties as following:

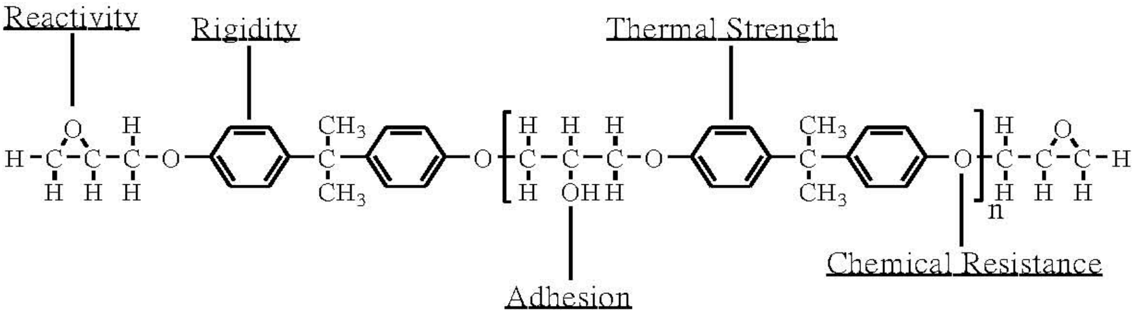


Figure 2.16 Sources of epoxy properties.

1. **Low viscosity**. The liquid epoxy resins and their curing agents can produce low viscosity, easy to process (or modify) systems.
2. **Easy cure**. Epoxy resins cure rapidly and easily at practically any temperature from 5 to 150'C, depending on the selection of curing agents.
3. **Low shrinkage**. Their low shrinkage during cure is one of the mast advantageous properties of the epoxy resins. Furthermore, epoxy resins react with very little rearrangement and without volatile by-products being evolved.
4. **High adhesive strengths.** Owing to the chemical makeup, mainly the presence of the polar hydroxyl and ether groups, the epoxy resins are excellent adhesives. They can be cured with low shrinkage, thus the various surface contacts set up between the liquid epoxy resins formulation and the adherents are not disturbed during cure. Adhesive strengths without the need for both open time and high pressure are perhaps the best available in the contemporary plastic technology.
5. **High mechanical properties**. The strength of appropriately formulated epoxy resins usually surpasses that of other types of casting epoxy resins. This is due to their low shrinkage and comparatively unstressed structure after curing.
6. **High electrical properties.** Cured epoxy systems exhibit good electrical properties over a range of temperatures and frequencies. They are excellent electrical insulators.
7. **Good chemical resistance.** The chemical resistance of the cured epoxy resin relies considerably on the curing agent used. Generally, most epoxy resins possess extremely high resistance to caustics and good to excellent resistance to acids.

8. **Versatility.** The epoxy resins are likely the most versatile of the modern plastics. The basic properties may be modified in many ways such as by blending of resin types, by selection of appropriate curing agents, and by application of modifiers.

Table 2.2 Curing agents for epoxy resins (Kroschwitz, 1991)

Type	Advantages	Disadvantages	Applications
Aliphatic amines	-low viscosity; -ambient cure temperature; -little color	-short pot life; -rapid heat evolution; -critical mix ratio; -moderately toxic; -high moisture absorption	-adhesives; -small castings; -electrical encapsulation; -civil engineering
Aromatic amines	-good elevated temperature performance; -good chemical resistance; -long pot life; -low moisture absorption	-incompatibility with epoxy resins; -long cure cycles at high temperature; -toxicity	-high performance composites and coatings; -adhesives; -filament winding; -electrical encapsulation
Polyamidoamines	-low viscosity; -ambient cure temperature; -good mix ratios, mechanical properties, and pot life	-poor performance at high temperature	-construction adhesives; -sealants; -floorings; -concrete bonding
Polyamides	-good mix ratios, pot life, flexibility, toughness, and corrosion resistance; -ambient cure temperature; -low toxicity	-low temperature performance; -high viscosity; -poor color	-maintenance coatings; -castings; -trade sale paints; -adhesives; -marine coatings
Anhydrides	-good mechanical and electrical properties; -low shrinkage and viscosity; -long pot life; -little color	-long cure cycles at high temperature	-castings; -potting; -encapsulation; -filament winding
Catalytic	-high temperature resistance; -very long pot lives	-long cure cycles at high temperature; -brittle	-powder coatings; -adhesives; -electrical encapsulation

Table 2.2 (Continued)

Type	Advantages	Disadvantages	Applications
Dicyandiamide	-good electrical properties; -high temperature resistance; -latent systems	-incompatibility with epoxy resins; -long cure cycles at high temperature	-electrical laminates; -powder coatings; -single-package adhesives
Polycarboxylic polyesters	-good weather ability, corrosion resistance, and mechanical properties; -low cost	-poor chemical resistance	-powder coatings
Isocyanates	-fast cure at low temperature; -good flexibility and solvent resistance	-moisture-sensitive; -toxicity	-powder coating; -maintenance coatings
Phenol-formaldehyde, novolacs	-good chemical resistance, electrical properties, shelf stability, and compatibility with epoxies; -high temperature resistance	-poor UV stability; -high melting; -high temperature cure	-molding compounds; -powder coatings
Polysulfides and polymercaptans	-rapid cure times; -flexible systems	-poor performance at high temperature; -odorous	-sealants; -adhesives
Melamine-formaldehyde	-good color and hardness; -stable one-component systems	-high temperature cure; -low compatibility with epoxy resins	-stove paints; -can coatings; -finishes
Urea-formadehyde	-stable one-component systems; -little color	-high temperature cure	-fast-bake enamels; -stove primers; -can and drum coatings; topcoats
Resole phenolics	-stable one-component systems; -good chemical resistance	-high temperature cure; -brittle; -poor weather ability	-baked enamels; -drum and pail coatings

In this research study, epoxy type EPON Resin 826 will be selected. EPON Resin 826 can be cross-linked with a variety of curing agents/depending on processing conditions and properties desired for the finished product. EPON 826 is commonly used to fabricate high strength fiber reinforced pipes and composites. The low viscosity of the resin provides rapid wet out of a wide range of reinforcing fibers including glass, graphite, aramid and boron. High fiber content with low void content can be achieved with this resin. Structural composites such as this have a high ratio of strength to weight. This makes them suitable for applications ranging from sporting goods equipment to aerospace structural members. EPON Resin 826 systems are also excellent electrical insulators. Such systems are used frequently in electrical encapsulations, laminates and molding compounds. Structures, linings and coatings made with EPON Resin 826 protect metal surfaces and resist attack from acids, bases, solvents and fuel. They find use in the oil, gas, mining and chemical industries. The higher shear strength obtained with EPON Resin 826 adhesives is due in part to the low internal stresses inherent in cured epoxy resins. Such adhesives are used to bond a broad range of substrates.

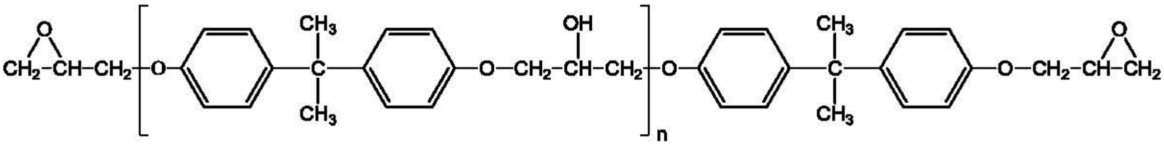


Figure 2.17 Structure of EPON Resin 826 (Merfeld et al., 2003).

Table 2.3 Typical properties of EPON Resin 826

Typical properties	
Approximate average molecular weight (Feninat, 2002), g/mol	365
Epoxide equivalent weight (EEW)	178–186
Viscosity, poise at 25°C	65–95
Density, g/ml at 25°C	1.16

Applications for EPON 826:

- Fiber reinforced pipe and composites
- Tooling and molding compounds
- Construction, electrical and aerospace adhesives
- Electrical castings and laminates
- Chemical resistant high solids tank linings
- Flooring
- Grouting compounds

For some types of processing the viscosity of the uncured resin system needs to be lowered. When it is not advisably, as in the case of hand lay-up, to use volatile solvents as diluents, reactive diluents must be used. In this research used Neopentyl glycol diglycidyl ether (NGDE) as diluents. They are low viscosity liquids containing epoxide groups.

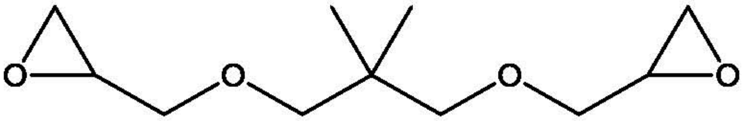


Figure 2.18 Structure of Neopentyl glycol diglycidyl ether (NGDE).

In this research used aliphatic amine as curing agents, Jeffamine D-230, the temperatures required to achieve cure with amine curing agents fall in a wide range, from 25°C to nearly 200°C, depending on the chemical structure of the amine. They can cure epoxides at room temperature or only slightly above. Aliphatic amine-cured systems also tend to have low glass transition temperatures (T_g) the temperature at which the mechanical behavior changes from rigid to rubbery.

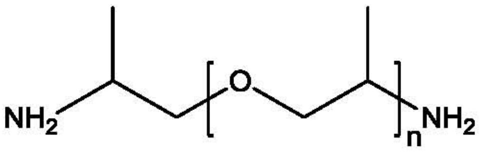
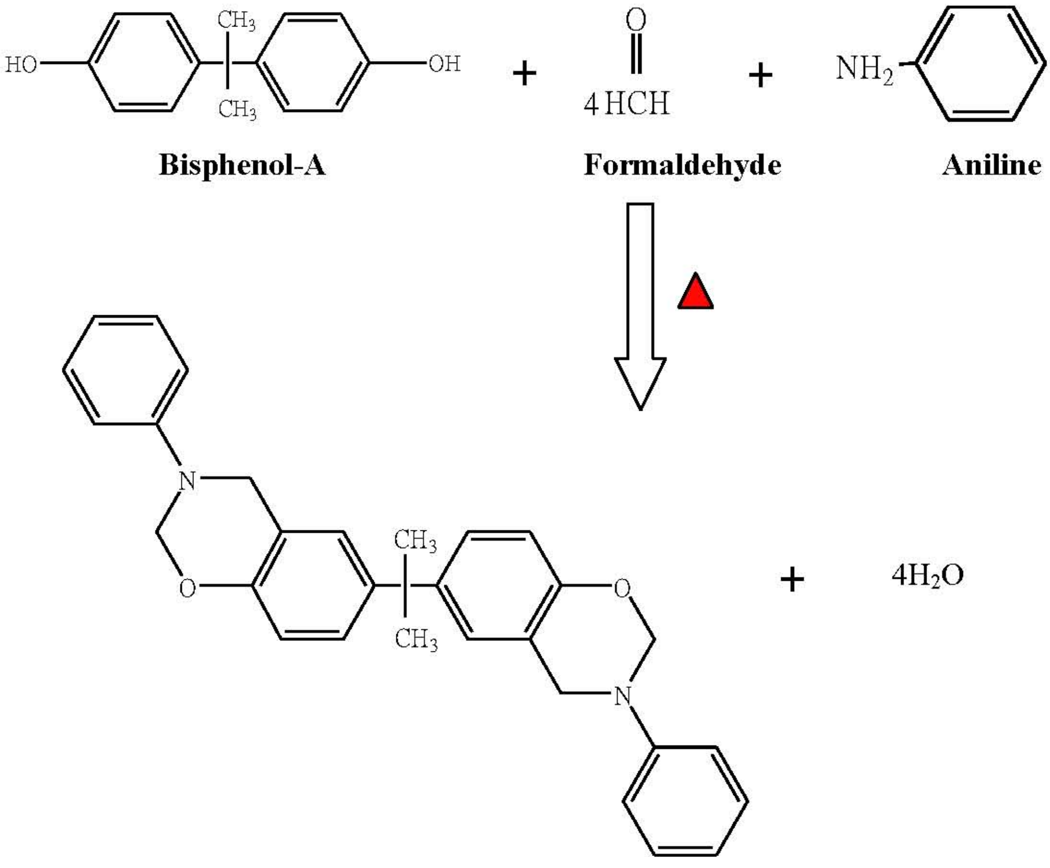


Figure 2.19 Structure of Jeffamine D-230 (n~2.5)

2.3 Benzoxazine Resin

Polybenzoxazine is a phenolic polymer in which generated by the Mannich-like condensation of phenol, formaldehyde and amine. It can be prepared by using solvent less synthesis technology (Rimdusit and Ishida, 2002). The general pattern for this process is:



Benzoxazine monomer (BA-a)

Figure 2.20 Schematic synthesis of bifunctional benzoxazine monomer.

Polybenzoxazine offers many advantages. First, a variety of reactants can be used to design desired molecular structures. Second, thermal polymerization is easy to carry out and is not dependent on the use of a strong acidic or basic catalyst. Third, processing is easier compared to traditional resins because of low viscosity. Fourth, benzoxazine polymerization does not produce any byproduct. Consequently, benzoxazine can be easily processed to make void free products.

The polymer network structures are responsible for high modulus of polybenzoxazines based on bisphenol-A compounds. Earlier, it was assumed that high flexural modulus and near zero shrinkage (or little expansion) upon polymerization are due to chemical crosslinking only. However, more recent studies demonstrated that extensive hydrogen bonding networks also contribute substantially. The intra and intermolecular hydrogen bonding were found to establish large networks, which in turn prevent shrinkage and lead to higher modulus.

Thermal properties of polybenzoxazine are the most studied properties besides mechanical properties. High glass transition temperature, flame retardancy, and high char yield are among the significant features. Furthermore, it has been reported in detail that polybenzoxazine can be tailored through two substitutions, preferably phenols and amines, to improve thermal stability. In this regard, polybenzoxazines containing propargyl, allyl, and maleimide functionalities were developed and investigated. The studies revealed that the modifications in chemical structure result in polymers stable in the temperature range between 200°C and 350°C, offering very high glass transition temperatures from 100°C to 250°C.

CHAPTER 3

LITERATURE REVIEWS

Ishida and Allen (1996) investigated mechanical characterization of benzoxazine and epoxy based on DGEBA. The benzoxazines are copolymerized with an epoxy resin in order to modify their performance. The addition of epoxy to the polybenzoxazine network greatly increases the crosslink density of the thermosetting matrix and strongly influences its mechanical properties. Copolymerization leads to significant increases in the glass transition temperature, flexural stress, and flexural strain at break over those of the polybenzoxazine homopolymer, with only a minimal loss of stiffness. By understanding the structural changes included by variations of epoxy content and their effect on material properties, the network can be tailored to specific performance requirements. Figure 3.1 show the glass transition temperature and the flexural strength of copolymer, respectively.

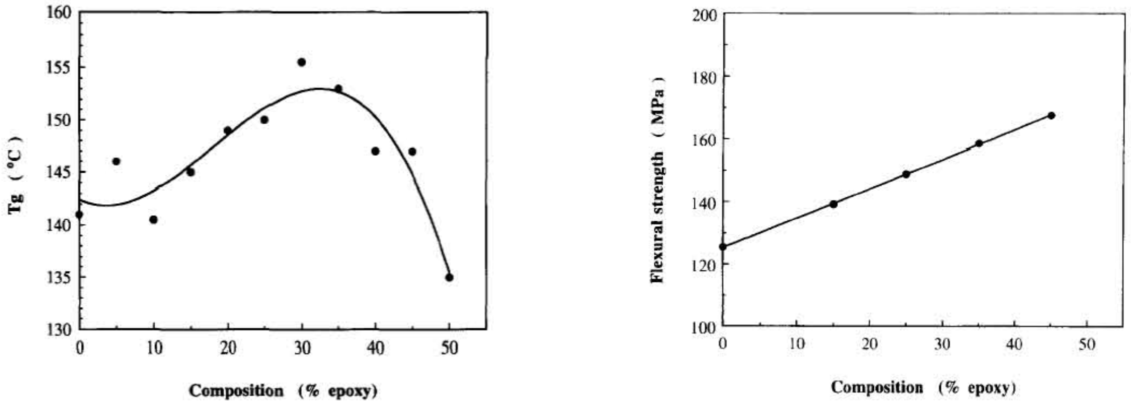


Figure 3.1 The glass transition temperature and the flexural strength of copolymer (Ishida and Allen, 1996).

Rimdusit and Ishida (2000) found the synergism in the glass-transition temperature (T_g) of ternary systems based on benzoxazine, epoxy, and phenolic resins. The systems showed the maximum T_g up to about 180°C in benzoxazine/epoxy/phenolic 5/4/1 mass ratio. Adding a small fraction of phenolic resin enhanced the crosslink density and, therefore, the T_g in the copolymers of benzoxazine and epoxy resins. To obtain the ultimate T_g in ternary system, 6-10 wt% phenolic resin was needed. The molecular rigidity from benzoxazine and the improved crosslink density from epoxy contribute to the synergistic behavior. The mechanical relaxation spectra of the fully cured ternary systems in a temperature range of –140 to 350°C showed four types of relaxation transitions: gamma transition at –80 to –60°C, beta transition at 60-80°C, alpha_1 transition at 135-190°C, and alpha at 290-300°C. The partially cured specimens showed an additional loss peak that was frequency-independent as a result of the further curing process of the materials. Effect of the epoxy content on glass transition temperature of the binary and ternary systems are shown in Figure 3.2.

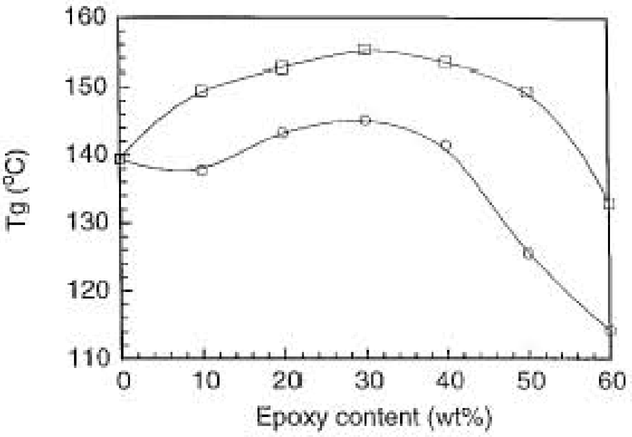


Figure 3.2 Effect of the epoxy content on glass transition temperature of the binary (○) and ternary (□) systems (Rimdusit and Ishida, 2000).

Rimdusit and Ishida (2000) have developed new polymeric systems based on the ternary mixture of benzoxazine, epoxy, and phenolic novolac resins. Low melt viscosity resins render void-free specimens with minimal processing steps. The material properties show a wide range of desirable reliability and processability, which are highly dependent on the composition of the monomers in the mixture. A glass transition temperature as high as 170°C and considerable thermal stability at 5%

weight loss up to 370°C can be obtained from these systems as shown in Figure 3.4. Phenolic novolac resin acts mainly as an initiator for these ternary systems while low melt viscosity, flexibility and improved crosslink density of the materials are attributed to the epoxy fraction. Polybenzoxazine imparts thermal curability, mechanical properties as well as low water uptake to the ternary systems.

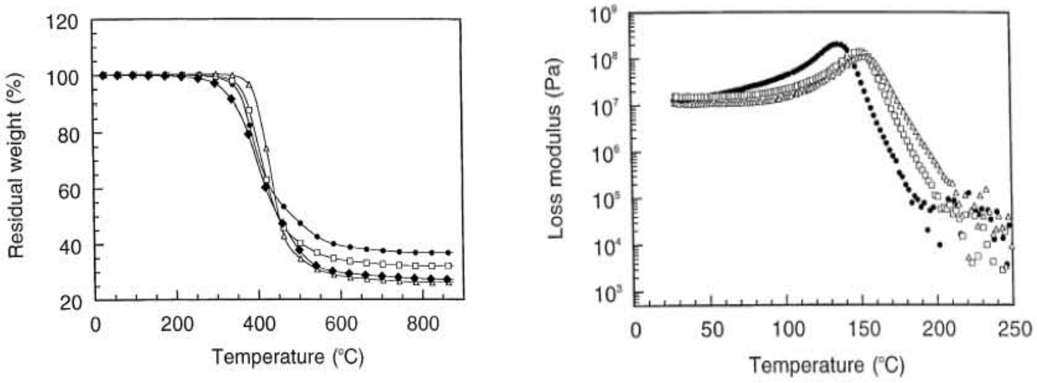


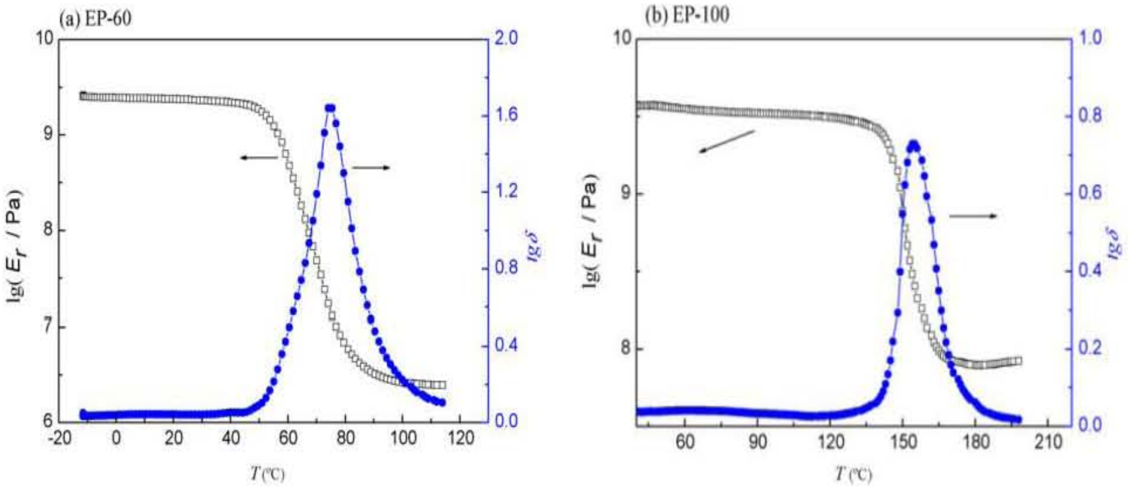
Figure 3.3 Loss moduli and TGA thermogram of ternary systems: (●) BEP 111, (□) BEP 121, (Δ) BEP 131 and (♦) BA-a.

Liu et al. (2010) have investigated the effect of crosslink density, recovery temperature and consecutive cycles on the shape memory properties. A series of shape memory epoxy resins (SMEPs) were prepared by epoxy and varying content of aromatic amine curing agent. The T_g values obtained from DSC analysis are also summarized in Table 3.1. These results show all samples possess distinctive glass transition temperatures ranging from 44.7°C to 145.3°C and the T_g values gradually increase with the addition of curing agent. More curing agent brings higher cross-linking density and closer structure, which can hinder the movement of segment.

Table 3.1 Glass transition temperatures of prepared epoxy resin systems.

Sample	**EP-50**	**EP-60**	**EP-70**	**EP-80**	**EP-90**	**EP-100**
T_g (°C)	44.7	63.7	80.8	93.9	113.5	145.3

This series of materials were marked as EP-x, where x represented the curing degree of epoxy resin (EP). From the Table 3.1 shown EP-50 for which the strength is too low to use as an SMP, is abandoned in the subsequent experiments. While EP-60 is primarily investigated because its T_g is in the suitable range of temperature needed by space deployable structures. EP-60 and EP-100 samples are further characterized by DMA. The spectra and data obtained are shown in Figure 3.5.



(a) (b)

Figure 3.4 Storage modulus and loss tangent (tan δ) as a function of temperature of (a) EP-60, (b) EP-100 (Liu et al., 2010).

According to the results, EP-60 has a decrease of 3 orders on storage modulus and E_r reaches 2.88×10^6 Pa at the rubbery state, while EP-100 has a decrease of only 1.5 orders and E_r reaches 8.17×10^7 Pa. Usually, a good SMP should have a change of storage modulus for more than 2 orders below and above T_g, and an appropriate value of E_r at rubbery state to guarantee large elastic deformation. Thus EP-60 meets the requirements, but EP-100 is abandoned because of too high storage modulus at rubbery state to accomplish large deformation.

The shape recovery ratio vs. temperature curves for SMEPs are presented in Figure 3.5. All samples have similar trend that the shape recovery ratio monotonically and sharply increases with the increase of temperature and finally reaches 100%. EP-

60, EP-70, EP-80 and EP-90 can all recover their original shape completely at a gradually higher temperature. These results declare that their SMEPs have excellent shape recovery ability. EP-60 starts shape recovery at 14°C below its T_g, EP-70 at 13°C below T_g, EP-80 at 8°C below T_g and EP-90 at the temperature of T_g. The reason can be explained that highly cross-linked structures have strong constrained force on their segments, so these highly cross-linked samples need larger free volume and more energy, which can be obtained at higher temperature, to accomplish shape recovery.

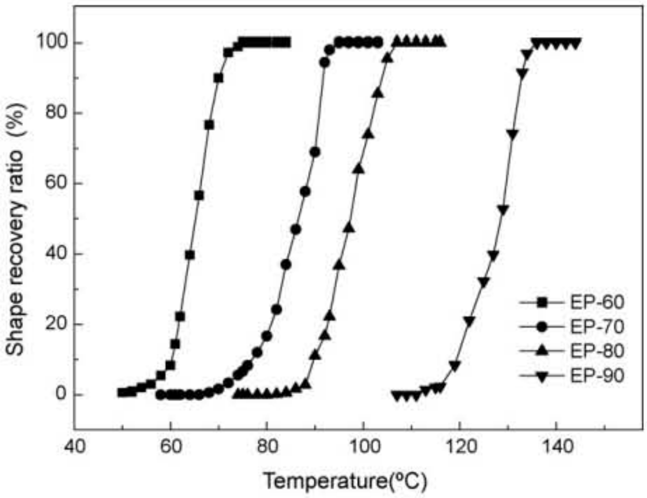


Figure 3.5 Shape recovery ratios of prepared epoxy resins vs. temperature (Liu et al., 2010).

Xie and Rousseau (2009) have developed methods to tailor T_g of shape memory epoxy polymer. Starting with an amine (Jeffamine D230) cured aromatic epoxy (EPON 826) system, epoxy polymers were synthesized by either reducing the crosslink density by substituting the diamine curing agent with a monoamine such as decylamine (DA) or introducing flexible by replacing the EPON 826 with a flexible aliphatic diepoxy NGDE. The molar compositions for all epoxy synthesized are summarized in Table 3.2.

All the other epoxy polymers in Table 3.2 show typical shape memory properties, with shape fixity above 90% and shape recovery around 100%.

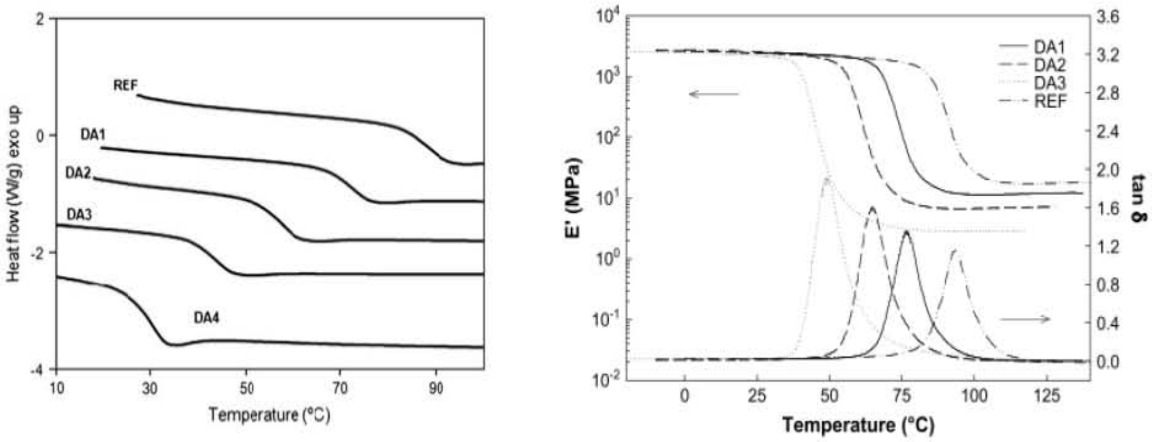
Interestingly, it appears that the shape fixity for the DA and NGDE series including the REF seems to increase as more and more DA and NGDE were present in the formulation. The difference in shape fixities for all the epoxy samples can be correlated to the difference in glassy modulus and rubbery modulus for each individual sample. The reduction in the crosslinker led to the decrease in crosslinking density, as reflected in the increase of M_c in Table 3.2.

All DA series samples showed distinctive glass transition temperatures ranging from 30 to 89°C (Figure 3.3a) and relatively constant storage moduli in their respective glassy and rubbery regions and the difference between the glassy modulus and rubbery modulus for each individual sample ranges from 2 to 3 orders of magnitude as shown Figure 3.7(b), the reduction in the crosslink density (increase in M_c) leads to the reduction in the rubbery modulus for the DA series.

Table 3.2 Compositions, shape fixity, and shape recovery of the epoxy samples.

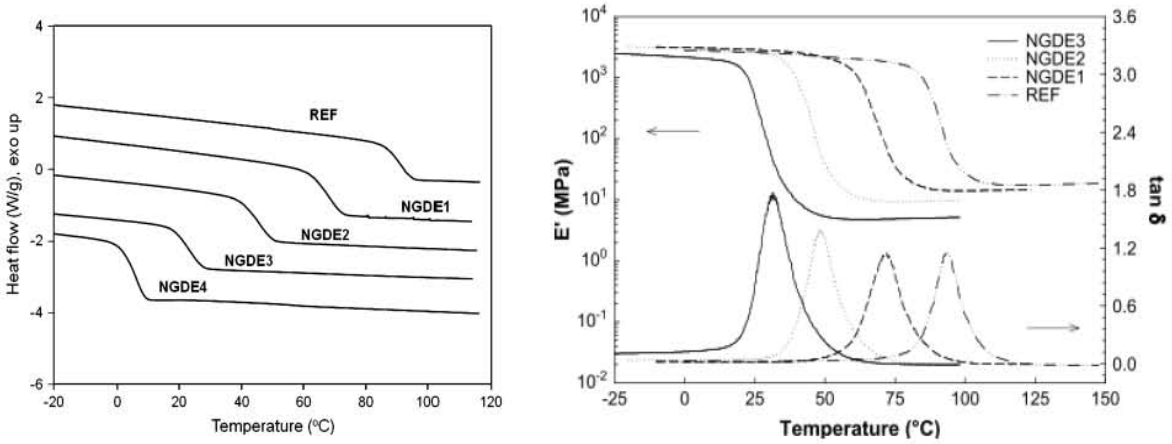
Sample	EPON 826 (mol)	D230 (mol)	DA (mol)	NGDE (mol)	Average molecular weights between crosslink points (M_c)	R_f (%)	R_r (%)
REF	0.02	0.01	0	-	475	91.3	99.1
DA1	0.02	0.0075	0.005	-	647	95.2	99.2
DA2	0.02	0.005	0.01	-	992	94.2	99.8
DA3	0.02	0.0025	0.015	-	2026	102.3	98.2
DA4	0.02	0	0.02	-	∞	-	-
NGDE1	0.015	0.01	-	0.005	439	92.3	99.2
NGDE2	0.01	0.01	-	0.01	403	96.4	99.7
NGDE3	0.005	0.01	-	0.015	367	96.8	99.3
NGDE4	0	0.01	-	0.02	331	-	-

In the NGDE series, increasing the crosslink density alone would increase the material rigidity, thereby reducing its T_g ranging from 88 to 6°C. The results, shown in Figure 3.6(a) and (b), suggest that the impact of increasing the crosslink density by introducing NGDE is more than compensated for by the increase in the overall chain flexibility, resulting in a net reduction in T_g and rubbery modulus.



(a) (b)

Figure 3.6 (a) DSC curves for the DA epoxy series, (b) DMA curves for the DA epoxy series (Xie and Rousseau, 2009).



(a) (b)

Figure 3.7 (a) DSC curves for the NGDE epoxy series. (b) DMA curves for the NGDE epoxy series (Xie and Rousseau, 2009).

Feldkamp and Rousseau (2010) have studied the effect of the deformation temperature on the shape memory behavior of epoxy networks. Two main approaches exist for increasing flexibility and ultimate elongation in epoxy systems. In this work used epoxy resins synthesized where a DEGBA-based monomer (EPON 826 or Dow D.E.R.383) is crosslinked with a mixture of a diamine cross-linker with either a second diamine cross-linker or a monoamine pendant chain both of high molecular weight.

Note that varying the chemical and structural design of these epoxies enabled tailoring of the glass transition temperature (alternatively, the transformation temperature) of the epoxy SMPs from 36.5 to 98.6^{o}C, thereby offering a strong and stable material solution to multiple applications ranging from low to high transformation temperature requirements. In addition, it can be noted that the modulus (E') of the epoxies in their glassy state (E'_s) is high (≈2 GPa) and remains high in their rubbery state (≈10–25 MPa) relative to that of other common SMPs in the rubbery state.

Figure 3.8 shows the data obtained upon testing the D-148(04) M600 samples. The stress/strain curves obtained for three specimens of the D-148(04) M600 samples are shown when tested at $\mathbf{T_g^{E'}}$ (dashed lines), and at T_d (solid lines). The presented data are representative of all other epoxy samples discussed herein.

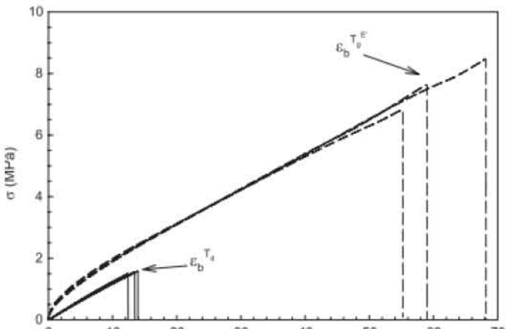


Figure 3.8 Stress/strain curves measured for D-148(04)M600 at the deformation temperature (T_d = 96^{o}C, solid lines) and at the onset temperature of the glass transition ($\mathbf{T_g^{E'}}$ = 44^{o}C, dashed lines). The respective average strain at break values are $\boldsymbol{\varepsilon_b^{T_d}}$= 13.3% and $\boldsymbol{\varepsilon_b^{T_g^{E'}}}$ = 60.7% (Feldkamp and Rousseau, 2010).

Leonardi et al., (2010) have investigated the epoxy network contains chemical crosslinks represented by m-xylylenediamine (MXDA) units and physical crosslinks represented by n-dodecylamine (DA) units, by the maximum ratio was 4:1. The increase in the rubbery modulus is ascribed to the increase of the fraction of physical crosslinks produced during the annealing period. The final result is shown in Figure 3.9 representing the dynamic-mechanical thermal response of the epoxy networks obtained before and after the annealing period. Both T_g and the rubbery modulus increased with the annealing. T_g measured by DSC also increased from 37.6°C to 41.2°C with the annealing.

Figure 3.9 shows the uniaxial tensile behavior of the epoxy network in the rubbery state, at three different temperatures. The strain at break shows a significant increase when decreasing temperature approaching the glass transition. At 55°C the material is located at about half of its transition while at 75°C it is close to the end value. They can speculate that the presence of local glassy regions increases the toughness of the material.

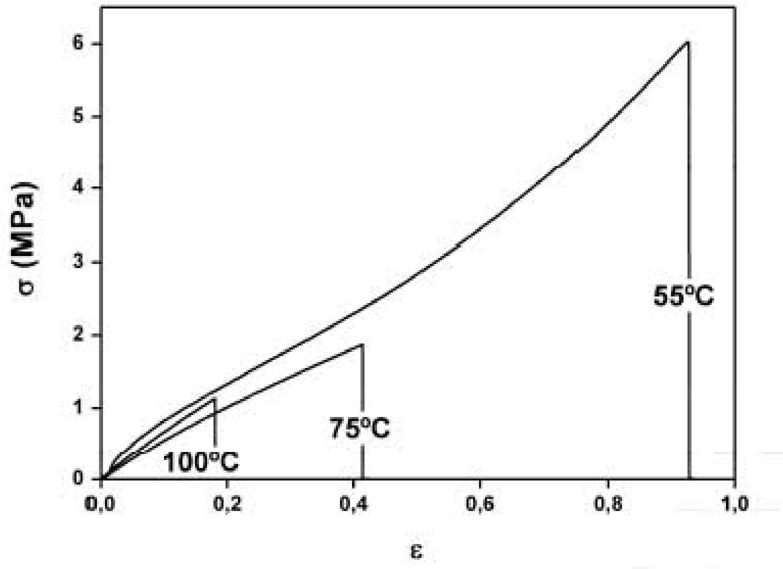


Figure 3.9 Typical uniaxial stress-strain curves at different temperatures in the rubbery state (Leonardi et al., 2010).

They selected a temperature of 55°C as the high temperature of the shape memory cycle. At this temperature the elastic modulus was 11 MPa and the sample could be strained to the desired value of 75%. The required stress is close to 3 MPa, as results from the curve at 55°C shown in Figure 3.9, a value that represents the stress recovery of the SMP for the selected strain.

Shape memory properties were determined employing 4 thermo-mechanical cycles (Figure 3.10), fixing 20°C and 55°C as the low and high temperatures of the cycle and 75 % as the prescribed tensile strain. Figure 3.11 shows the stress-strain curves at 55°C for the 4 cycles. There is a small difference between the first and subsequent curves and almost no difference from the second to the fourth cycle. The resulting values of shape fixity and shape recovery are shown in Table 3.3. They were close to 98% and 96%, respectively, for the 4 cycles. A significant result is the absence of a strain hysteresis in the first cycle with respect to subsequent cycles, as reported for other shape memory epoxies.

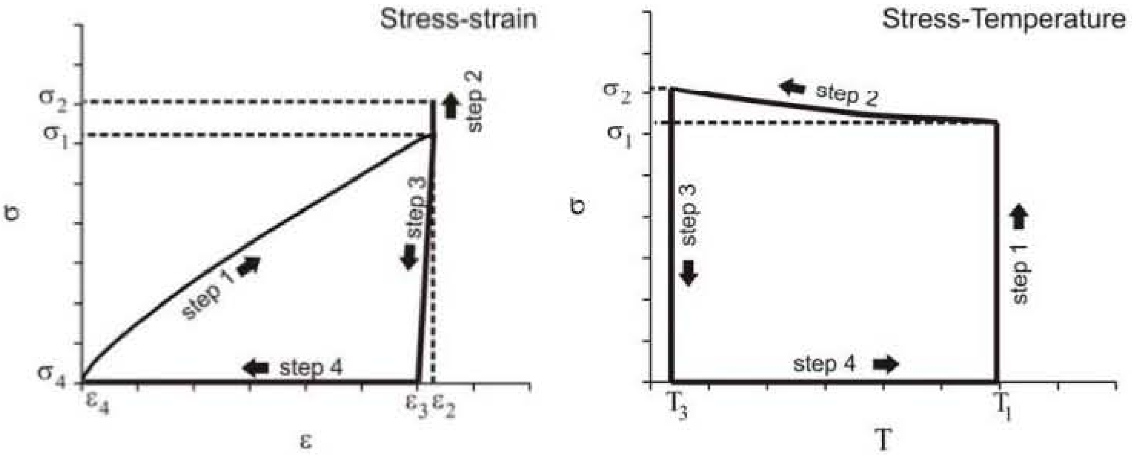


Figure 3.10 Scheme of the shape memory cycle (Leonardi et al., 2010).

Table 3.3 Shape fixity and shape recovery at various cycle

Cycle	**1**	**2**	**3**	**4**
R_f (%)	98.0	98.5	98.1	98.2
R_r (%)	96.8	95.7	95.5	95.5

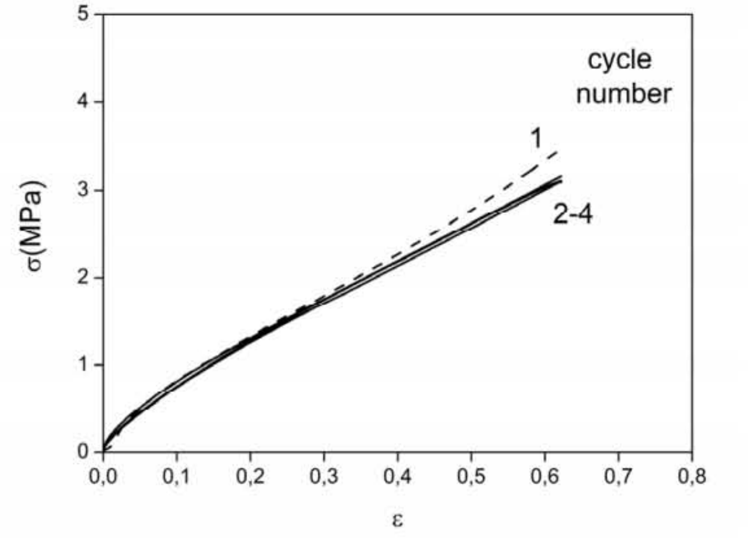


Figure 3.11 Uniaxial stress-strain curves at 55°C during the 4 cycles used to determine shape memory properties (Leonardi et al., 2010).

Erden and Jana (2009) examined the properties of polyurethane-polybenzoxazine based shape memory polymers by using many techniques such as DSC, DMA, TGA, FTIR, AFM etc. In the experiment, he synthesized 3 samples which are consist of 4,4'-methylene diphenyl diisocyanate (MDI), Polytetramethylene glycol (PTMG), 1, 4-butanediol (BD),and benzoxazine (B-a). The molar ratios of each sample and hard segment percentage (HS%) are shown in Table 3.4.

Table 3.4 Corresponding molar ratios of raw materials

Sample	MDI	PTMG	BD	B-a	HS%
1	5	1	4.0	0	71.2
2	5	1	3.5	0.5	73.4
3	5	1	3.0	1.0	75.3

The results from DMA test are shown in Table 3.5. There is strong evidence on a result showing the improvement of shape memory properties and T_g. The larger the value of E'(T_g-20 °C)/ E'(T_g+20 °C) mean the higher values of shape fixity and rapid shape recovery. Also the increasing of T_g is due to the increasing amount of benzoxazine in the sample.

Table 3.5 Viscoelastic properties of the samples

Sample	E' (glassy)(Pa)	E' (T_{room}) (Pa)	E' (T_g+20) (Pa)	E'(T_g-20)/ E'(T_g+20)	T_g(°C)
1	$7.5x10^9$	$4.1\ x10^9$	$5.3\ x10^8$	11.3	51
2	$5.3x10^9$	$3.8x10^9$	$3.4\ x10^7$	147	65
3	$4.7\ x10^9$	$3.9\ x10^9$	$1.4\ x10^7$	271	91

Furthermore, he used Universal testing machine (tensile mode) to explore the tensile properties of the samples. The results are shown in Table 3.6. With the increasing of the amount of benzoxazine, the value of young's modulus and the ultimate stress is clearly rising. However, the elongation percentage at break and toughness is reduced due to the presence of benzoxazine. Sample 1 and 2 showed the yielding behavior but sample 3 showed brittle failure.

Table 3.6 Tensile properties of the samples

Sample	Young's Modulus (MPa)	Elongation at break (%)	Yield Stress (MPa)	Ultimate Stress (MPa)	Toughness (MPa)
1	228	478	41	50	216
2	258	95	44	35	36
3	475	32	N/A	160	6

Moreover, the stress recovery and shape recovery ratio had been observed. As the results in Figure 3.12, sample 1 obtained the lowest stress recovery value, which is around 6.8 MPa, while sample 2 and 3 are at 11.2 and 13 MPA respectively. Figure 3.13 implied the shape recovery (%) of each sample. Sample 1 can retain only 72% of its length; on the other hands, sample 2 and 3 can recover up to 93% of their shapes.

In conclusion, many properties are affected by the presence of benzoxazine especially the shape memory behavior and the increasing of T_g.

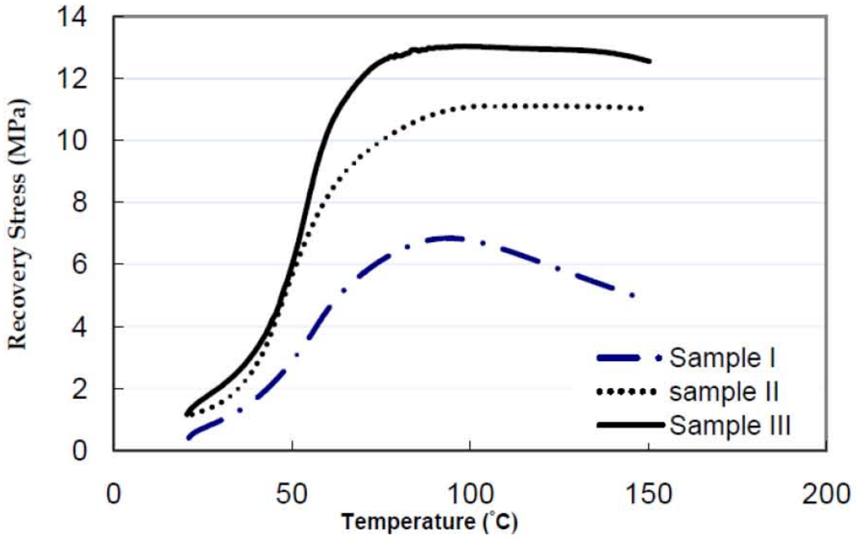


Figure 3.12 Recovery stress behaviors of 100% strained samples. Heating rate was 4°C/min and stretching rate was 50 mm/min (Erden and Jana, 2009).

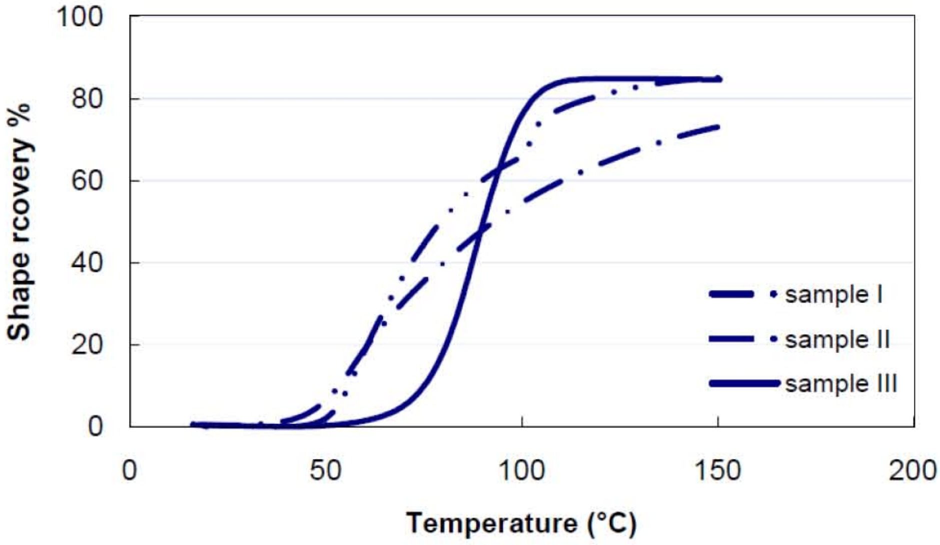


Figure 3.13 Shape recovery ratio of 100% strained samples. Heating rate was 4°C/min and stretching rate was 50 mm/min (Erden and Jana, 2009).

CHAPTER 4

EXPERIMENTAL

4.1 Raw Materials

Materials used in this research are benzoxazine resin, aromatic epoxy, aliphatic epoxy and aliphatic curing agent. Benzoxazine resin is based on bisphenol-A, aniline and formaldehyde. The bisphenol-A (polycarbonate grade) was supported by Thai Polycarbonate Co.,Ltd. (TPCC). Para-formaldehyde (AR grade) was purchased from Merck Company and aniline (AR grade) was contributed by Panreac Quimica S.A. Company. The diglycidyl ether of bisphenol A epoxy monomer (EPON 826) and Neopentyl diglycidyl ether (NGDE) were available from Aditya Birla Chemical (Thailand). The curing agent poly(propylene glycol)bis(2-aminopropyl) ether (Jeffamine D230) was purchased from Aldrich. All chemicals were used as received.

4.2 Resin Preparation

4.2.1 Benzoxazine Resin Preparation

Benzoxazine resin (BA-a) was synthesized from bisphenol-A, paraformaldehyde, and aniline at a mole ratio of 1:4:2. The mixture was heated to 110^{o}C in an aluminum pan and was mixed until a homogeneous mixture was obtained for 30 min to yield a light yellow solid monomer product, according to the patented solventless method. The resulting benzoxazine monomer is solid at room temperature with transparent yellow color. The as-synthesized monomer was ground into fine powder and taken for material characterization.

4.2.2 Preparation of Benzoxazine-Epoxy Alloying Specimens

The benzoxazine monomer was mixed with aromatic epoxy, flexible epoxy and curing agent to provide epoxy-modified benzoxazine at the desirable mole ratio. The mixture was heated to about 70°C in an aluminum pan for about ten minutes until a homogeneous mixture. The molten resin was poured into the aluminum foil mold and was thermally cured at 80°C for 4 hrs in vacuum oven, 100°C/2 hrs, 130°C/1 hr, 150°C/24 hrs, 170°C/1 hr, 190°C/1 hr and 200°C/2 hrs. The samples were demolded and taken to characterization.

Table 4.1 Compositions of the benzoxazine-modified epoxy SMP

Samples	EPON 826 (mol)	NGDE (mol)	Jeffamine D230 (mol)	BA-a (mol)
ENDB 1/1/1/0	1	1	1	-
ENDB 1/1/0.8/0.2	1	1	0.8	0.2
ENDB 1/1/0.6/0.4	1	1	0.6	0.4
ENDB 1/1/0.4/0.6	1	1	0.4	0.6
ENDB 1/1/0.2/0.8	1	1	0.2	0.8
ENDB 1/1/0/1	1	1	-	1

In the nomenclature of the mixtures, the notation E, N, D and B stands for EPON 826, NGDE, Jeffamine D230 and BA-a, respectively. The digits after the notation are 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.

4.3 Characterization Methods

4.3.1 Differential Scanning Calorimetry (DSC)

Curing behaviors of each resin and its mixture with epoxy were studied using a differential scanning calorimeter (DSC) model 2910 from TA Instruments. Each specimen with a mass in a range of 3−5 mg was sealed in an aluminum pan with lid. The heating rate used was 10°C/min and the sample temperature was scanned from room temperature to 300°C under nitrogen purging. The purge nitrogen gas flow rate was maintained to be constant at 50 ml/min.

The degree of conversion (α) of a sample was determined according to the following relationship:

$$\alpha=1-\left(\frac{H_{rxn}}{H_0}\right) \tag{4.1}$$

where H_{rxn} = the heat of reaction of the partially cured specimen as determined from the DSC experiment, mW/mg.

H_o = the heat of reaction of the uncured resin, mW/mg.

4.3.2 Dynamic Mechanical Analysis (DMA)

A dynamic mechanical analyzer (NATZSH, model DMA 242) was used to obtain a storage modulus (E′), loss modulus (E″) and loss tangent (tan δ) of the polymeric specimens. The specimen, with a dimension of $10\times50\times3$ mm^3, was tested using a three-point bending mode at the frequency of 1 Hz and heating rate of 2^oC/min from room temperature to the temperature beyond the glass transition temperatures (T_g) of each specimen. The glass transition temperature was taken as the maximum point on the loss modulus.

4.3.3 Universal Testing Machine (Flexural Mode)

The mechanical properties of the polymers or polymer alloy were determined using a universal testing machine (model 5567) from Instron Co., Ltd. The test method was a three-point loading with the supporting span of 32 mm and tested at a crosshead speed 1.0 mm/min. A dimension of a specimen is $10\times50\times2$ mm^3. Flexural properties were determined based on ISO 178:2001. The flexural strength, flexural strain and the modulus were calculated by the following equations:

$$E_B=\frac{L^3m}{4bd^2} \tag{4.2}$$

$$S = \frac{3PL}{2bd^2} \tag{4.3}$$

Where E_B = Flexural modulus, GPa.

S = Flexural strength, MPa.

P = Load at a given point on the load-deflection curve, N.

L = Support span, mm.

b = Width of beam tested, mm.

d = Depth of beam tested, mm.

m = Slope of the tangent to the initial straight-line portion of the load deflection curve, N/mm.

4.3.4 Shape Recovery Performance

The shape recovery performance is essential important. Therefore, a systematic shape recovery test of SMPs specimens depend on bending was performed. The procedure for the thermo-mechanical bending cycling of the SMPs includes the following steps (see Figure 4.1): First, the specimen in its permanent shape is kept in an oil bath for 5 min at T_g+20°C; then the SMPs is bent to a storage angle θ_0 in a "U" shape with the radius of 2 mm in the soft rubbery state, and then the SMPs is kept in room temperature with the external constraint to freeze the elastic deformation energy for 5 min; (3) the SMP specimen fixed on the apparatus is immersed into oven at an elevated temperature, and then it recovers to an angle θ_N. Five specimens were used in each test. The method used to quantify the precision of deployment is illustrated in Figure 4.1, where r denotes the radius of the mandrel, t represents the thickness of the SMP specimen, θ_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 θ_0. θ_N is the residual angle in the recovery state during the N^{th} thermo-mechanical bending cycle (N = 1, 2, 3,...). $R(x_N, y_N)$ is a testing point in order to calculate θ_N:

$$\theta_N = \mathrm{ArcCot}\ x_N$$

$$(N = 1, 2, 3, \ldots, 0 \leq \theta_N \leq 180^{\circ}) \tag{4.4}$$

The value of the shape recovery ratio is calculated by

$$R_N = \frac{\theta_0 - \theta_N}{\theta_0} \times 100\% \qquad (N = 1, 2, 3, \ldots) \quad (4.5)$$

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, θ_N and R_N are obtained through equations (4.4) and (4.5). In the following tests, the radius r of the mandrel and thickness t of SMP specimen is 2 mm and 3 mm, respectively.

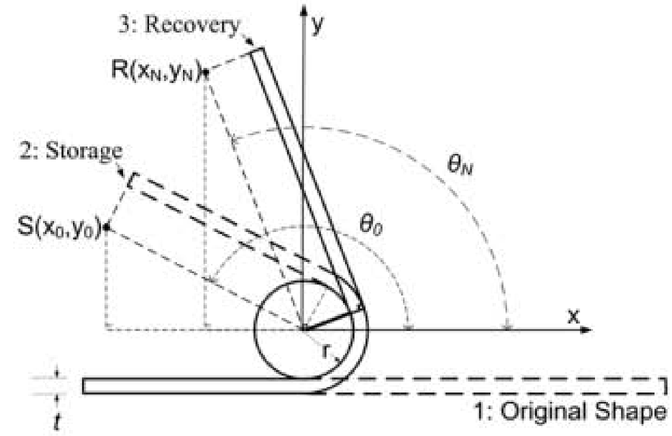


Figure 4.1 Schematic illustration of the setup for the shape recovery performance test (Lan et al., 2009).

4.3.5 Recovery Stress Test

The experimental procedure in the recovery stress test is schematically shown in Figure 4.2.

(1) First, the maximum deflection y_{max}=10 mm was applied at T_g+20°C. At the point of y_{max}, force took the maximum value which was observed at T_g+20°C in the deformation test at various temperatures.

(2) The specimen was cooled down to room temperature by keeping y_{max} constant. Stress decreased almost to zero during cooling.

(3) Then the force was removed perfectly at T_g+20°C. The deflection after unloading was measured.

(4) The specimen was heated up to T_g+20°C by keeping the fixed deflection constant. Stress during heating was measured and the recovery stress was obtained.

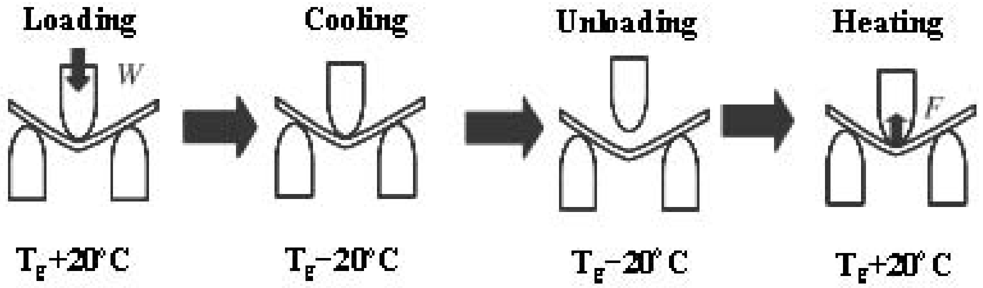


Figure 4.2 Experimental procedures in the recovery stress test (Tobushi, 2006).

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Effect of Benzoxazine and Jeffamine D230 Content on Curing Behavior

Curing mechanisms of BA-a resin and BA-a alloyed with epoxy were investigated by a differential scanning calorimeter (DSC). Figure 5.1 shows the curing exothermic peaks of BA-a and the binary mixtures i.e. BA-a/Jeffamine D230, epoxy resins/Jeffamine D230, BA-a/aromatic epoxy (EPON 826) and BA-a/ aliphatic epoxy (NGDE) mixture. From this graph, the exothermic peak of the neat benzoxazine resin (Figure 5.1(a)) was located at 230°C while BA-a/Jeffamine D230 mixture (Figure 5.1(b)) revealed two exothermic peaks at 122°C and 229°C. This result suggested that curing reaction of BA-a takes place by either with and without any curing agent. The exothermic peaks of EPON 826/Jeffamine D230 and NGDE/Jeffamine D230 appeared at 133°C and 136°C as shown in Figures 5.1(c) and 5.1(d), respectively. It can be seen that EPON 826 as aromatic epoxy was cured with Jeffamine D230 at higher temperature than that of NGDE as aliphatic epoxy. The mixture of BA-a/EPON 826 and BA-a/NGDE showed exothermic peaks at 252°C and 251°C, respectively. This result implied that BA-a resin can also act as curing agent for epoxy. It is due to the formation of phenolic moieties, which is well known as one curing agent of epoxy resin, during polymerization of BA-a resin (Jubsilp et al., 2010).

In this investigation, the effect of curing agent system comprised of BA-a resin and Jeffamine D230 mixture on eopxy resins system was also studied by DSC as shown in Figure 5.2. The ratio of aromatic and aliphatic epoxy was fixed at 1:1 mole ratio whereas the ratio of curing agents mixed between BA-a resin and Jeffamine D230 was varied from 0 to 1 mole ratio. Figure 5.3(a) exhibits the exothermic peak of ENDB 1/1/1/0 located at 134°C attributed to polymerization of epoxy by the Jeffamine D230. In case of epoxy cured with mixture of curing agent between

Jeffamine D230 and BA-a resin at various mole ratios exhibit two exothermic curing peaks. The first peak was observed at about 120°C which corresponding to the peak of epoxy cured by Jeffamine D230. The second peak showed overlapped exothermic peaks or a shoulder beside the main peak at 201°C as clearly seen when 0.6 and 0.8 mole ratio of BA-a was added as shown in Figures 5.2(d) and 5.2(e), respectively. The shoulder corresponded to the exothermic of BA-a/Jeffamine D230 mixture as seen in Figure 5.1(b). The second peaks of the alloys were observed at temperature of 254°C to 259°C which was assigned to the BA-a/epoxy curing, as mentioned in Figures 5.1(e) and 5.1(f). Furthermore, the thermogram also revealed a decrease of area under the curve of the first peak when the amount of BA-a increased. On the other hand, the area under the curve of second peak was observed to increase with increasing amount of BA-a. It is due to the increase in the number of moles of reacted functional groups between epoxy-benzoxazine and benzoxazine-benzoxazine itself. The curing temperature of benzoxazine-modified epoxy resins at a fixed mole ratios of ENDB 1/1/0/1, which, in principle, required the highest curing temperature at 259°C among the investigated resin mixtures, was depicted in Figure 5.2(f). Therefore, BA-a resin at composition of 1.0 mole ratio (ENDB 1/1/0/1) was selected for further study the curing condition of the system.

The curing condition of the benzoxazine-modified epoxy mixtures was determined from the disappearance of the area under the curve of the exothermic peak in DSC experiment. Figure 5.3 illustrated the DSC thermogram of the epoxy modified with benzoxazine at 1 mole ratio of BA-a content at various curing conditions. The heat of reaction of the uncured ENDB 1/1/0/1 was 160.8 J/g corresponding to the 0% conversion. After curing at 80°C for 4 hrs, the heat of reaction decreased to 81.42 J/g (49% conversion) and decreased to 80.27 J/g (51% conversion), 70.99 J/g (56% conversion), 20.45 J/g (87% conversion), 9.60 J/g (94% conversion) and 6.99 J/g (96% conversion) after further curing at 100°C for 2 hrs, 130°C for 1 hr, 150°C for 24 hrs, 170°C for 1 hr and 190°C for 1 hr, respectively. After the curing temperature was elevated to 200°C for 2 hrs, complete disappreance of exothermic peak was observed indicating to 100% conversion of monomers to polymers which corresponded to the fully cured stage of the alloys. The degree of conversion of each sample was determined according to the following relationship:

$$\% \text{ conversion} = (1 - \frac{H_{rxn}}{H_o}) \times 100 \qquad (5.1)$$

where, H_{rxn} = the heat of reaction of the partially cured specimen.

H_o = the heat of reaction of the uncured resin.

As a consequence, the curing temperature at 80°C for 4 hrs, 100°C for 2 hrs, 130°C for 1 hr, 150°C for 24 hrs, 170°C for 1 hr, 190°C for 1 hr and 200°C for 2 hrs was chosen as an optimum curing condition of all the benzoxazine-modified epoxy SMP samples.

Glass transition temperature, T_g, is one of the major characteristic parameters of thermomechanical deformation and shape recovery in SMP materials at which polymers transform from a glassy state to a rubbery state. Polymer segments are assumed to be locked into a glassy state when the polymer segmental motion is limited greatly at temperatures below T_g. T_g of benzoxazine-modified epoxy SMP samples at various BA-a mole ratio were evaluated from DSC as shown in Figure 5.4. In this experiment, the T_g values were taken as the midpoint temperature of the change in specific heat in the transition region.

The T_g of the benzoxazine-modified epoxy SMPs at BA-a content of 0, 0.2, 0.4, 0.6, 0.8 and 1.0 mole ratios were 47°C, 53°C, 59°C, 82°C, 84°C and 116°C, respectively. It clearly seen that an increasing in BA-a mole ratio resulted in an increasing in T_g of epoxy-based SMP. The highest T_g, 116°C, is demonstrated by the material containing 1 mole ratio of BA-a resin. The T_g of the benzoxazine-modified epoxy SMPs can be altered substantially by controlling the amount of BA-a and Jeffamine D230 content.

5.2 Effect of Benzoxazine-Modified Epoxy SMPs on Dynamic Mechanical Properties

Dynamic mechanical analysis (DMA) is useful to investigate thermomechanical properties of polymeric materials, especially the transitions and relaxations of the materials. Knowledge of the transitions and relaxations of the materials will lead to an understanding of how materials behave at different temperatures and to an identification of a suitable service temperature. The change in molecular mobility of the specimen when temperature changed was sensed by dynamic mechanical analysis. The viscoelastic behaviors of benzoxazine-modified epoxy SMPs at various compositions were characterized by DMA at temperature of 30–300°C and a heating rate of 2°C/min. The dynamic mechanical properties of the system were presented in Figures 5.5–5.9.

The thermal 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 (Menard, 1999).

The plot of the loss modulus (MPa) as a function of temperature (°C) of the benzoxazine-modified epoxy SMP samples was illustrated in Figure 5.5. T_g of 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 the 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 prevoius work reported by Rimdusit and Ishida (2000).

Figure 5.6 illustrates a plot of storage modulus (MPa), a material stiffness, as a function of temperature (°C) of the benzoxazine-modified epoxy SMP samples. The storage modulus of a solid polymer at its glassy state (35°C) was 3.18, 3.90, 4.34, 4.44, 4.62 and 4.70 GPa at BA-a content of 0, 0.2, 0.4, 0.6, 0.8 and 1 mole ratio, respectively. The storage modulus tended to increase with increasing BA-a fraction in the alloys as a result of the more rigid characteristics of the BA-a resin.

Effects of BA-a resin on the storage modulus in the rubbery plateau region of the ploymer alloys are illustrated in Figure 5.7. The plateau moduli in the rubbery plateau region were systematically increased from 21 MPa to 54 MPa with addition of the BA-a mole ratio from 0 to 1 mole. This revealed that the increase in the BA-a content in the polymer alloys possibly resulted in an enhancement of the crosslink density of the SMPs alloy which was closely related to the rubbery platueau modulus. The crosslink density of each component may be estimated from the rubbery plateau modulus of the specimen using equation from the statistical theory of rubber elasticity i.e. Nielsen's equation (equation 5.2) (Rimdusit et al., 2011).

$$\log\left(\frac{E'}{3}\right) = 6 + 293\left(\frac{\rho}{M_c}\right) \tag{5.2}$$

Where E' (Pa) is storage modulus in a rubbery plateau region, ρ (g/cm^3) the density of the material at room temperature, and M_c (g/mol) is the molecular weight between crosslink points. As displayed in Table 5.1, the crosslink density values of benzoxazine-modified epoxy SMPs at BA-a content of 0, 0.2, 0.4, 0.6, 0.8 and 1 mole were 2.90×10^{-3}, 3.25×10^{-3}, 3.62×10^{-3}, 3.79×10^{-3}, 3.81×10^{-3} and 4.29×10^{-3} mol/cm^3, respectively. It was observed that the crosslink density tended to increase with an increasing in BA-a content.

In addition, the effect of molecular weight between crosslinks (i.e., inversely proportional to its crosslink density) on a T_g of a copolymer or a non-uniform polymer network can be accounted for using the equation also proposed by Neilsen (Rimdusit et al., 2011).

$$T_g - T_{g(0)} = \frac{k}{M_c} \tag{5.3}$$

The number average molecular weight between crosslinks is M_c. $T_{g(0)}$ is the glass transition temperature of the uncrosslink polymer. Figure 5.8 exhibits the T_g from loss modulus and crosslink density of SMPs alloys at various compositions. As shown in this Figure, the T_g of the polymer network increased when its crosslink density in the alloys increased which is in good agreement with our DMA results.

Tan delta (tan δ) or loss tangent curves relate to the ratio of energy loss or viscous part (E") to storage energy or elastic part (E') of dynamic modulus of material. Moreover, T_g of system can be investigate from the maximum peak of tan δ curve. Tan δ curve of benzoxazine-modified epoxy SMP samples at various mole ratios of

BA-a were illustrated in Figure 5.9. The T_g of the benzoxazine-modified epoxy SMP samples at 0, 0.2, 0.4, 0.6, 0.8 and 1.0 mole ratio BA-a content were found to be 57, 80, 88, 97, 105 and 129°C, respectively. T_g's of the alloys were observed to shift to higher temperature with increasing the mole ratio of the BA-a. Furthermore, an inset of Figure 5.9 also illustrated the magnitude of maximum peak, reflecting the large scale mobility associated with α relaxation. The peak height of the tan δ was found to decrease when BA-a content increase. This confirmed the reduction in segmental mobility of polymer chains with increasing crosslink density. In addition, the width at half height of the maximum peak of tan δ curve relates to the network homogeneity. The width at half height of the tan δ curves of our SMP alloys was observed to be broadest at ENDB of 1/1/0.4/0.6. This behavior implied network heterogeneity to be more pronounced with the presence of mixture of two curing agents.

5.3 Effect of BA-a Content of Benzoxazine-Modified Epoxy SMPs on Mechanical Properties

5.3.1 Mechanical Properties of Benzoxazine-Modified Epoxy SMP at Glassy State

Mechanical properties of benzoxazine-modified epoxy SMPs play important role on their effective utilization. In this work, the mechanical properties of the SMP samples were investigated at glassy state (room temperature) and rubbery state (T_g+20°C). Generally, SMPs were commonly used over these temperatures.

Figures 5.10(a) and 5.10(b) exhibit the plots of the flexural strength and flexural modulus of 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 were 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 increased with an increasing in the BA-a resin fraction. The flexural modulus values of 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 resulted 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 increaseing the stiffening of the resulting polymer alloys. The flexural strength of thermosetting resin was influenced by a number of interrelated parameters including T_g, molecular weight between crosslink, free volume, chemical structure, network regularity and perfection, and many other contributing factors (Rimdusit et al., 2011).

5.3.2 Mechanical Properties of Benzoxazine-Modified Epoxy SMP at Rubbery State

Mechanical properties of benzoxazine-modified epoxy SMPs at a rubbery state are also important parameters that affect deploying ability of the SMP samples. The flexural strength of the benzoxazine-modified epoxy SMPs was measured using three-point bending tests with a Universal testing mechine, 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 5.11(a) exhibited the plot of the flexural strength as a function of the BA-a content (mole ratio) of benzoxazine-modified epoxy SMPs at T_g+20°C. The flexural strength at rubbery state values of benzoxazine-modified epoxy SMPs were 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 at rubbery state of the benzoxazine-modified epoxy SMPs increased with increasing of the BA-a resin fraction from 0 to 1 mol.

Figure 5.11(b) exhibited the plot of the flexural modulus as a function of the BA-a content (mole ratio) of benzoxazine-modified epoxy SMPs at T_g+20°C. The addition of BA-a resin also resulted in a systematic increase of the modulus in the rubbery state with increasing amount of the BA-a resin. The flexural modulus values of benzoxazine-modified epoxy SMPs were 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.

In the T_g+20°C, the system with 1 mole of BA-a content without Jeffamine D230, the flexural strength and flexural modulus rapidly increased. These results suggested that BA-a showed a stronger positive effect on mechanical properties of epoxy over Jeffamine D230. Furthermore, macromolecular chain motion of the benzoxazine-modified epoxy SMP plays a critical role in mechanical resistive loading. Therefore, the mechanical properties of the benzoxazine-modified epoxy SMP would be dependent on the BA-a and Jeffamine D230 composition. The motion of the macromolecular chains would be hindered by the network of the BA-a and Jeffamine D230 and epoxy through friction interactions, helping the benzoxazine-modified epoxy SMP to resist external loading, resulting in a significant improvement in mechanical properties (Lu et al., 2010).

5.4 Shape Memory Properties

5.4.1 Shape Memory Behavior of Benzoxazine-Modified Epoxy-based SMPs

The thermomechanical cyclic tests involve the use of special equipment. In contrast, bending tests are much simpler and is easily approached by many researchers. Liu et al., (2002); Lin and Chen (1998); Li and Larock (2000); Lan et al., (2009) and Biju et al., (2012) investigated the shape memory of SMPs by bending test at temperature between 20°C above T_g and room temperature. The obtained benzoxazine-modified epoxy SMPs incorporating with 0, 0.2, 0.4, 0.6, 0.8 and 1 mole ratio of BA-a resin are illustrated in Figures 5.12(a)–(f). The samples had the appearence of transparence yellow colour which suggested that the blends of the components were mixed well (Lu et al., 2008). The benzoxazine-modified epoxy SMPs at ENDB 1/1/0/1 was used as representative sample to demonstrate the shape memory behavior as shown in Figure 5.13. First, The original rectangular shape (a) was heated at $T \geq T_g$ and deformed into different shapes through bending and twisting. Then, the deformed temporary shapes (b) were fixed by cooling under load.

After re-heating above T_g, the sample recovered into its original rectangular shape (c). The samples were then reheated to recover to their original shape. The recovered shape was indistinguishable from the original shape, confirming the excellent shape fixity and recovery.

5.4.2 Effect of BA-a Content on Shape Fixity

The shape fixity is one key parameter used to describe the extent of a temporary shape being fixed during shape memorization. A high glassy state modulus (E'_g) provided the materials high shape fixity. It is due to the fact that high glassy modulus is indicative of high cohesive energy (mostly highly cross linked) which leads to minimized propensity for creep related shape change. High glassy modulus is not always mandatory for high shape fixity but is desirable, whereas the high rubbery modulus (E'_r) implied high elastic recovery at high temperature (Byung et al., 1996). The modulus ratio (E'_g/E'_r) was taken as (E'_{Tg-20^oC} /E'_{Tg+20^oC}). Where, E'_{Tg-20^oC} and E'_{Tg+20^oC} attributed to the storage modulus at temperature at 20°C below T_g and 20°C above T_g, as described in section 5.2. The modulus ratio was summarized in Table 5.2. The modulus ratio of benzoxazine-modified epoxy SMPs were 102 in ENDB 1/1/1/0, 86 in ENDB 1/1/0.8/0.2, 22 in ENDB 1/1/0.6/0.4, 14 in ENDB 1/1/0.4/0.6, 18 in ENDB 1/1/0.2/0.8, and 20 in ENDB 1/1/0/1. It can be observed that the storage modulus increased with increasing in mole ratio of BA-a resin whereas E'_g/E'_r ratio decreased with increase in mole ratio of BA-a resin. The modulus ratio can be used to represent the shape fixity of the samples. Since reversibility of the samples depend on the modulus ratio. The relationship between shape fixity and modulus ratio was described by the following mathematical equation 5.4 (Ratna and Kocsis, 2008).

$$\text{Shape fixity } (R_f) = 1 - \frac{E'_r}{E'_g} \tag{5.4}$$

Where E'_g is the glassy modulus (T_g–50°C), E'_r is the rubbery modulus (T_g+50°C). The shape fixity values of benzoxazine-modified epoxy SMPs are 99.5% in ENDB 1/1/1/0, 99.3% in ENDB 1/1/0.8/0.2, 99.2% in ENDB 1/1/0.6/0.4, 99.2% in

ENDB 1/1/0.4/0.6, 99.2% in ENDB 1/1/0.2/0.8, and 98.8% in ENDB 1/1/0/1, the value was also summarized in Table 5.2. The samples showed excellent shape fixity values of about 98–99%. These range of value corresponded to the publication of Leonardi et al. (2011). The shape fixity of an epoxy (DGEBA type) network consisted of n-dodecylamine (DA) units as physical crosslinks and m-xylylenediamine (MXDA) units as chemical crosslinks. The prepared epoxy SMPs at molar ratio of 6:4:1 (DGEBA/DA/MXDA) was reported to be 98%.

5.4.3 Shape Recovery Ratio at Different Active Temperature

Shape recovery is used to reflect how well an original shape of the sample has been memorized. The diverse and complex utilization of shape recovery performance take place not only to notation but also to mathematical expressions of various parameters.

In this study, 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 (Lan et al., 2009; Leng et al., 2009 and Lu et al., 2010). The rectangular specimens were used to investigate the recovery phonomenon. As shown in Figure 5.14, the ENDB 1/1/0.8/0.2 sample was heated up to the transition temperature ($T \geq T_g$) in an oven and held for 20 min. Then, sample became elastic and was bent into a u-shape of mandrel with a diameter of 4 mm. The fixed sample was subsequently cooled to room temperature, and then held for 20 min to ensure that the sample retained u-shape. In the next step, the bent sample was placed in an oven at certain temperatures for further study on their shape recovery performance. All of the SMP samples showed the similar shape recovery performance as illustrated in Figure 5.14.

From the bending test as mention in 5.4.1, we investigate the shape recovery ratio (R_N) of the SMP at different active temperatures, the samples were set at different active temperatures as T_g–20^{o}C, T_g–10^{o}C, T_g^{o}C, T_g+10^{o}C and T_g+20^{o}C. Shape recovery ratio was obtained through calculating the ratio of shape recovery angle to 180^o. The value of the shape recovery ratio is calculated by:

$$R_N = \frac{\theta_0 - \theta_N}{\theta_0} \times 100\% \qquad (5.5)$$

Where R_N denotes the shape recovery ratio of the Nth thermomechanical bending cycle. θ_0 is the original storage angle of the specimen. θ_N is the residual angle in the recovery state during the N^{th} thermomechanical bending cycle (N = 1).

Figure 5.15 showed the plot of shape recovery ratio at T_g–20°C, T_g−10°C, T_g°C, T_g+10°C and T_g+20°C. The experimental results demonstrated that the epoxy modified with benzoxazine ranging from 0 to 1 mole ratio presented fast responsive behaviors 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 temperatures, e.g. T_g, T_g+10°C, T_g+20°C. Whereas at temperature below T_g (T_g–20°C), the recovery ratio decreased with increasing BA-a content. Moreover, the recovered ratio of 1 molar ratio of BA-a content clearly decreased with every temperature. However, 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°C and T_g, which is associated with the partial glass transition. However, the shape recovery ratio dropped sharp when the active temperature decreased to T_g–20°C. The shape recovery effect cannot be released below an active temperature of T_g–20°C. The R_N values of all samples were 100%. The R_N values of all specimens were significantly higher compare to that of shape memory polymers from polyurethane-benzoxazine systems (Erden et al., 2009) which were reported to 72–84%. R_N value of some epoxy based SMPs was 99% (Leng et al., 2011). Based on the results, active temperature at T_g and T_g+20°C provide recovery ratio about 90–100% within 150 s therefore these temperatures i.e. T_g and T_g+20°C are selected to be used as the condition for measurement recovery time of benzoxazine-modified epoxy SMP samples.

5.4.4 Effect of BA-a Content on Shape Recovery Time

The shape recovering time for benzoxazine-modified epoxy at different active temperatures i.e. T_g and T_g+20°C, are shown in Figures 5.16 and 5.17. According to the results, all samples need a few minutes to recover their original shape which indicated a good shape memory performance.

Figure 5.16 illustrats the relationship between recovery angle and recovery time of benzoxazine-modified epoxy SMP specimens at T_g. The slope of curve in Figure 5.16 keeps at a constant from 50^o to 150^o. Below and above this range, it was observed to be slightly increase. It indicated that epoxy-based SMP has a relative low recovery rate at the start and last stage. At incipient stage, the release of constrained force was followed by heavy friction among molecules, so that the slope was found to be a little high. After incipient stage, friction force reduced under the gradual adjustment of segments. At terminal stage, shape recovery rate becomes slowly once again because most of the constrained force has been released, with little left of the force (Liu et al., 2010).

Figure 5.17 shows the plot of recovery angle as a function of recovery time for benzoxazine-modified epoxy SMP specimens at T_g+20°C. As can be seen in Figure 5.17, the epoxy based SMP cured by mixture of curing between benzoxazin resin and Jeffamine D230 at various mole ratios could deploy quickly within the initial 30 s, and then deployment velocity dropped quickly due to the termination of strain energy dissipation. The similar observation was also reported in carbon fiber reinforced styrene based SMPs (Lan et al., 2009). The shape recovery time of the benzoxazine-modified epoxy SMPs having BA-a content of 0 to 1 mole ratio was observed to be ranging from 40 s to 140 s. The shape recovery time was found to increase with increasing amount of BA-a resin. Shape recovery depends on both the structures of polymers and the thermomechanical conditions of shape memorization (Leng et al., 2009). This result implied that the addition of BA-a can control the shape recovery time, therefore broadening the applications of the epoxy based SMPs.

Shape recovery speed of the benzoxazine-modified epoxy SMP samples were evaluated by the time period of their full recovery. Figure 5.18 showed the relationship of the shape recovery time and BA-a content at the active temperature (T_g and T_g+20°C). According to the results, all of the samples took only a few minutes to completely recover to their original shape, suggesting the 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 SMPs samples with 0, 0.2, 0.4, 0.6, 0.8 and 1.0 mole ratio of BA-a spent 47, 74, 88, 112, 131 and 173 s, respectively, to fully recover. At T_g+20°C, the shape recovery time also increased with an increasing in BA-a content. The benzoxazine-modified epoxy SMPs samples with 0, 0.2, 0.4, 0.6, 0.8 and 1.0 mole ratio of BA-a spent 40, 57, 61, 72, 83 and 142 s, respectively. This observation suggested that increasing of the active temperature, the shape recovery time certainly decreased whereas the increasing amount of benzoxazine affected to the increasing of recovery time at same temperature. This could be due to the shape recovery of SMPs depended on the relaxation of chain segments. At high temperature, the movement of chain segment became intense that affected to the increasing of recovery force on the samples. Thus, the shape recovery time of the specimens decreased with an increasing in active temperature. At the same deformation condition of samples, the movement of chain segment would be expected to be more restrictive because increasing of crosslink density which resulted in the decrease of molecular weight between crosslink points, as shown in Table 5.1. Hence, benzoxazine-modified epoxy SMP samples with higher BA-a content has a lower shape recovery time.

5.4.5 Effect of BA-a Content on Recovery Stress

To obtain potential applications being in the area of actuators and reconfigurable structures, two key merits of performance for an SMP-based device were return force and response time (Xie, 2010). The return force quantified the tendency of the SMP to return to its original shape. The test was conducted by restricting the strain of a deformed SMP. Recovery stress from the elastic recovery stress generated in the deformation process. When SMPs were heated and deformed, the elastic stress was generated and the elastic stress was stored when SMPs were cooled below T_g. If the deformed and fixed SMPs were reheated above T_g, the stress stored in SMPs was released as shape recovery stress (Hu, 2007).

At first, maximum stress (σ_m) was applied at 20°C above T_g. The strain (ε_m) at the maximun stress point was maintained by cooled down to room temperature. Note that stress was reduced to zero at this stage and the sample was held at room temperature under the unload condition for 15 min, then it was heated to 20°C above

T_g by maintaining the strain (ε_m). Final stage, the sample was held at 20°C above T_g for 15 min (Tobushi et al., 2003).

Figure 5.19 shows photographs of bending in recovery stress process for benzoxazine-modified epoxy SMPs at four stages. Initial stage showed the rectangular original shape of ENDB 1/1/0/1 as depicted in Figure 5.19(a). The deformed state at the maximum deflection (y_{max})=10 mm was shown in Figure 5.19(b). The sample was fixed by cooling to below T_g at this stage. Figure 5.19(c) exhibits the shape-fixed state of sample after cooling to room temperature and final stage, the bent shape of sample recovered considerably, as can be seen in Figure 5.19(d). The recovery stress of SMPs was measured from transition stage of the shape-fixed stage to recovery shape stage.
The benzoxazine-modified epoxy SMPs samples with 0, 0.2, 0.4, 0.6, 0.8 and 1.0 mole ratio of BA-a showed the recovery stress about 20.42±0.39, 23.36±2.39, 29.77±0.87, 30.97±0.97, 33.70±3.01 and 38.18±2.82 kPa, respectively, as shown in Figure 5.20. Based on the result, benzoxazine resin can improve recovery stress of epoxy based SMP. It is due to that the BA-a may store elastic strain energy. When reheating the specimen, this stored elastic strain energy will release and BA-a/epoxy-based SMP obtain higher recovery stress (Gall et al., 2002; Ni et al., 2007).

From the results, introduced BA-a resin in the epoxy-based SMP resulting in an increase of the rubbery modulus from 21 to 54 MPa while maintaining acceptable shape fixity and recovery (≥ 90%) after shape memory effect. Therefore, the obtained SMPs were highly useful in some applications such as actuator and temerature sensor etc.

5.4.6 Mechanical Properties of the Samples after Repeated Recovery Cycles

In order to evaluate the degradation of SMP based benzoxazine-modified epoxy, the relationship between flexural strength and the number of bending cycles was tested at T_g+20°C. The test results in the plots of flexural strength and number of recovering 100 cycles was shown in Figure 5.21. 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 1.0 mole ratio of BA-a showed the flexural strength in 100 cycles 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. The little change of flexural strength values was observed in Figure 5.21. This phenomenon can be explained by the fatigue of material during repeated shape recovery process.

However, the benzoxazine-modified epoxy polymers maintained flexural strength after testing at 100 cycles. It indicated the excellent cycling capability of the SMP alloys due to the excellent thermal stability of benzoxazine-modified epoxy polymers and its chemical crosslink nature.

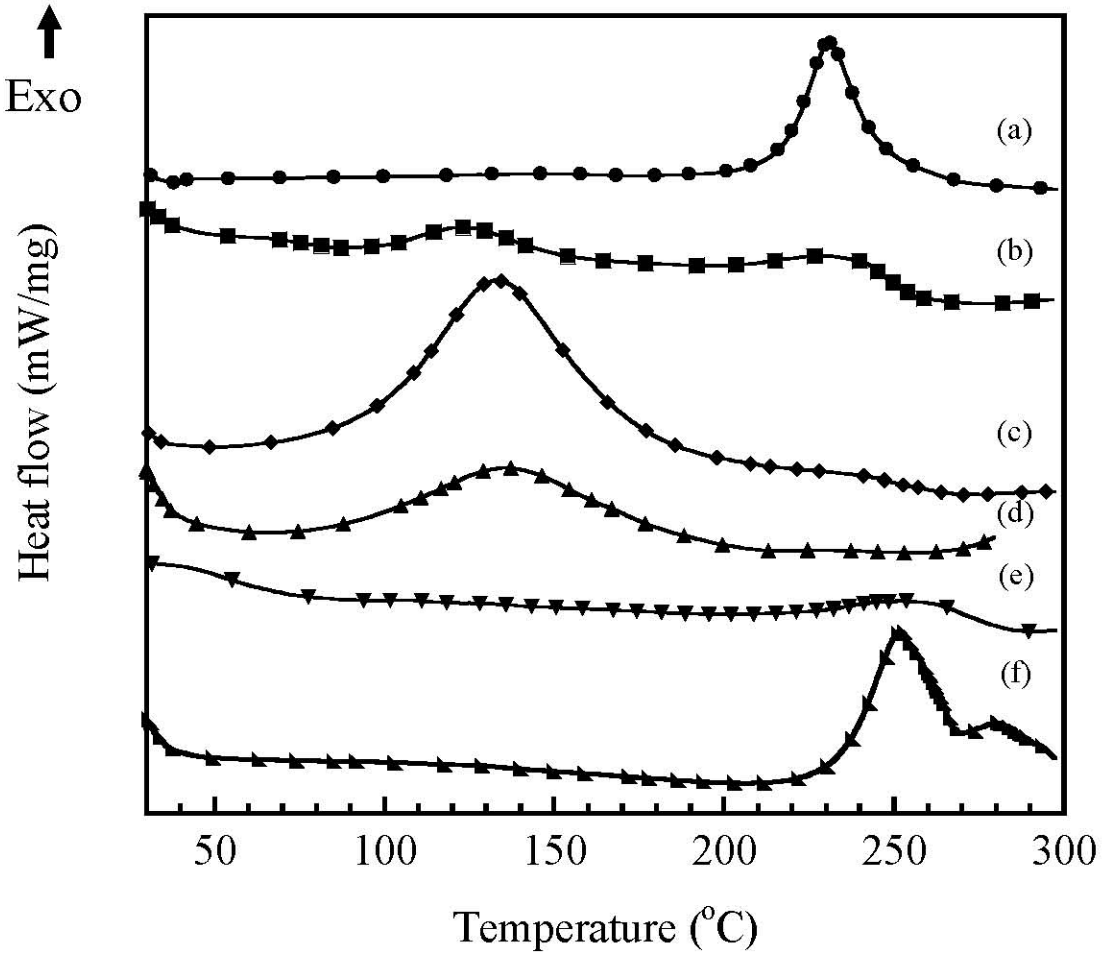


Figure 5.1 DSC thermograms of (●) benzoxazine monomer (BA-a), (■) BA-a/curing agent (Jeffamine D230), (♦) aromatic epoxy (EPON 826)/curing agent (Jeffamine D230), (▲) aliphatic epoxy (NGDE)/curing agent (Jeffamine D230), (▼) BA-a/aromatic epoxy (EPON 826) and (◣)BA-a/aliphatic epoxy (NGDE).

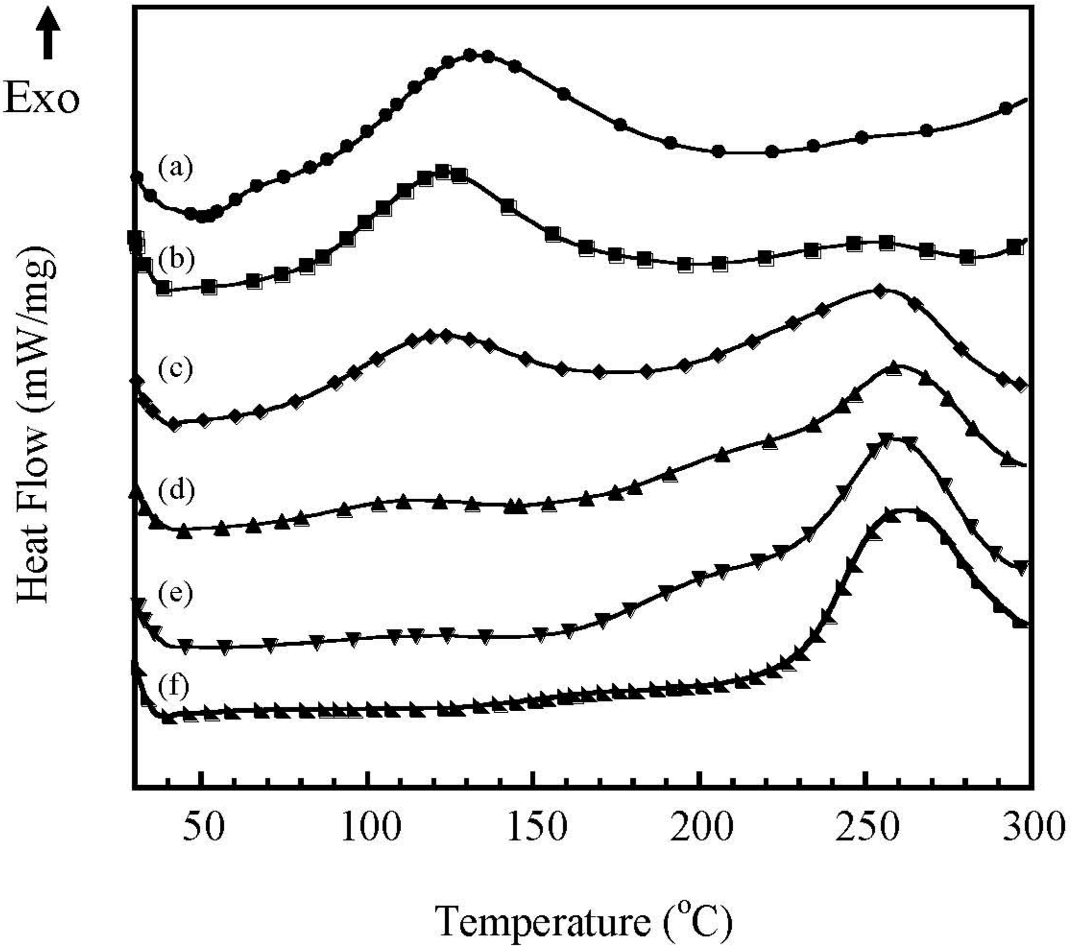


Figure 5.2 Curing behaviors of the benzoxazine-modified epoxy SMP samples at various compositions: (●) ENDB 1/1/1/0, (■) ENDB 1/1/0.8/0.2, (♦) ENDB 1/1/0.6/0.4, (▲) ENDB 1/1/0.4/0.6, (▼) ENDB 1/1/0.2/0.8 and (◣) ENDB 1/1/0/1.

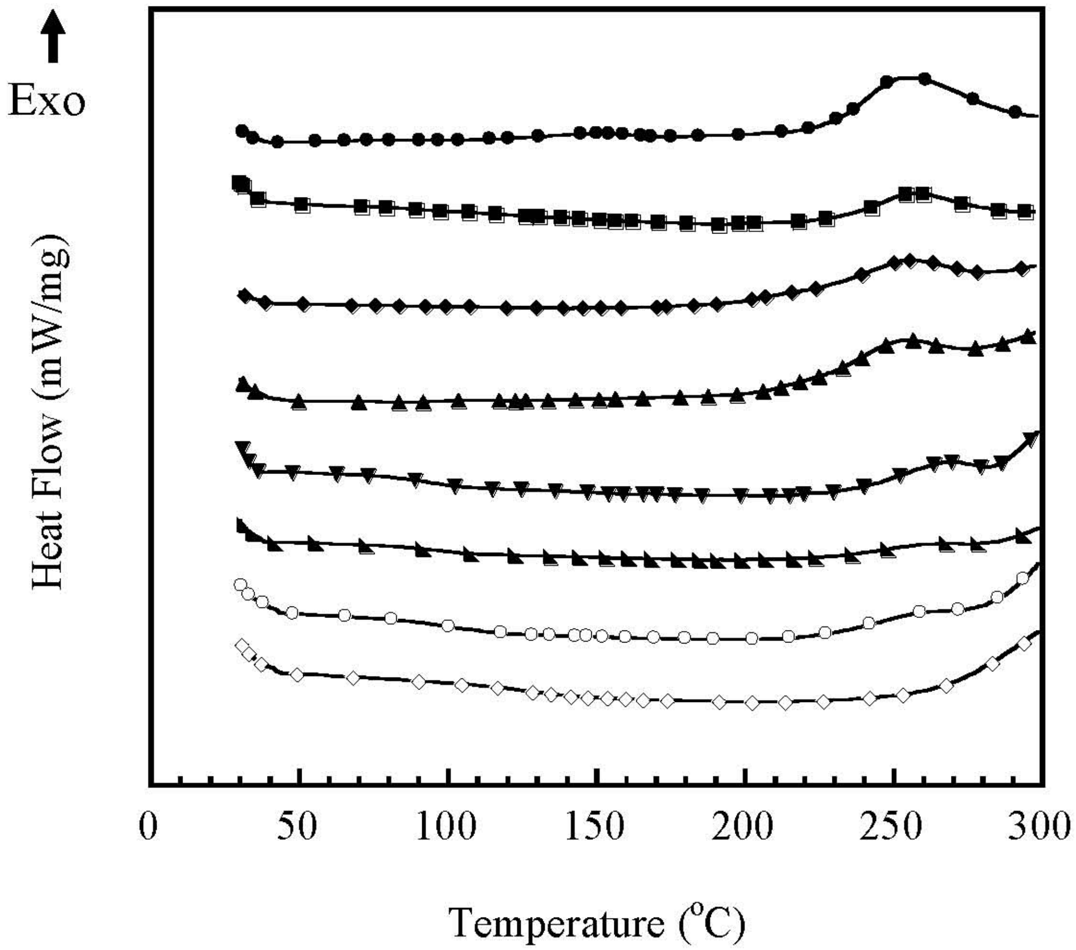


Figure 5.3 DSC thermograms the benzoxazine-modified epoxy SMP samples at various compositions at a mole fraction of ENDB 1/1/0/1 at various curing conditions: (●) uncured, (■) 80^{o}C/4hrs, (♦) 80^{o}C/4hrs + 100^{o}C/2hrs, (▲) 80^{o}C/4hrs + 100^{o}C/2hrs + 130^{o}C/1hr, (▼) 80^{o}C/4hrs + 100^{o}C/2hrs + 130^{o}C/1hr + 150^{o}C/1hr, (◣) 80^{o}C/4hrs + 100^{o}C/2hrs + 130^{o}C/1hr + 150^{o}C/1hr + 170^{o}C/1hr, (○) 80^{o}C/4hrs + 100^{o}C/2hrs + 130^{o}C/1hr + 150^{o}C/1hr + 170^{o}C/1hr + 190^{o}C/1hr, and (◊) 80^{o}C/4hrs + 100^{o}C/2hrs + 130^{o}C/1hr + 150^{o}C/1hr + 170^{o}C/1hr + 190^{o}C/1hr + 200^{o}C/2hrs.

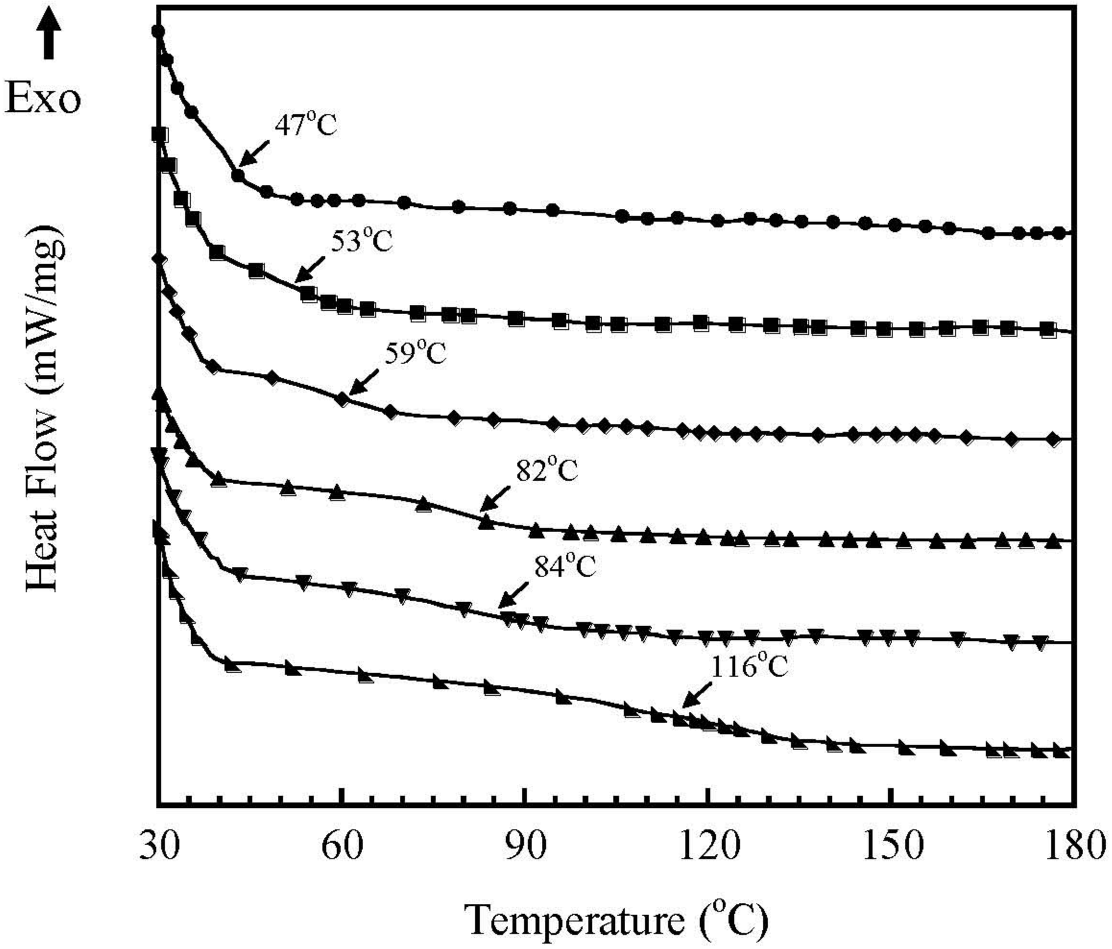


Figure 5.4 Glass transition temperature the benzoxazine-modified epoxy SMP samples at various compositions samples from DSC thermograms at various compositions: (●) ENDB 1/1/1/0, (■) ENDB 1/1/0.8/0.2, (♦) ENDB 1/1/0.6/0.4, (▲) ENDB 1/1/0.4/0.6, (▼) ENDB 1/1/0.2/0.8 and (◣) ENDB 1/1/0/1.

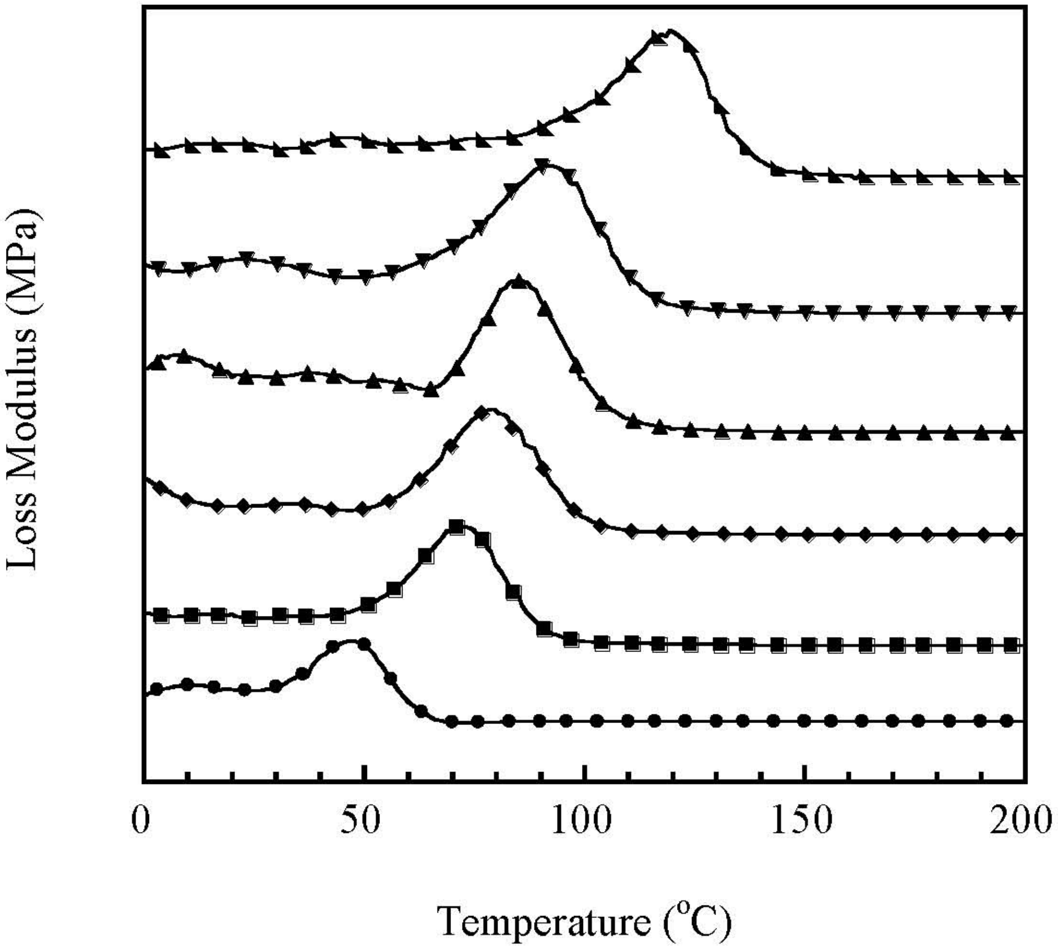


Figure 5.5 Loss modulus as a function of temperature of the benzoxazine-modified epoxy SMP samples at various compositions: (●) ENDB 1/1/1/0, (■) ENDB 1/1/0.8/0.2, (♦) ENDB 1/1/0.6/0.4, (▲) ENDB 1/1/0.4/0.6, (▼) ENDB 1/1/0.2/0.8 and (◣) ENDB 1/1/0/1.

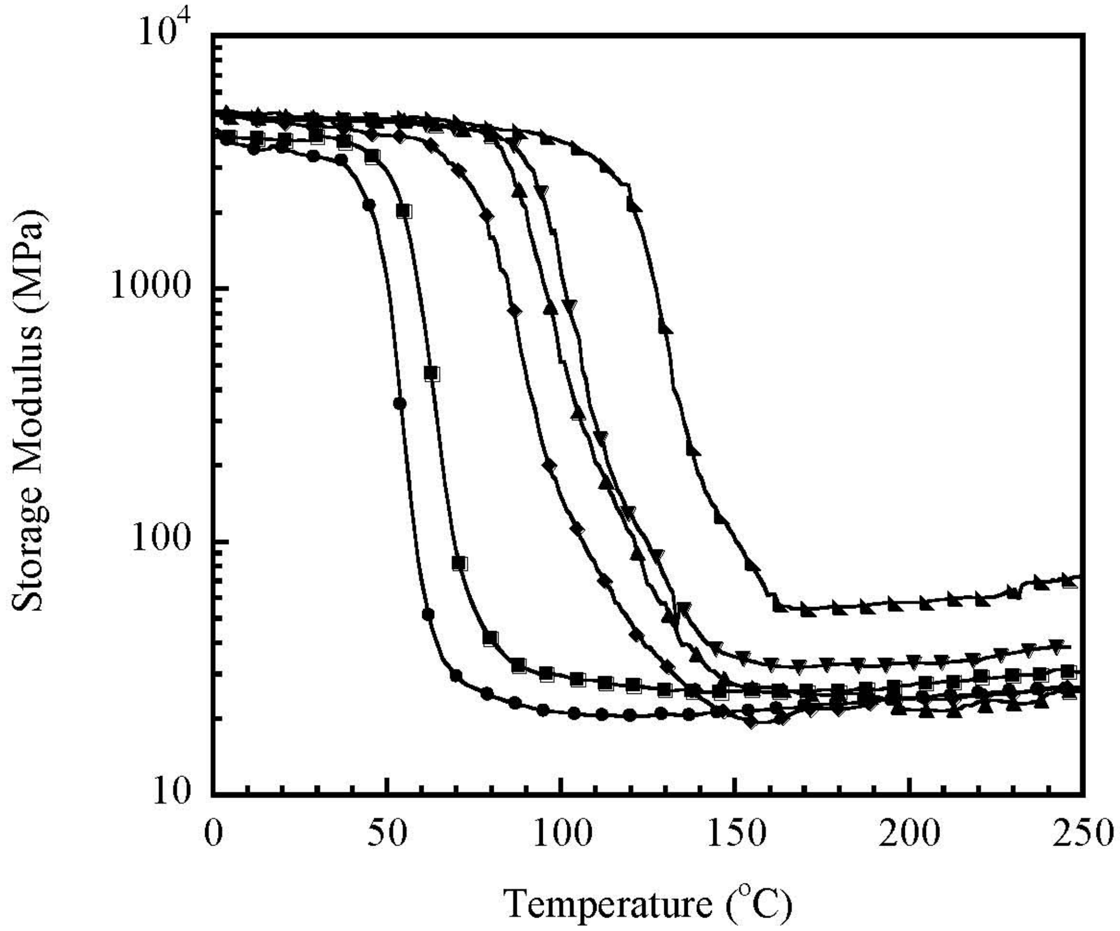


Figure 5.6 Storage modulus of the benzoxazine-modified epoxy SMP samples at various compositions: (●) ENDB 1/1/1/0, (■) ENDB 1/1/0.8/0.2, (♦) ENDB 1/1/0.6/0.4, (▲) ENDB 1/1/0.4/0.6, (▼) ENDB 1/1/0.2/0.8 and (◣) ENDB 1/1/0/1.

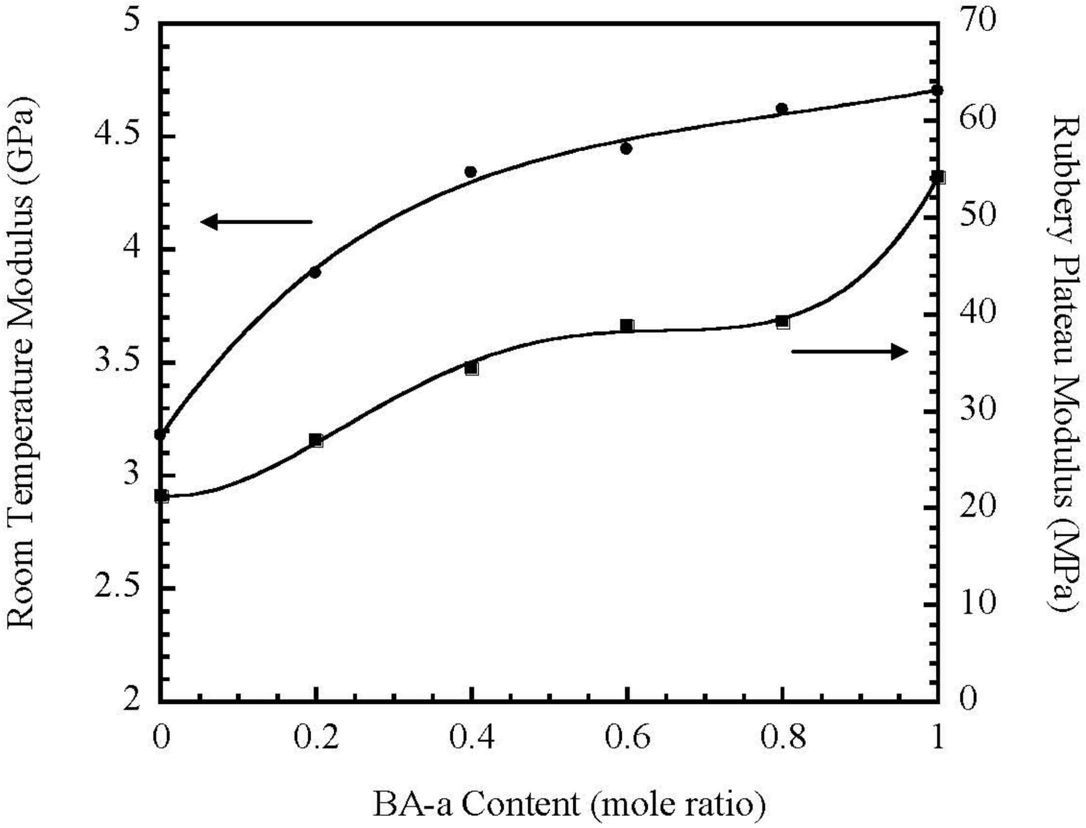


Figure 5.7 Plot of the room temperature storage modulus and rubbery plateau modulus as a function of the BA-a content in the benzoxazine-modified epoxy SMP samples: (●) room temperature modulus and (■) rubbery plateau modulus.

Table 5.1 Properties of benzoxazine-modified epoxy SMP samples from DMA analysis

Samples	**Storage modulus (E') at 35^{o}C (GPa)**	**Crosslink density (mol/cm^3)**	**Molecular weight between crosslink points, M_c (g/mol)**	**Glass transition temperature, T_g (^{o}C)**
ENDB 1/1/1/0	3.18	2.90×10^{-3}	394	47.15
ENDB 1/1/0.8/0.2	3.90	3.25×10^{-3}	354	71.93
ENDB 1/1/0.6/0.4	4.34	3.62×10^{-3}	320	79.66
ENDB 1/1/0.4/0.6	4.44	3.79×10^{-3}	310	85.07
ENDB 1/1/0.2/0.8	4.62	3.81×10^{-3}	309	92.31
ENDB 1/1/0/1	4.70	4.29×10^{-3}	277	119.55

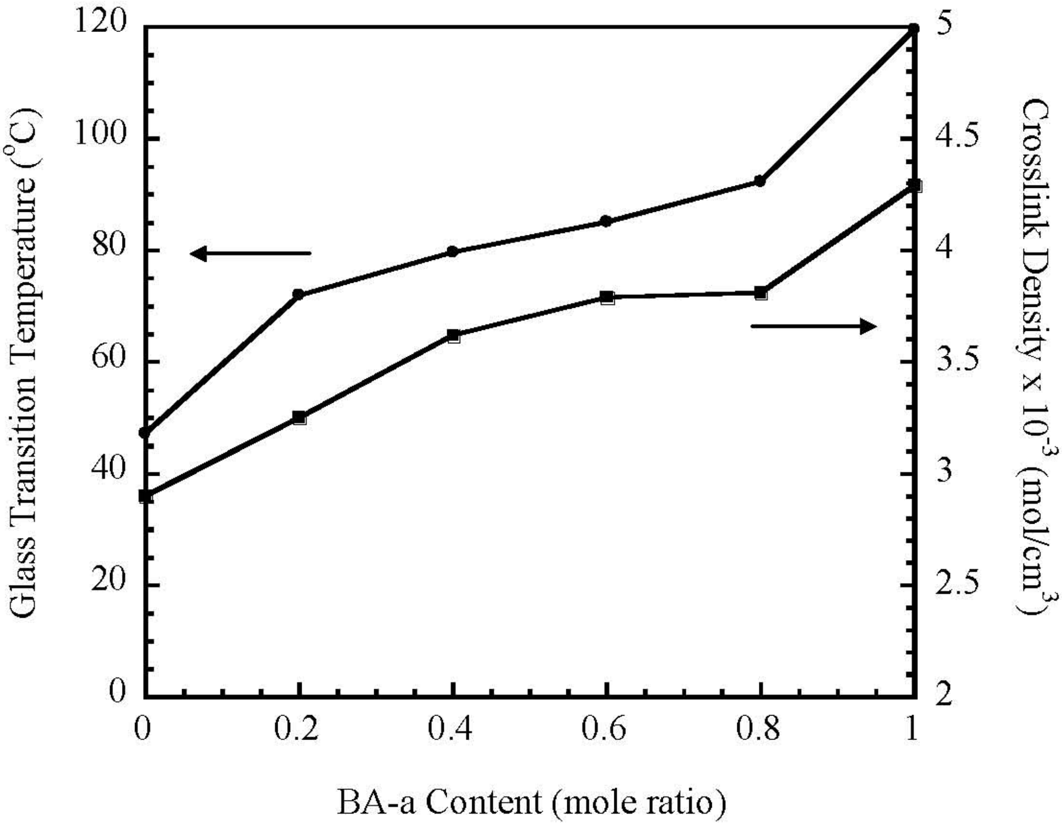


Figure 5.8 Glass transition temperature (●) and Crosslink density (■) and from loss modulus of benzoxazine-modified epoxy SMP at various compositions.

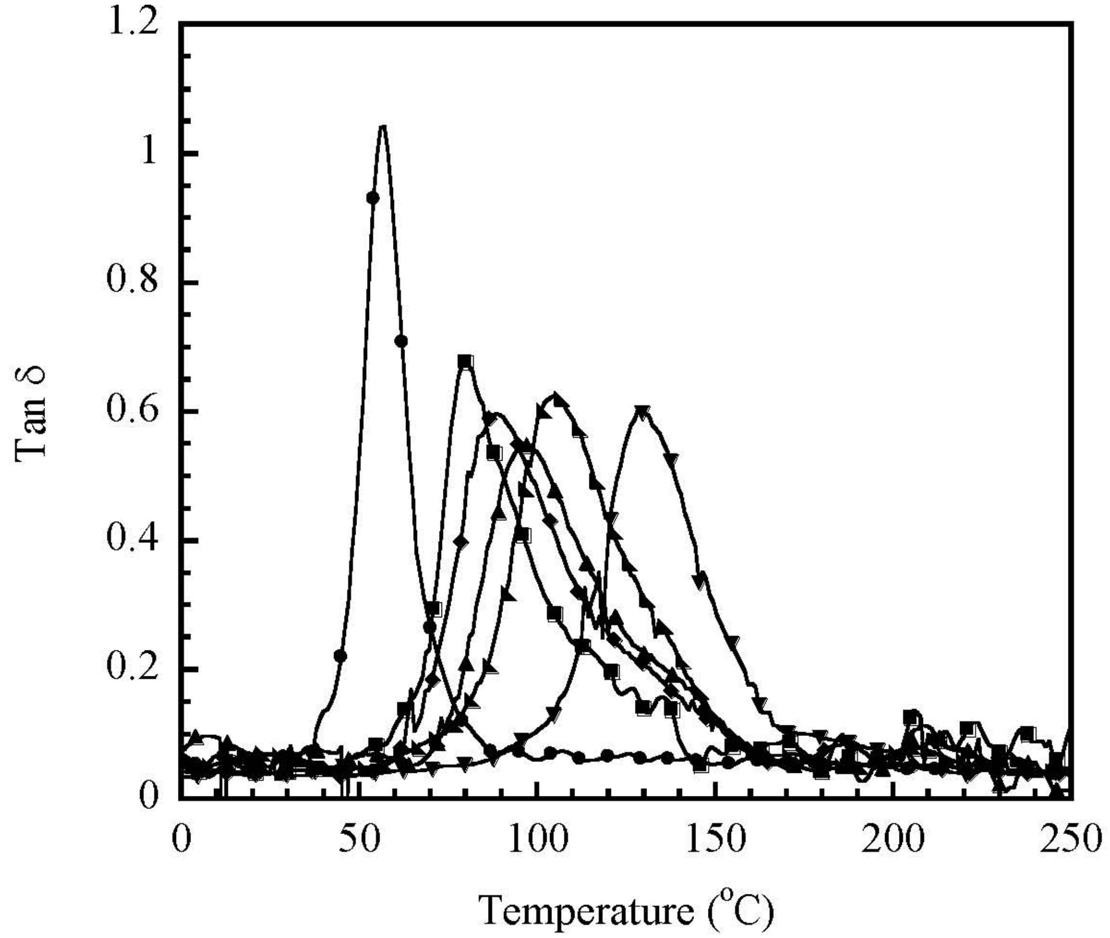
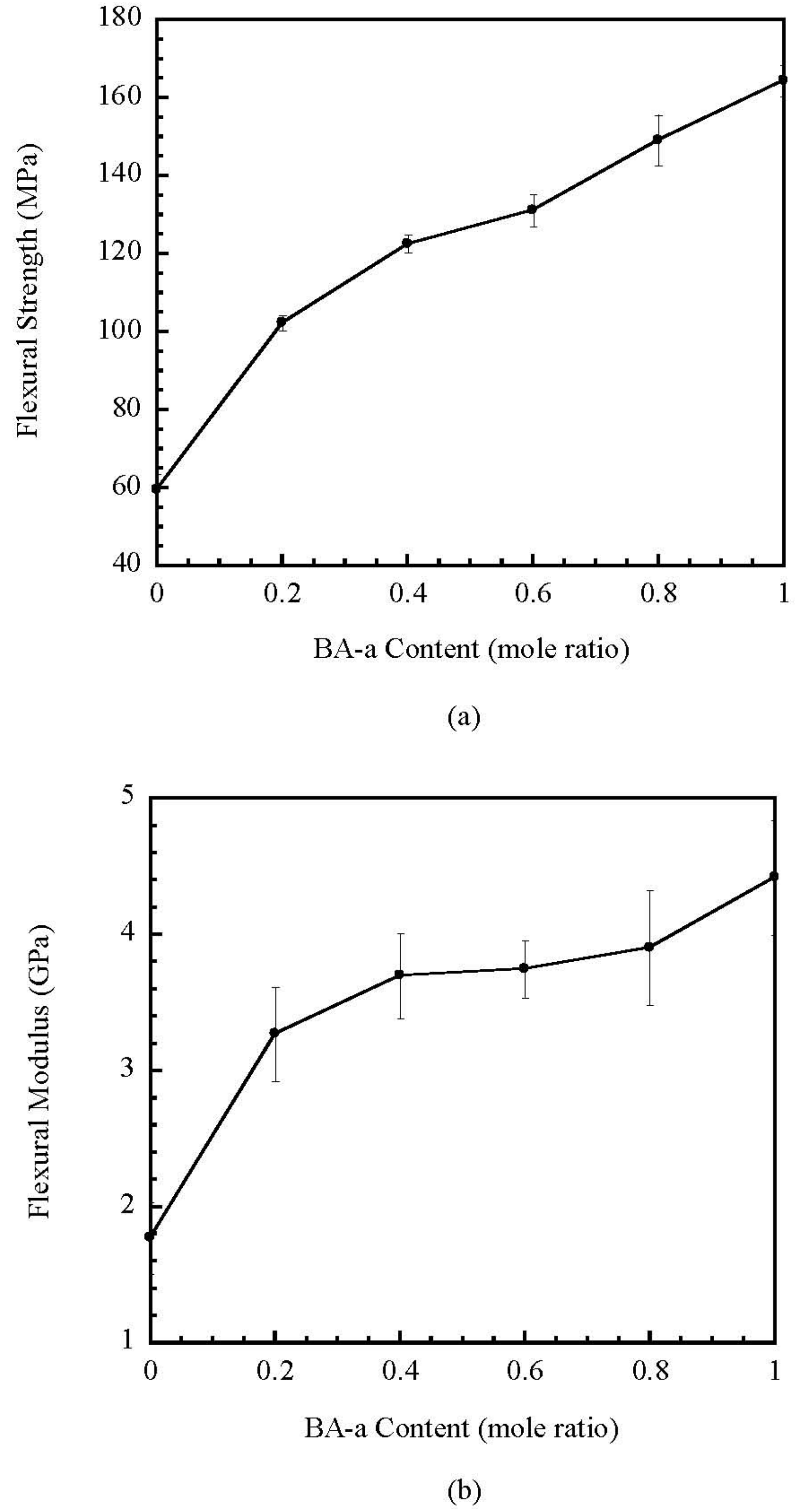


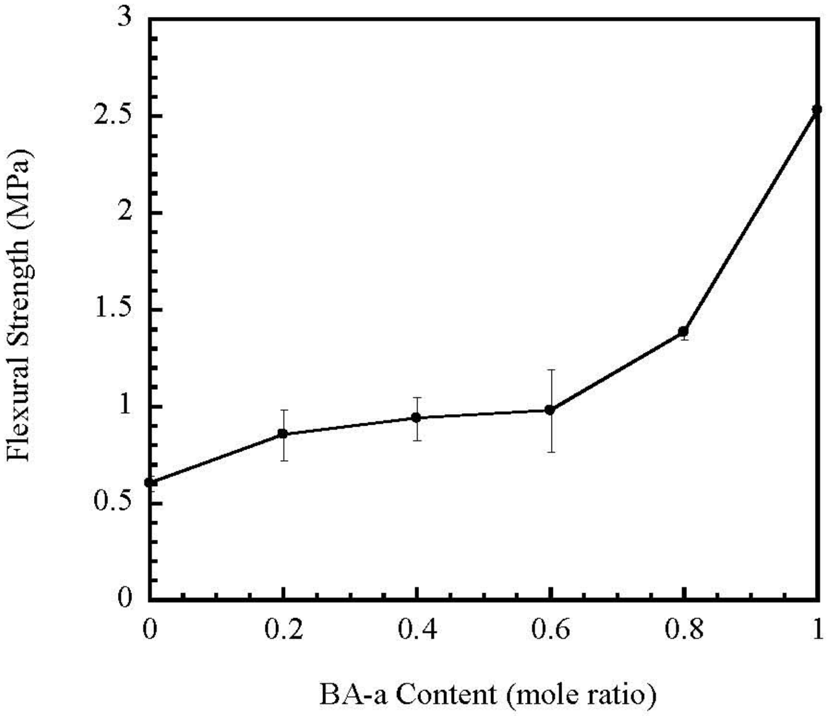
Figure 5.9 Loss tangent as a function of temperature of the benzoxazine-modified epoxy SMP samples at various compositions: (●) ENDB 1/1/1/0, (■) ENDB 1/1/0.8/0.2, (♦) ENDB 1/1/0.6/0.4, (▲) ENDB 1/1/0.4/0.6, (▼) ENDB 1/1/0.2/0.8 and (◣) ENDB 1/1/0/1.



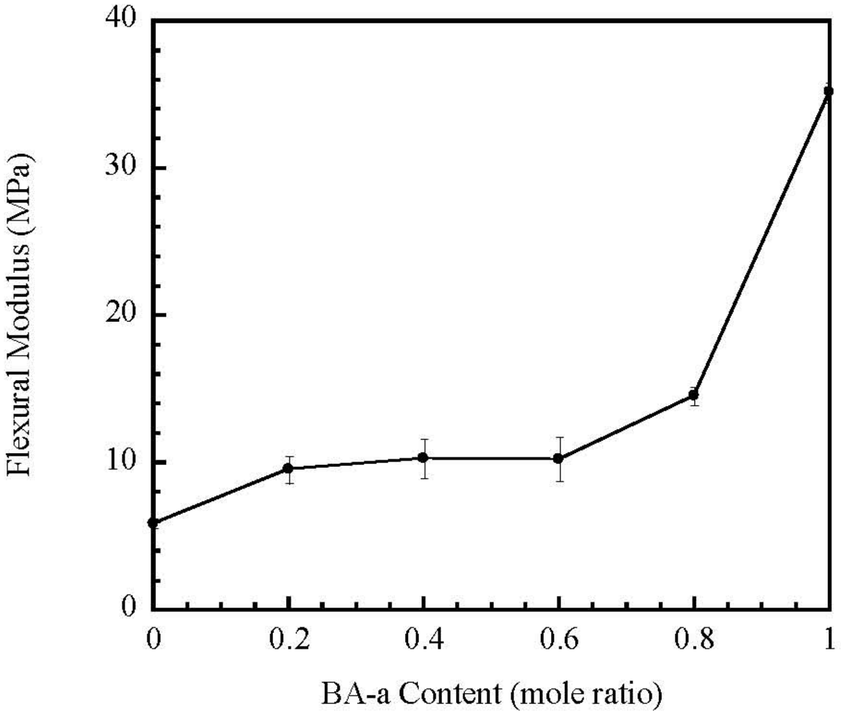
(a)

(b)

Figure 5.10 Flexural strength (a) and flexural modulus (b) of the benzoxazine-modified epoxy SMP samples at various compositions at room temperature.



(a)



(b)

Figure 5.11 Flexural strength (a) and flexural modulus (b) of the benzoxazine-modified epoxy SMP samples at various compositions at T_g+20°C.

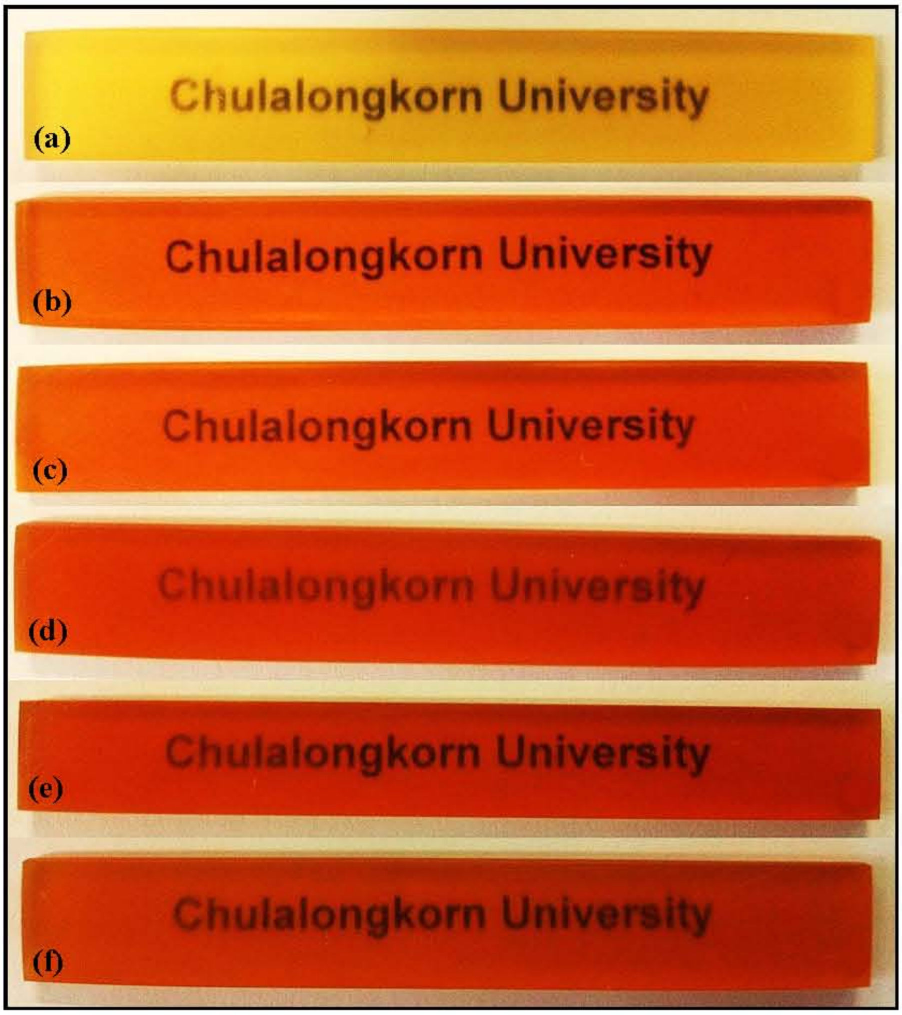
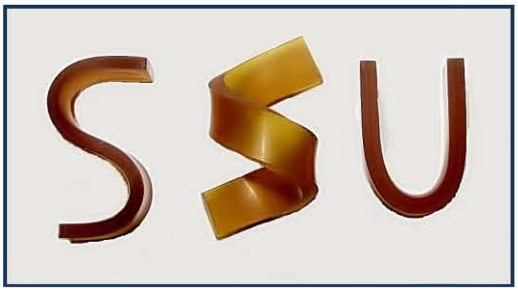


Figure 5.12 Photograph of transparent benzoxazine-modified epoxy SMP samples at (a) ENDB 1/1/1/0, (b) ENDB 1/1/0.8/0.2, (c) ENDB 1/1/0.6/0.4, (d) ENDB 1/1/0.4/0.6, (e) ENDB 1/1/0.2/0.8, (f) ENDB 1/1/0/1.

(a) Original shape



(b) Temporary shape

(c) Recovered shape

Figure 5.13 Shape memory behavior of benzoxazine-modified epoxy SMP sample at ENDB 1/1/0/1 (a) original shape, (b) temporary shape and (c) recovered shapes at T_g+20°C.

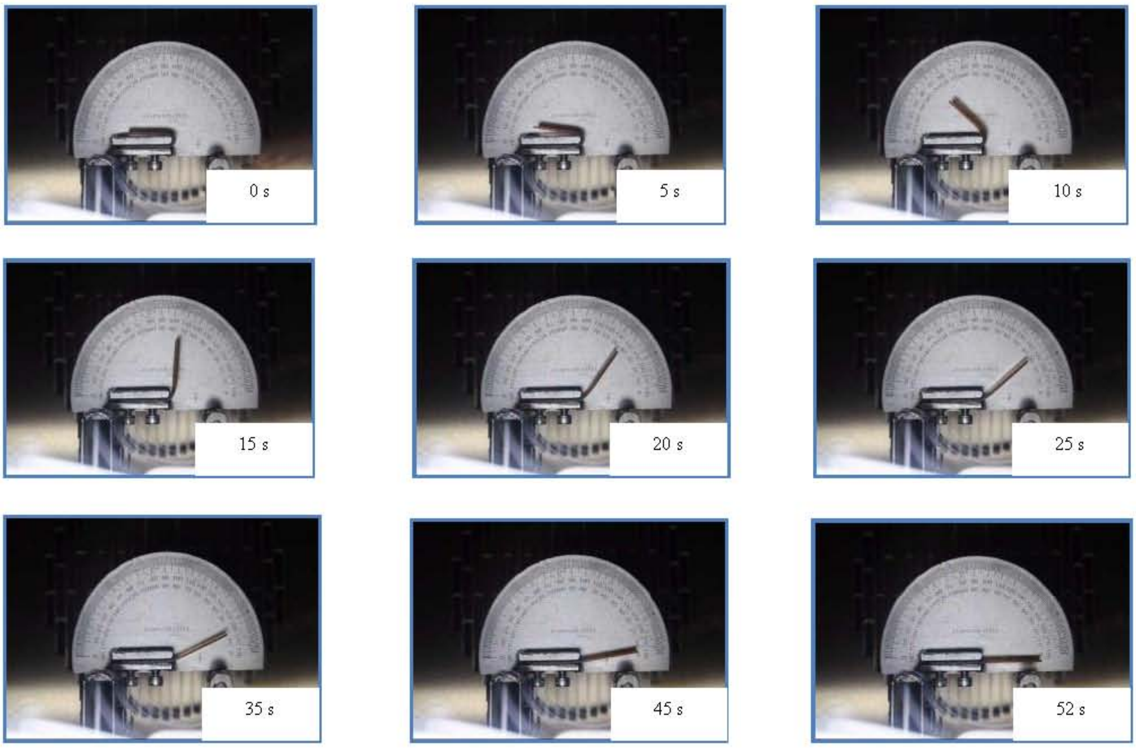


Figure 5.14 Series of images showed the shape recovery of the benzoxazine-modified epoxy SMP sample with ENDB 1/1/0.8/0.2 at T_g+20°C (91°C). The permanent and temporary shape were rectangular and u-shape, respectively.

Table 5.2 Shape fixity of benzoxazine-modified epoxy SMP samples.

Samples	E'_g/E'_r	Shape fixity (%)
ENDB 1/1/1/0	102	99.5
ENDB 1/1/0.8/0.2	86	99.3
ENDB 1/1/0.6/0.4	22	99.2
ENDB 1/1/0.4/0.6	14	99.2
ENDB 1/1/0.2/0.8	18	99.2
ENDB 1/1/0/1	20	98.8

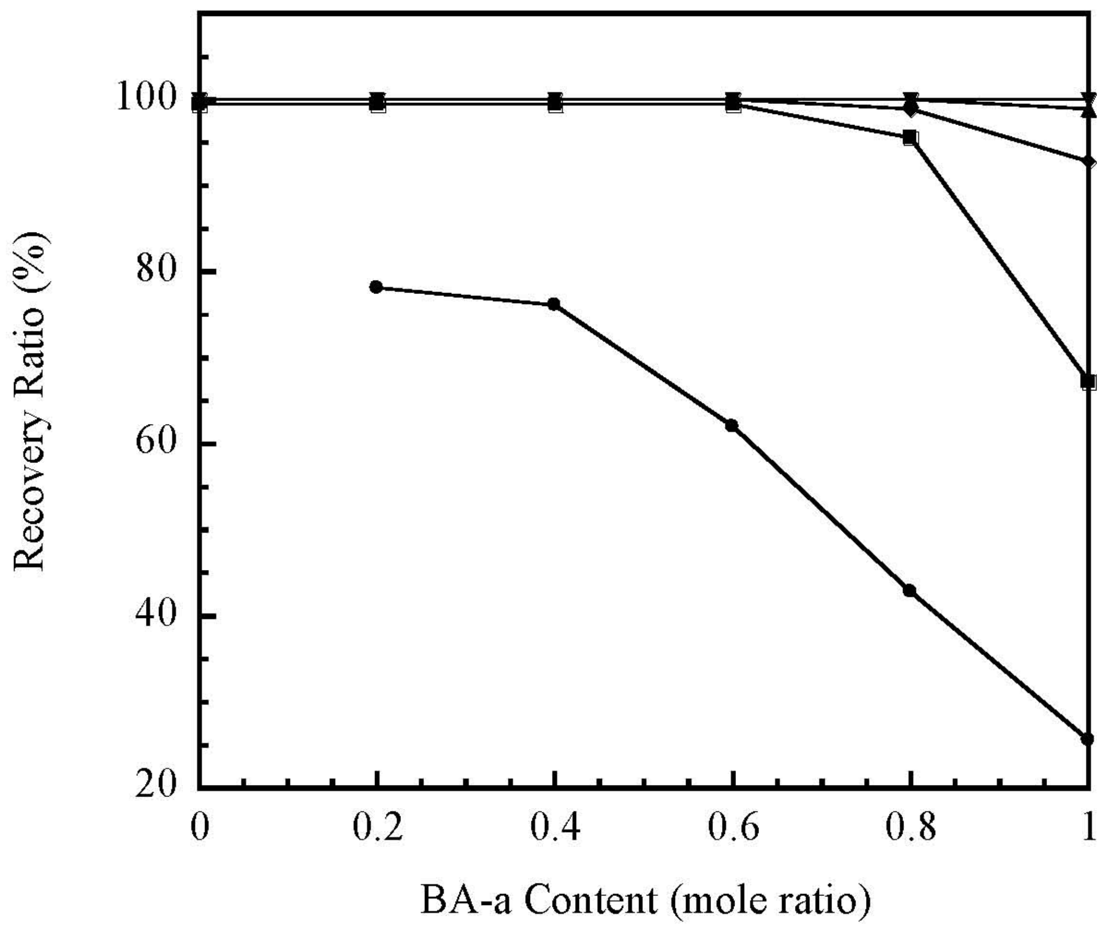


Figure 5.15 Shape recovery ratio as a function of BA-a content at different active temperatures. The original storage angle θ_0 is 180^o in the storage state is selected at the 150th second during the shape recovery cycle: (●) T_g–20°C, (■) T_g–10°C, (♦) T_g, (▲) T_g+10°C, (▼) T_g+20°C.

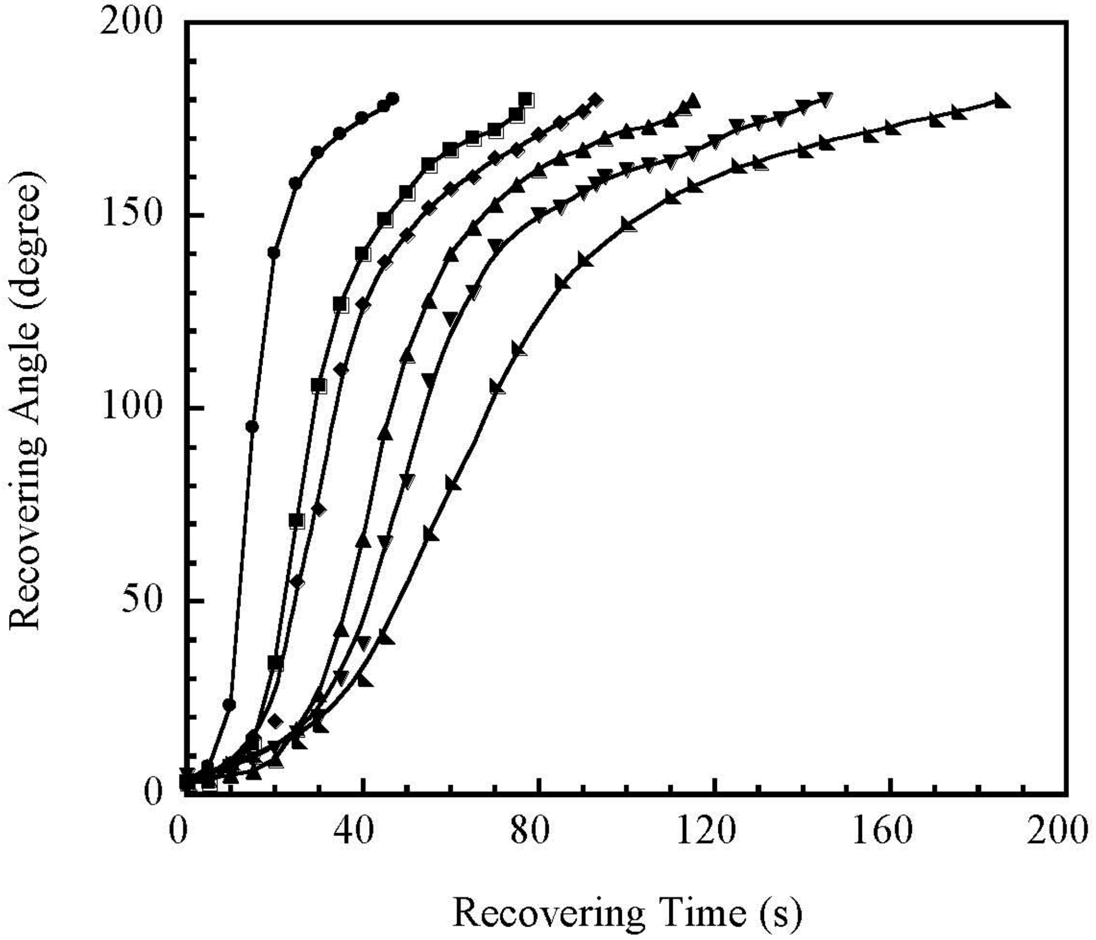


Figure 5.16 Recovery angle as a function of recovery time during the shape recovery process at T_g of the benzoxazine-modified epoxy SMP samples at various compositions: (●) ENDB 1/1/1/0, (■) ENDB 1/1/0.8/0.2, (♦) ENDB 1/1/0.6/0.4, (▲) ENDB 1/1/0.4/0.6, (▼) ENDB 1/1/0.2/0.8 and (◣) ENDB 1/1/0/1.

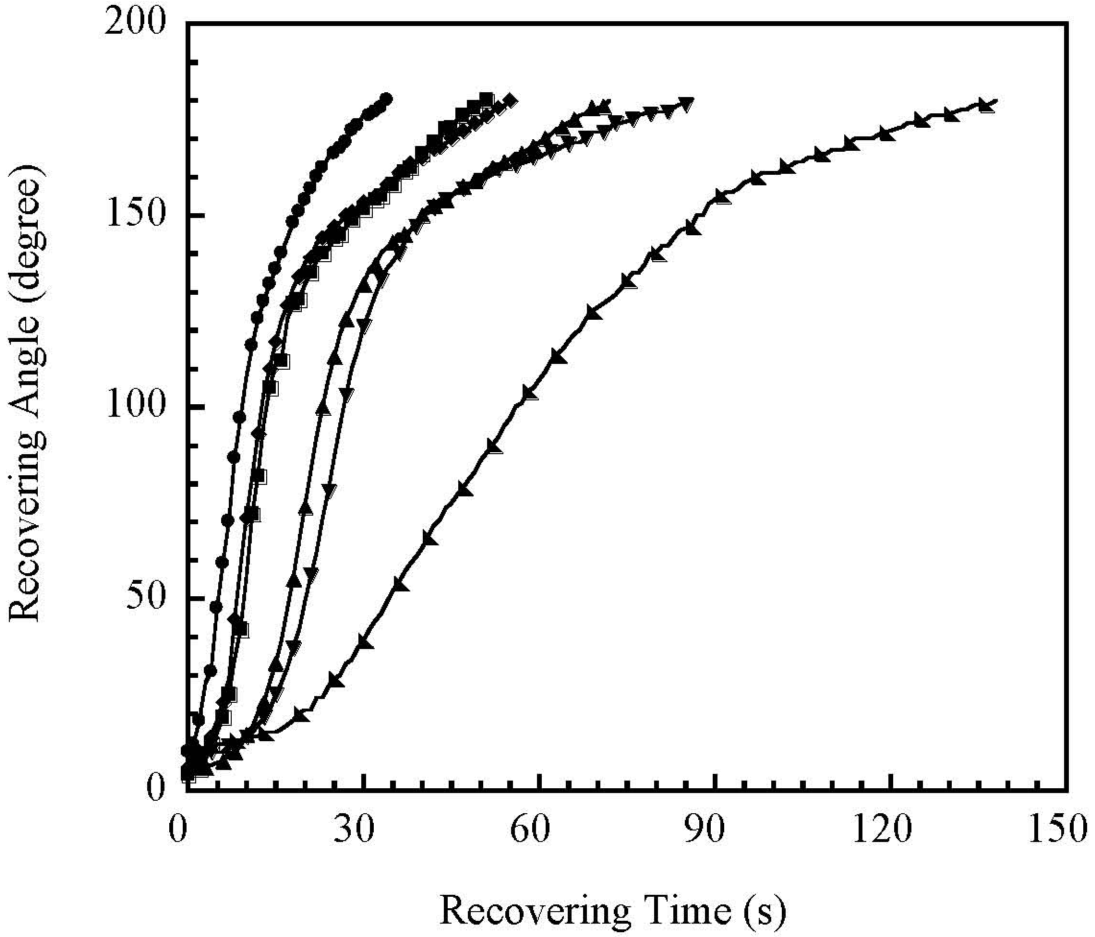


Figure 5.17 Recovery angle as a function of recovery time during the shape recovery process at T_g +20°C of the benzoxazine-modified epoxy SMP samples at various compositions: (●) ENDB 1/1/1/0, (■) ENDB 1/1/0.8/0.2, (♦) ENDB 1/1/0.6/0.4, (▲) ENDB 1/1/0.4/0.6, (▼) ENDB 1/1/0.2/0.8 and (◣) ENDB 1/1/0/1.

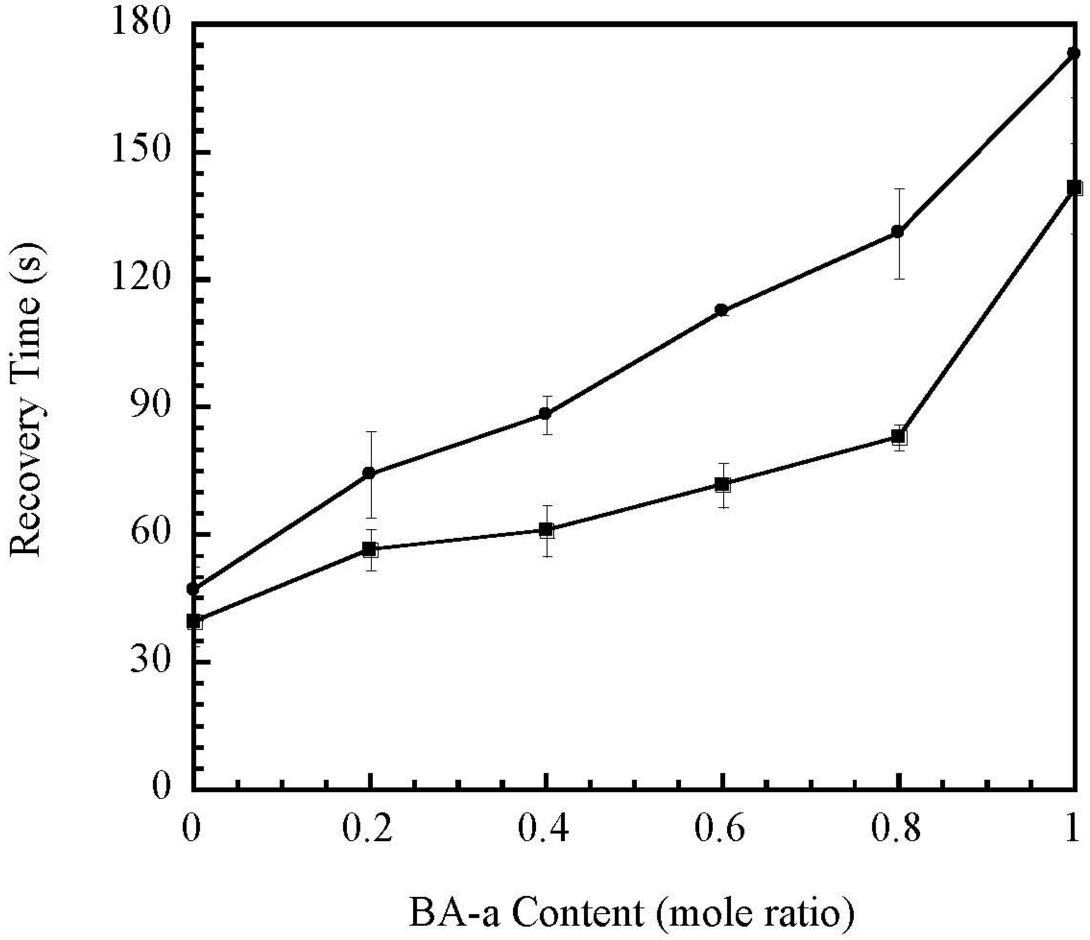
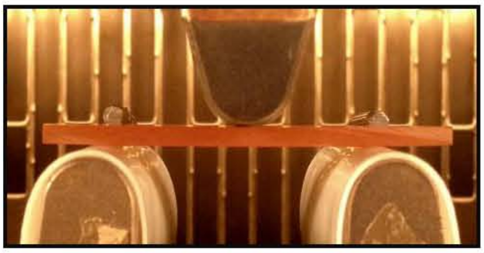
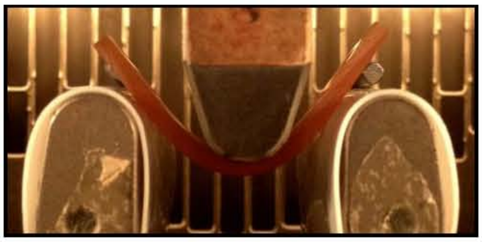


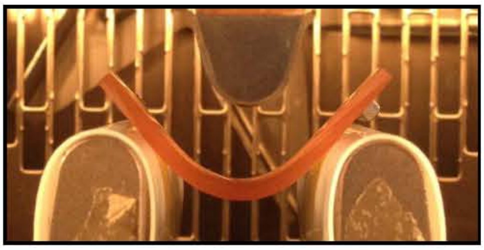
Figure 5.18 Recovery time as a function of BA-a content of the benzoxazine-modified epoxy SMP samples at various compositions: (●) T_g, (■) T_g+20°C.



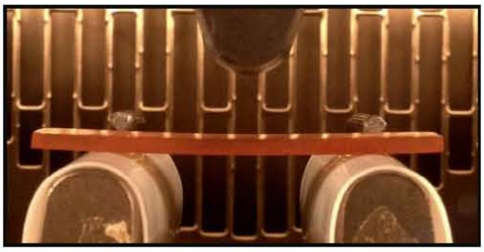
(a) Initial state



(b) Maximum deflection



(c) Shape-fixed state after cooling



(d) Recovered state after reheating

Figure 5.19 Photographs showing various states of bending in recovery stress process for benzoxazine-modified epoxy SMP sample: (a) original state of the sample, (b) deformed state of y_{max}=10 mm., (c) shape-fixed state after cooling and (d) shape-recovered state after reheating.

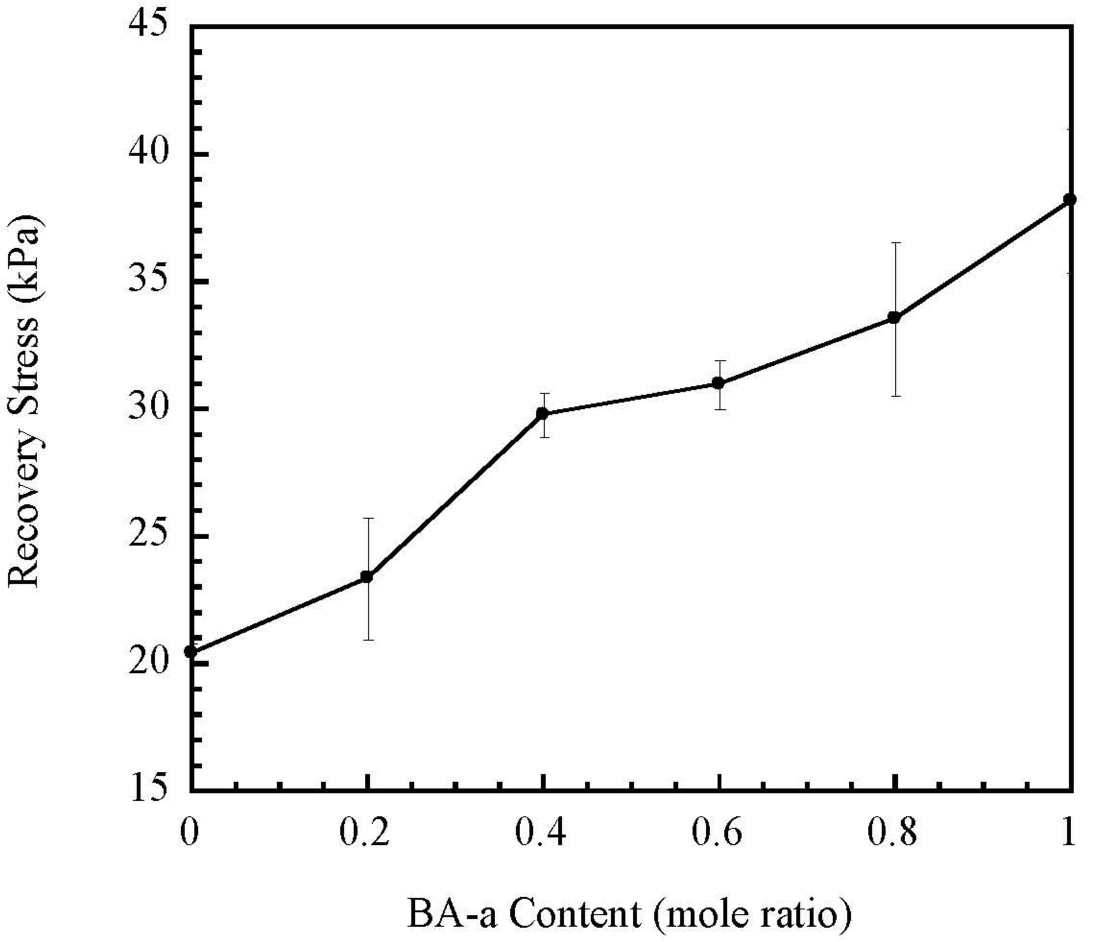


Figure 5.20 Recovery stress as a function of BA-a content of the benzoxazine-modified epoxy SMP samples at various compositions.

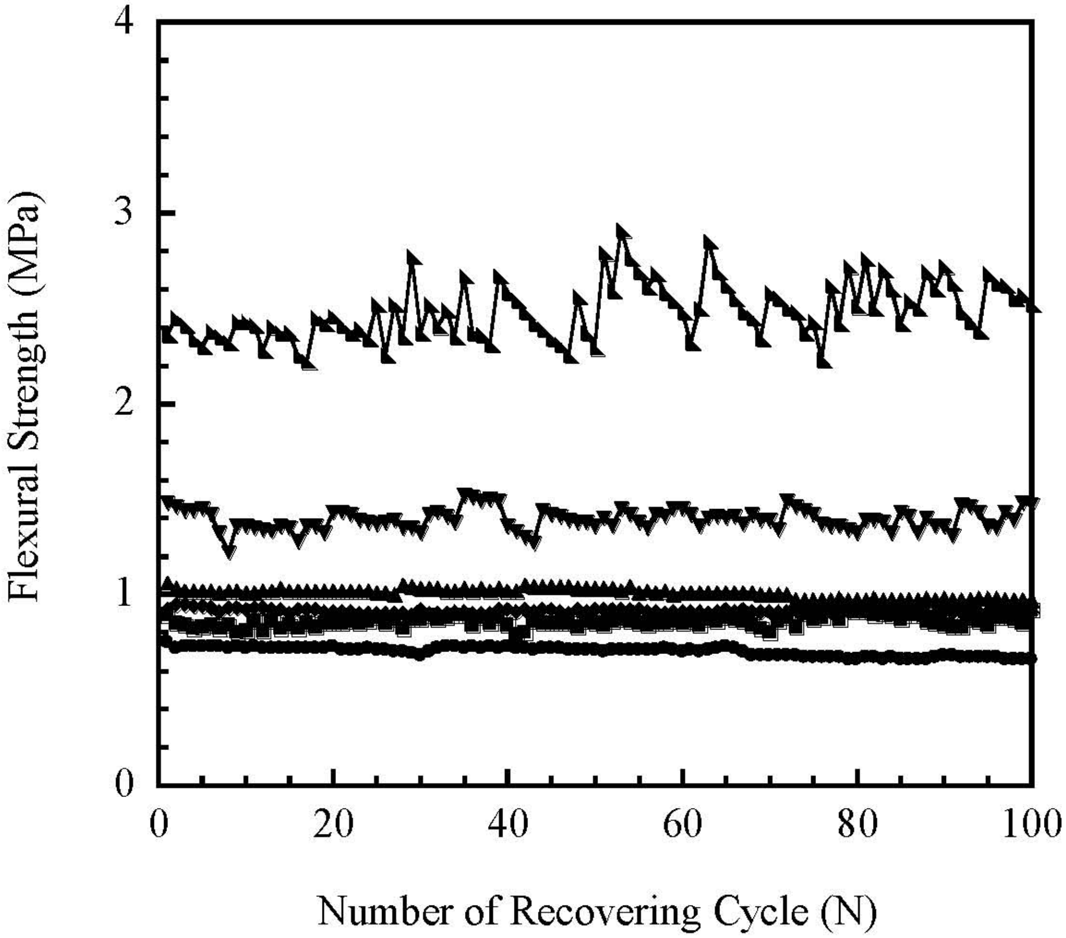


Figure 5.21 Flexural strength versus number of recovering cycle from consecutive shape memory cycles of the benzoxazine-modified epoxy SMP samples at various compositions: (●) ENDB 1/1/1/0, (■) ENDB 1/1/0.8/0.2, (♦) ENDB 1/1/0.6/0.4, (▲) ENDB 1/1/0.4/0.6, (▼) ENDB 1/1/0.2/0.8 and (◣) ENDB 1/1/0/1.

CHAPTER 6

CONCLUSIONS

Polybenzoxazine alloying with epoxy-based shape memory polymer (SMP) was developed to be used in wider range of shape memory application. In this thesis, BA-a mixed with Jeffamine D230 at the mole fractions of Jeffamine D230/BA-a = 1/0, 0.8/0.2, 0.6/0.4, 0.4/0.6, 0.2/0.8 and 0/1 were used as curing system for shape memory epoxy. Effect of addition of BA-a resin into epoxy-based SMP on thermal stability, mechanical properties and shape memory performance were evaluated.

In DSC experiment, a heat treatment at 80°C for 4 hours, 100°C for 2 hours, 130°C for 1 hour, 150°C for 24 hours, 170°C for 1 hour, 190°C for 1 hour and 200°C for 2 hours was chosen as an optimum curing condition of all benzoxazine-modified epoxy SMP due to the complete disappearance of an exothermic under their curing peak. From DMA experiment, glass transition temperature (T_g) values were obtained from the maximum peaks of loss moduli. An incorporation of BA-a resin in the epoxy-based SMP resulted in an increase of the T_g with increasing the BA-a mole fraction in the alloys.

Enhanced thermo-mechanical performance epoxy SMPs was also achieved by alloying with benzoxazine resin. The incorporation of the benzoxazine fraction contributed to higher of storage modulus at a glassy state, higher crosslink density, enhanced flexural strength and greater flexural modulus at room temperature than those of the epoxy-based SMP cured solely by Jeffamine D230. In addition, the flexural strength and flexural modulus at a rubbery state of the obtained SMPs also provided a relatively high shape fixity value of 98−99%. The recovery stress of BA-a/epoxy-based SMP was also found to be larger than that of epoxy-based SMP. The shape recovering time for various compositions of benzoxazine-modified epoxy SMP at different active temperatures i.e. T_g and T_g+20°C. All samples need only several minutes to fully recover their original shape. Interestingly, the obtained SMPs also provided an outstanding shape recovery ratio value of about 99−100%, indicative of a good shape memory performance. Finally, an addition of benzoxazine resin as a co-curing agent for epoxy enables the control of the shape recovery time which made the obtained samples attractive as a good candidate for shape memory material to be used in broader range of applications.

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APPENDIX

APPENDIX

Characterization of Polybenzoxazine and Epoxy-based Shape Memory Polymer Alloying Specimens

Appendix 1 Glass transition temperature of benzoxazine-modified epoxy SMP samples at various compositions from DSC analysis

ENDB	T_g from DSC (^oC)
1/1/1/0	47
1/1/0.8/0.2	53
1/1/0.6/0.4	59
1/1/0.4/0.6	82
1/1/0.2/0.8	84
1/1/0/1	116

Appendix 2 Storage modulus and rubbery plateau modulus of benzoxazine-modified epoxy SMP samples at various compositions

ENDB	Storage modulus (E') at 35^oC (GPa)	Rubbery Plateau Modulus at T_g+50^oC (MPa)
1/1/1/0	3.18	21.27
1/1/0.8/0.2	3.90	26.96
1/1/0.6/0.4	4.34	34.50
1/1/0.4/0.6	4.44	38.73
1/1/0.2/0.8	4.62	39.25
1/1/0/1	4.70	54.17

Appendix 3 Density of benzoxazine-modified epoxy SMPs

ENDB	**Density (g/cm^3)**
1/1/1/0	1.14±0.00328
1/1/0.8/0.2	1.15±0.00025
1/1/0.6/0.4	1.16±0.00144
1/1/0.4/0.6	1.17±0.00161
1/1/0.2/0.8	1.18±0.00591
1/1/0/1	1.19±0.00209

Appendix 4 Flexural strength and flexural modulus of benzoxazine-modified epoxy SMP samples at various compositions at room temperature and T_g+20°C

ENDB	**At glassy state (room temperature)**		**At rubbery state (T_g+20°C)**	
	Flexural strength (MPa)	**Flexural modulus (GPa)**	**Flexural strength (GPa)**	**Flexural modulus (MPa)**
1/1/1/0	59.49±4.01	1.77±0.26	0.60±0.04	5.85±0.32
1/1/0.8/0.2	102.17±1.94	3.27±0.35	0.86±0.13	9.53±0.93
1/1/0.6/0.4	122.49±2.24	3.70±0.31	0.94±0.11	10.29±1.31
1/1/0.4/0.6	131.11±4.15	3.75±0.21	0.98±0.21	10.23±1.49
1/1/0.2/0.8	149.09±6.53	3.90±0.92	1.38±0.04	14.52±0.59
1/1/0/1	164.34±3.99	4.42±0.42	2.53±0.02	35.14±0.70

Appendix 5 Shape recovery ratio at different active temperatures, the original storage angle θ_0 is 180° in the storage state is selected at the 150 second during the shape recovery cycle

ENDB	Recovery ratio, R_N (%) within 150 s				
	T_g–20°C	T_g–10°C	T_g	T_g+10°C	T_g+20°C
1/1/1/0	-	99.44	100	100	100
1/1/0.8/0.2	78.12	99.44	100	100	100
1/1/0.6/0.4	76.11	99.44	100	100	100
1/1/0.4/0.6	62.00	99.44	100	100	100
1/1/0.2/0.8	42.78	95.56	98.89	100	100
1/1/0/1	25.56	67.22	92.78	98.89	100

Appendix 6 Recovery time of the benzoxazine-modified epoxy SMP samples at various compositions

ENDB	Recovery time (s)	
	T_g (°C)	T_g+20°C
1/1/1/0	47±5.60	40±5.70
1/1/0.8/0.2	74±10.13	57±4.79
1/1/0.6/0.4	88±4.57	61±6.04
1/1/0.4/0.6	112±0.71	72±5.38
1/1/0.2/0.8	131±10.56	83±3.00
1/1/0/1	173±9.90	142±10.61

Appendix 7 Recovery stress of benzoxazine-modified epoxy SMP samples

ENDB	**Recovery stress (kPa)**
1/1/1/0	20.42±0.39
1/1/0.8/0.2	23.36±2.39
1/1/0.6/0.4	29.77±0.87
1/1/0.4/0.6	30.97±0.97
1/1/0.2/0.8	33.55±3.01
1/1/0/1	38.18±2.82

VITAE

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