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EFFECT OF BENZOXAZINE RESIN ON NETWORK FORMATION OF ALIPHATIC EPOXY FOR SHAPE MEMORY POLYMERS

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A Thesis Submitted in Partial Fulfillment of the Requirements
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ธชณัฏฐ์ ตันพิทักษ์สิทธิ์ : ผลของเบนซอกซาซีนเรซินต่อการเกิดโครงข่ายของอะลิฟาติกอีพอกซีสำหรับพอลิเมอร์จำรูปร่าง. (EFFECT OF BENZOXAZINE RESIN ON NETWORK FORMATION OF ALIPHATIC EPOXY FOR SHAPE MEMORY POLYMERS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.ศราวุธ ริมดุสิต, 76 หน้า.

พอลิเมอร์จำรูปร่าง (SMPs) คือพอลิเมอร์ที่สามารถกำหนดรูปร่างชั่วคราวได้และสามารถคืนรูปไปสู่รูปร่างดั้งเดิมได้เมื่อได้รับสิ่งกระตุ้นจากภายนอก เช่น อุณหภูมิ ความชื้น ความเป็นกรด-ด่าง ฯลฯ อีพอกซีเรซิน บางประเภทสามารถใช้งานเป็นพอลิเมอร์จดจำรูปร่าง เนื่องจากมีเสถียรภาพในการใช้งานค่อนข้างดี มีความทนทาน และมีความสามารถในการจดจำรูปร่างที่สูง อย่างไรก็ตาม การที่หมู่อีพอกไซด์ในอีพอกซีเรซินจะเปิดวงเพื่อทำปฏิกิริยาพอลิเมอไรเซชันนั้นต้องใช้สารช่วยบ่มด้วย ซึ่งสารบ่มอีพอกซีที่ใช้งานปัจจุบันในอุตสาหกรรมมีข้อเสียอยู่ที่สำคัญบางประการ เช่น มีราคาแพง เป็นพิษต่อผู้ใช้งาน หรืออาจมีสมบัติกัดกร่อนอุปกรณ์ และมักไม่ช่วยเสริมสมบัติการจำรูปร่าง ในงานวิจัยนี้ได้ศึกษาระบบพอลิเมอร์จำรูปร่างที่เตรียมจากอะลิฟาติกอีพอกซีเป็นส่วนของเฟสผันกลับได้ของโครงข่ายโมเลกุลของพอลิเมอร์จำรูปร่างได้ และบ่มด้วยเบนซอกซาซีนเรซิน ซึ่งสามารถทำหน้าที่เป็นส่วนของโครงข่ายพอลิเมอร์คงรูปไปในตัว โดยอัตราส่วนของเบนซอกซาซีนของพอลิเมอร์จำรูปร่างจากอีพอกซี ถูกควบคุมอยู่ในช่วง 30 ถึง 50 % โดยโมลของเบนซอกซาซีน โดยทำการวิเคราะห์สมบัติทางกลพลวัติ, สมบัติทางกลภายใต้แรงดัดโค้ง และสมบัติการจดจำรูปร่าง จากผลการทดลองพบว่า มอดูลัสสะสมที่อุณหภูมิห้องของพอลิเมอร์จำรูปร่างจากอีพอกซี สูงขึ้นจาก 2.8 กิกะปาสคาล ที่ปริมาณเบนซอกซาซีนเท่ากับ 30% โดยโมล เป็น 4.5 กิกะปาสคาล ที่ 50% โดยโมล ของเบนซอกซาซีน และให้อุณหภูมิเปลี่ยนสถานะคล้ายแก้วที่สูงขึ้นเมื่อเพิ่มอัตราส่วนของเบนซอกซาซีนมากขึ้นโดยมีค่าอยู่ในช่วงกว้างตั้งแต่ 51 ถึง 140 องศาเซลเซียสทำให้สามารถใช้งานได้กว้างขึ้น นอกจากนั้น ค่ามอดูลัสภายใต้แรงดัดโค้งและค่าความแข็งแรงภายใต้แรงดัดโค้งของพอลิเมอร์จำรูปร่าง อยู่ที่ 3.97 จิกะปาสคาล และ 132 เมกะปาสคาลที่อุณหภูมิห้อง และที่สถานะคล้ายยางอยู่ที่ 10.39 และ 2.3 เมกกะปาสคาลตามลำดับ จากการทดสอบการจดจำรูปร่าง พบว่า ทุกๆ ชิ้นงานพอลิเมอร์จำรูปร่างจากอีพอกซีบ่มด้วยเบนซอกซาซีนข้างต้น มีค่าการจำรูปร่าง (shape fixity) เข้าใกล้ 100% และใช้เวลาในการคืนรูปร่างสู่รูปร่างเดิมอย่างสมบูรณ์เพียง 1-3 นาที รวมไปถึงมีค่าความเค้นในการคืนรูป (recovery stress) ค่อนข้างสูง อยู่ในช่วง 0.25 ถึง 1.59 เมกะปาสคาล เมื่อทำการทดสอบสมบัติทางกลภายใต้แรงดัดโค้งซ้ำ 100 รอบ พบว่า พอลิเมอร์ที่ได้สามารถกลับสู่รูปร่างเดิมได้อย่างสมบูรณ์ ดังนั้นพอลิเมอร์จำรูปร่างจากอะลิฟาติกอีพอกซีและเบนซอกซาซีนนี้ จึงมีความน่าสนใจสำหรับใช้งานเป็นวัสดุจำรูปร่างที่สามารถนำไปใช้งานได้หลากหลายที่ช่วงอุณหภูมิค่อนข้างกว้าง เช่น บานพับหรือโครงสร้างพับงอต่างๆ เป็นต้น

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต ....

สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก ....

ปีการศึกษา 2556

5570210821 : MAJOR CHEMICAL ENGINEERING
KEYWORDS: SHAPE MEMORY POLYMERS / BENZOXAZINE RESIN / ALIPHATIC EPOXY / SHAPE RECOVERY

THACHANAT TANPITAKSIT: EFFECT OF BENZOXAZINE RESIN ON NETWORK FORMATION OF ALIPHATIC EPOXY FOR SHAPE MEMORY POLYMERS. ADVISOR: ASSOC. PROF. SARAWUT RIMDUSIT, Ph.D., 76 pp.

Shape memory polymers (SMPs) are polymers that can fix the temporary shape and recover to the permanent shape by external stimuli such as heat. Epoxy resins are an important family of SMPs due to their excellent stability, thermomechanical endurance and the high values of shape fixity. However, epoxide ring opening polymerization of epoxy requires a curing agent which typically possesses some disadvantages such as high cost, toxic problem to the user, corrosion to the processing apparatus, as well as no direct benefit to the shape memory performance. In this research, novel series of SMPs were prepared from aliphatic epoxy as reversible switching transition and cured by benzoxazine resin (BA-a) which also acted as stable polymer networks. The composition of BA-a in aliphatic epoxy/benzoxazine SMPs was controlled to be in the range of 30 to 50 mol%. Thermomechanical properties and flexural properties as well as essential shape memory properties of the BA-a/aliphatic-epoxy SMPs were characterized by dynamic mechanical analysis (DMA), flexural test and shape memory test. The results revealed that storage modulus at room temperature of the obtained SMPs was increased from 2.8 GPa at BA-a content of 30 mol% to the value of 4.5 GPa at 50 mol% of BA-a. The glass transition temperature (T_g) was substantially increased with an increase in BA-a content and reported to be in the range of 51 to 140°C. At benzoxazine content 50 mol%, the flexural modulus and flexural strength of the SMP samples were found to be as high as 3.97 GPa and 132 MPa at room temperature, at rubbery state 10.39 and 2.3 MPa respectively. From the shape memory test, all SMP samples exhibited a high value of shape fixity close to 100% and needed only a few minutes to fully recover to their permanent shape. Furthermore, the presence of BA-a content in aliphatic epoxy/benzoxazine SMPs imparted a greater recovery stress ranging from 0.25 to 1.59 MPa or about 6 times improvement. All of the SMP samples fully recovered to their permanent shape at the end of 100 cycles with minimum change on their flexural strength. These SMPs based on aliphatic epoxy/benzoxazine are highly attractive for shape memory materials to be used in a broader range of applications at elevated temperature such as hinge or deployable structure.

Department:	Chemical Engineering	Student's Signature	....
Field of Study:	Chemical Engineering	Advisor's Signature	....
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Finally, I would like to dedicate this paragraph to my parents who give their unfailing love, understanding, and generous encouragement during my study.

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CHAPTER I

INTRODUCTION

1.1 Overview

Shape memory polymers (SMPs) belong to a novel class of smart materials developed in the last few years [1]. That have the ability to return from the temporary shape to their permanent shape induced by an external stimulus such as light, humidity, solvents, electric or magnetic fields, ionic strength, pH or most typically thermal activation [2]. SMPs have advantages over their shape memory alloys (SMAs) such as high elastic deformation (strain up to more than 200% for most of materials), low cost, low density, a broad range of application temperatures which can be tailored, easy processing, potential biocompatibility and biodegradability. SMPs have found wide applications in self-deployable structures in spacecraft [3], orthodontic applications, intelligent medical devices [4] smart textiles and apparels [5].

Thermoplastics and thermosets can be SMPs. Thermoplastics have no chemical crosslinks. Consequently, they are easy to reshape or reform. However, they can potentially melt at high temperature, and can lose their memory properties over time [6]. In contrast, thermoset SMPs have chemical crosslinks; and they soften but do not melt at elevated temperatures [7]. Epoxy resins have many great advantages of thermoset that they have been used as structure, electrical system and many other applications [8]. Shape memory epoxies have been developed because they were found to be excellent shape memory performance [9].

Recently, Xie and Rousseau [10] developed methods to tailor epoxy SMP's transition temperature (T_g) and shape recovery properties by aromatic epoxy as hard segments, aliphatic epoxy as soft segments and aliphatic amine as curing agents. The authors found that, the T_g of epoxy SMPs ranged from room temperature to 89 ^{o}C and their shape recovery abilities were around 100%. However, curing agent of epoxie have more disadvantages such as toxic to the user, corrosion to the processing apparatus and high viscosity [11].

Benzoxazine resin is a relatively new developed class of thermosetting resin derived from ring-opening polymerization of their precursors. The polymer possesses various good properties such as high thermal stability and excellent mechanical properties thus showing high potential in many applications. Moreover, polybenzoxazines have some reported outstanding properties such as high glass-transition temperature, high thermal stability, low melt viscosity before cure resulting in its high process ability, low water absorption and excellent mechanical performance [12]. The resin has also been reported to act as a curing agent of epoxy and to yield synergism in some properties of resulting copolymers with epoxy [13, 14].

In the recent study by Erden and Jana [15], benzoxazine resin (BA-a) was selected for alloying with shape memory polyurethane with the following reasons. Firstly, benzoxazine resin can be either chemically bonded with SMPU chains by copolymerization or grafting reactions or can be blended with SMPU as a separate phase. Secondly, polybenzoxazine can act as an additional hard phase of SMPU due to its high glass transition temperature and much greater storage modulus than the soft segment phase of SMPU. The authors reported a substantially recovery stress of up to 13 MPa and shape recovery ratio 93% of the polymer alloy with only 17% by weight of the BA-a compared to the values of 6.8 MPa and 72% of the starting PU.

Consequently, the purpose of this study was to develop aliphatic epoxy/benzoxazine based SMPs with improved thermal stability and mechanical properties in order to use at elevated service temperature, and for greater load-bearing applications. Some essential properties, such as glass transition temperature, flexural modulus, flexural strength, recovery stress and shape recovery performance were investigated. Twofold benefits were to be expected from this aliphatic epoxy/benzoxazine SMPs, i.e. the potential improvement of recovery stress and shape recovery behaviors of SMEs and to simultaneously use benzoxazine resins as stable polymer network to replace rigid aromatic epoxy system and also as epoxy curing agent thus significantly simplify the formulation of currently used shape memory epoxy systems.

1.2 Objectives

1. To develop shape memory polymers based on binary system of aliphatic epoxy and benzoxazine resin with enhanced thermal stability, mechanical properties and shape memory properties.
2. To study the effects of benzoxazine resin as stable polymer network and curing agent on other essential properties of the obtained shape memory polymers from aliphatic epoxy/benzoxazine.

1.3 Scopes of the Study

1. Synthesis of BA-a typed benzoxazine resin by solventless synthesis technology.
2. Preparation of mixtures between benzoxazine resins (BA-a) and aliphatic epoxy at various benzoxazine contents ranging from 30-50 mol%
3. Property evaluation of aliphatic epoxy/benzoxazine as follows.

    3.1. Physical properties

    - Curing and crosslink behaviors (Fourier transform infrared spectroscopy)

    3.2. Thermal properties

    - Curing behaviors (Differential scanning calorimeter)

    3.3. Mechanical properties

    - Dynamic mechanical properties (Dynamic mechanical analyzer)
    - Flexural properties (Universal Testing Machine)

    3.4. Shape memory properties

    - Shape fixity ratio
    - Shape recovery ratio
    - Deformation temperature
    - Recovery time
    - Recovery stress
    - Number of shape memory cycles

1.4 Procedures of the Study

1. Prepare chemicals, apparatus, and equipment for this research such as aliphatic epoxy, bisphenol A, aniline etc.
2. Determine mixing or processing conditions of aliphatic epoxy and benzoxazine resin.
3. Examine aliphatic epoxy/benzoxazine by varying compositions of benzoxazine at 30, 35, 40, 45, 50 mol%.
4. Evaluate thermal, mechanical and shape memory properties of aliphatic epoxy-benzoxazine alloys.

CHAPTER II

THEORY

2.1 Shape Memory Polymers (SMPs)

Shape memory materials (SMMs) are a class of active materials that have dual-shape capability. The dual-shape capability, or shape memory effect, is characterized by the ability to recover a permanent shape from an initial level of pre-deformation when exposed to the appropriate external stimulus. Certain polymers, metal alloys, ceramics, and gels can be classified as SMMs [16]. Of all SMMs, shape memory alloys (SMAs) and shape memory polymers (SMPs) are by and large the most widely studied. The shape memory effect was seen in metal alloys as early as 1951 [17], and the shape memory effect in polymers was reported a decade earlier [18, 19]. However, SMAs are more prominent and more widely used than SMPs. Shape memory alloys and polymers differ in nearly every material aspect from the basic mechanism for the shape memory effect to the capability of tailoring specific material properties (i.e. elastic modulus and transition temperature). Looking at the basic material characteristics of SMAs and SMPs, it becomes very apparent that the properties of SMPs are more desirable. SMAs have been reported to have high stiffness, high cost, complicated processing demands, and very low recoverable strains, on average less than 8%. In direct contrast, SMPs are generally low cost, low density, and can recover strain levels of nearly 200% [20]. Other advantages of SMPs are the ability to specially adapt material properties for specific applications, and SMPs do not require costly or complicated procedures of manufacturing. Furthermore, SMPs can be activated by several stimuli including heat, light, chemical, or perhaps a combination of these stimuli. Additionally, most SMPs are biocompatible and biodegradable [21]. Accordingly, all of these advantages lead to SMPs being capable of application in a variety of areas.

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 shape, 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 SMPS by introducing a permanent network (e.g. chemical crosslinking). The process of programming and recovery of a shape was shown schematically in Figure 2.1

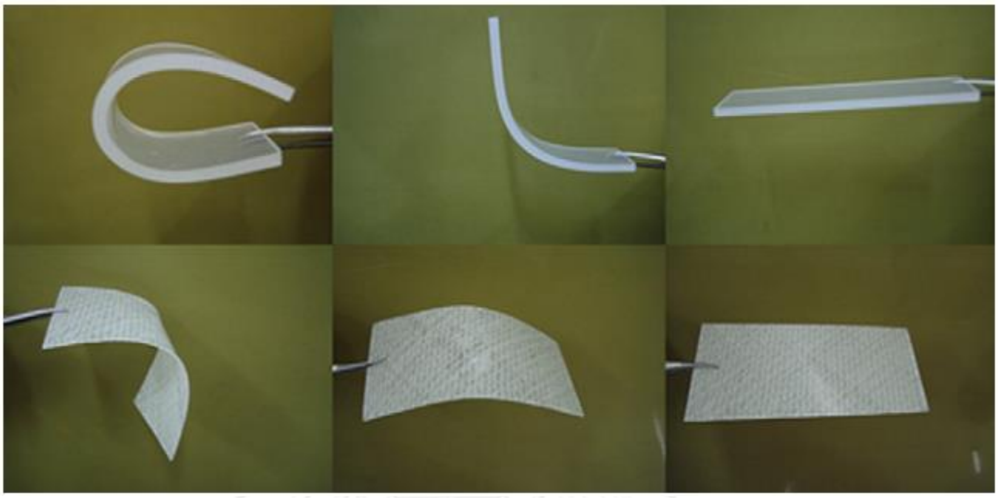


Figure 2.1 Time series photographs that show the recovery of a pure SMP (top row), and a glass-fiber-reinforced SMP (bottom row) [2].

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.

2.1.1 Class of Shape Memory Polymers

The four classes of SMPs are defined below. 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.

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 [22].

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 [22].

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, 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. [23] 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 [24] 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 [22].

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 [25] to 33% [26] have been reported as optimum values for increased SM behavior in the PU systems.

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.

2.1.2 Effect of Shape Memory Polymer

The shape-memory effect is not an intrinsic property, meaning that polymers do not display this effect by themselves. Shape memory results from a combination of polymer morphology and specific processing and can be understood as a polymer functionalization. By conventional processing, e.g. extruding or injection molding, the polymer is formed into its initial, permanent shape B. Afterwards, in a process called programming, the polymer sample is deformed and fixed into the temporary shape A. Upon application of an external stimulus, the polymer recovers its initial permanent shape B. This cycle of programming and recovery can be repeated several times, with different temporary shapes in subsequent cycles. In comparison with metallic shape-memory alloys, this cycle of programming and recovery can take place in a much shorter time interval and polymers allow a much higher deformation rate between shapes A and B in Figure 2.2.

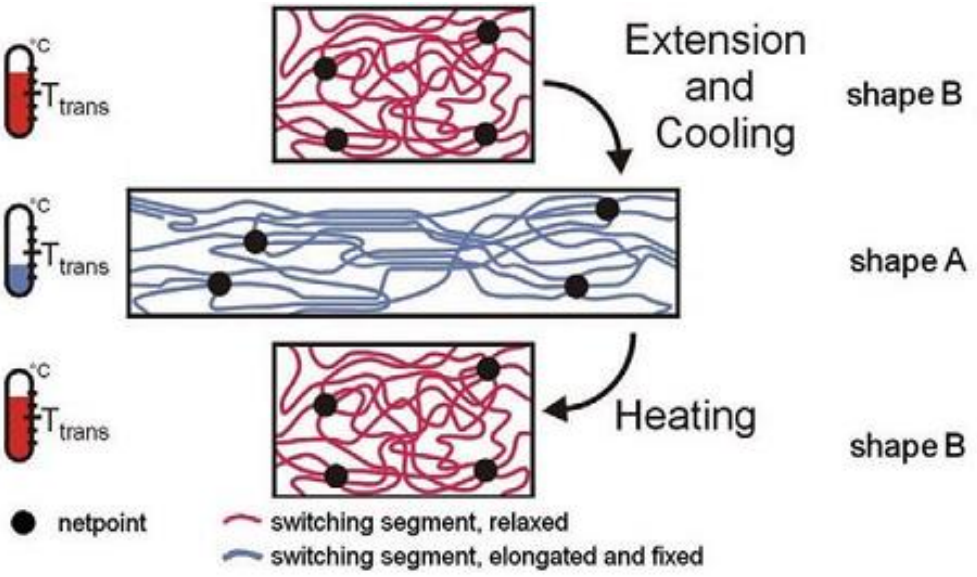


Figure 2.2 Molecular mechanism of the thermally induced shape-memory effect T_{trans} = thermal transition temperature related to the switching phase [27].

Shape-memory polymers are elastic polymer networks that are equipped with suitable stimuli-sensitive switches. The polymer network consists of molecular switches and netpoints (Figure 2.2). The netpoints determine the permanent shape of the polymer network and can be of a chemical (covalent bonds) or physical (intermolecular interactions) nature. Physical cross-linking is obtained in a polymer whose morphology consists of at least two segregated domains, as found for example in block copolymers. Here, domains related to the highest thermal transition temperature (T_{perm}) act as netpoints (a hard segment), while chain segments in domains with the second highest thermal transition (T_{trans}) act as molecular switches (a switching segment). If the working temperature is higher than T_{trans}, then the switching domains are flexible, resulting in an entropic elastic behavior of the polymer network above T_{trans}. If the sample has been previously deformed by application of an external stress, it snaps back into its initial shape once the external stress is released. The molecular mechanism of the shape-memory effect is illustrated for the thermally induced shape-memory effect in Figure 2.2.

2.1.3 Parameters for Characterization of SMPs

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 followings [28].

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 (Tg), it can develop large deformations which can be mostly fixed by cooling to a temperature below Tg. 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, which is given by 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.

Shape recovery (R_r)

A given SMP holding a deformation by low temperature can restore its original shape by being heated up above Tg. 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.

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 Tg. If the deformed and fixed SMPs are reheated above Tg, 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 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 consequence, 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 term.

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 are also called as speed of recovery process, deformation recovery speed or shape recovery speed. The parameter can be measured qualitatively and quantitatively.

Liu et al. [29] 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. [30] and Luo et al. [31] 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 Polymers

SMPs currently cover a broad range of applications such as structures in aerospace, medical devices, toy smart, clothing, cosmetics, robotic assembly process, homeware. Specific examples from recent works are detailed below.

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].

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 2.3, 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 [2].

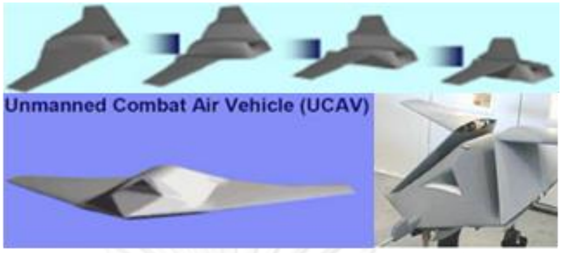
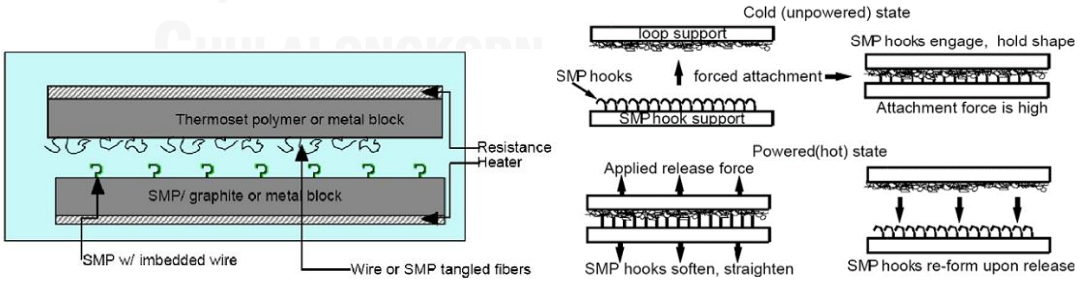


Figure 2.3 Z-shaped morphing wings produced by Lockheed Martin [2].

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 [2].



(a) (b)

Figure 2.4 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 [2].

As a typical example, SMPs are proposed to be used for the reversible attachments, as shown in Figure 2.4. In this embodiment (see Figure 2.4a), 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 2.4b). 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 [2].

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 2.5). 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 2.6, the SMP composite system can recover 75-85 % of flexural strength upon bending test [2].

Figure 2.5 Self-healing system based on SMP [2].

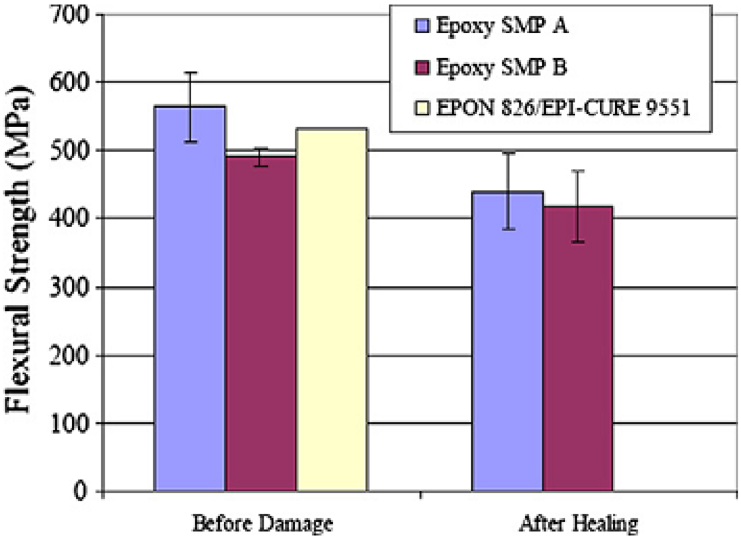


Figure 2.6 Flexural strength of epoxy-based composites before damage and after healing [2].

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 2.7. 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 [8].

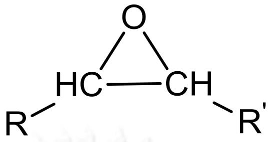


Figure 2.7 General structure of an epoxy resin [8].

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). These are the epoxides used in most commercial application.

Diglycidyl Ether of Bisphenol A (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 2.8.

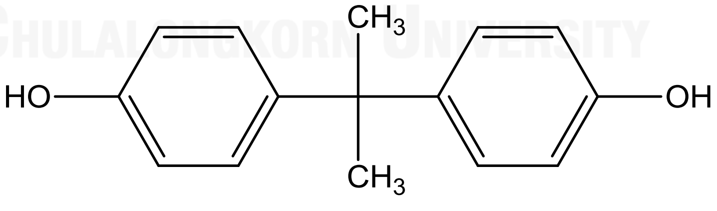


Figure 2.8 Chemical structure of bisphenol A [8].

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 2.9. 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.

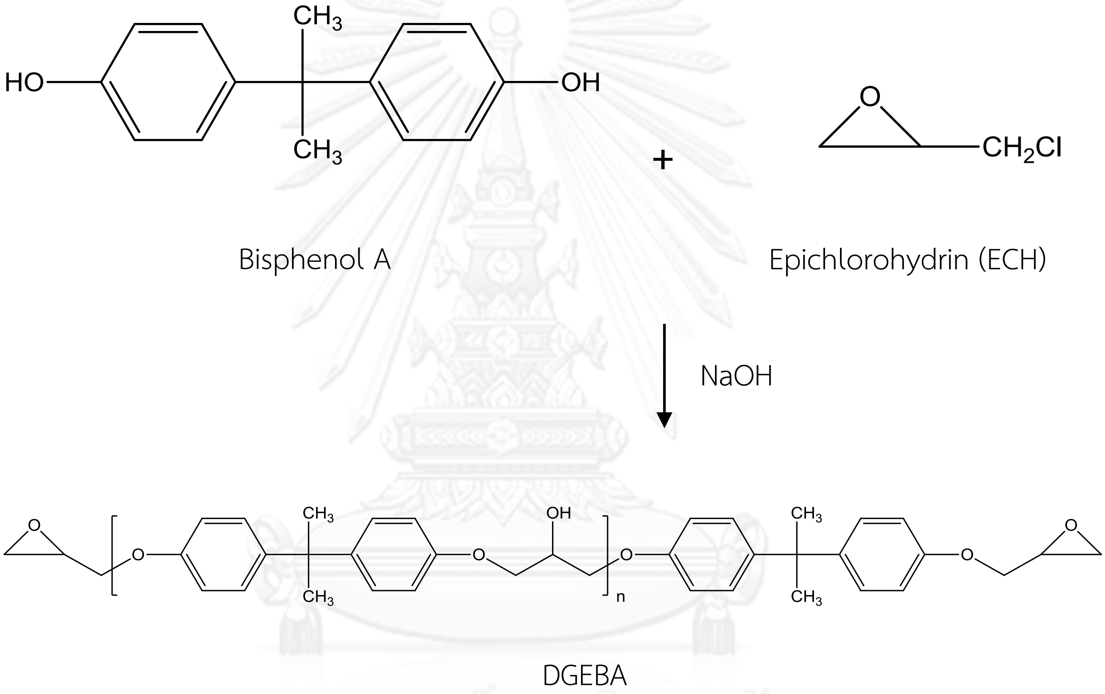


Figure 2.9 Formation of diglycydyl ether of bisphenol A (DGEBA) [8].

Basic characteristics of epoxy resins

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

1. Low viscosity. The liquid epoxy resins and their curing agents can produce low viscosity, easy to process (or modify) systems.

2. 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.

3. 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.

4. 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.

5. High electrical properties. Cured epoxy systems exhibit good electrical properties over a range of temperatures and frequencies. They are excellent electrical insulators.

6. 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.

7. 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.

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 (see in Figure 2.10)

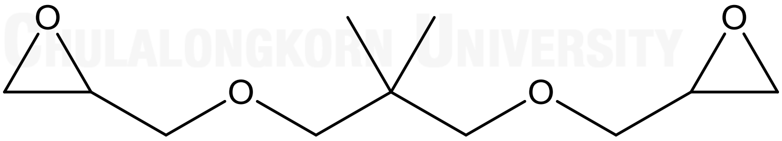


Figure 2.10 Structure of neopentyl glycol diglycidyl ether (NGDE) [8].

2.3 Benzoxazine Resin

Polybenzoxazine is a phenolic polymer generated by the Mannich-like condensation of phenol, formaldehyde and amine. It can be prepared by using solvent less synthesis technology [32]. The general pattern for this process is shown in Figure 2.11

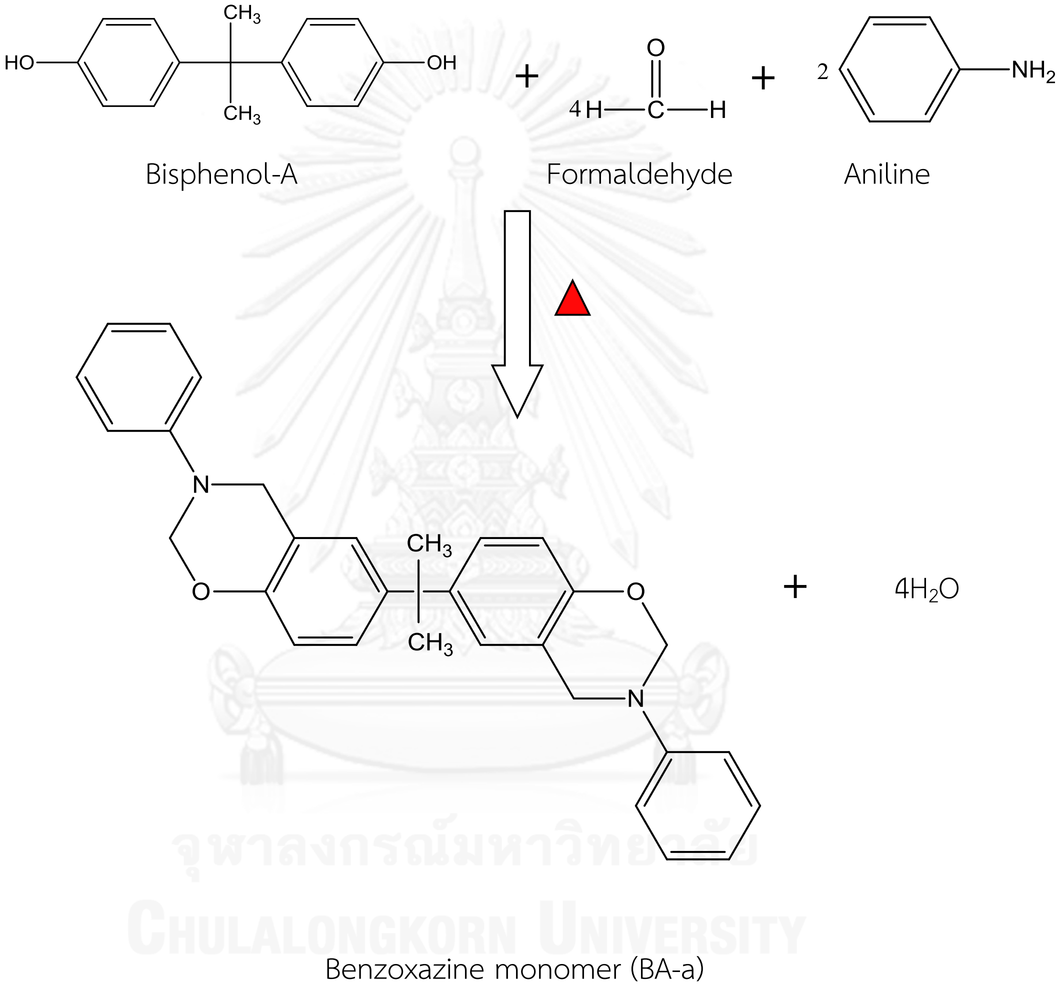


Figure 2.11 Schematic synthesis of bifunctional benzoxazine monomer.

The 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 III

LITERATURE REVIEWS

Ishida and Allen (1996) [33] 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. Figure 3.1 show the infra-red spectrum of a 60wt% benzoxazine/40wt% epoxy sample at different curing temperature. It was found that the consumption of epoxy can be monitored by the 913 cm^{-1} and 864 cm^{-1} epoxide ring modes that disappear as the ring is opened. As can be seen in Figure 3.1, the epoxide peak have almost completely disappeared by the end of the 160 °C stage of cure without a curing accelerator. Moreover, the obtained copolymer leads to significant increases in the glass transition temperature and flexural strength as invidence in Figure 3.2a and 3.2b, respectively.

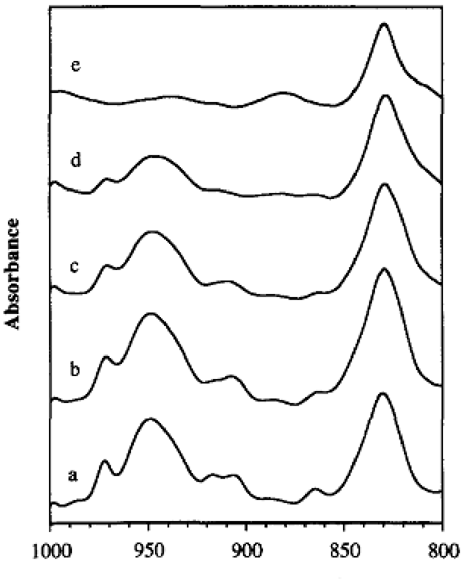
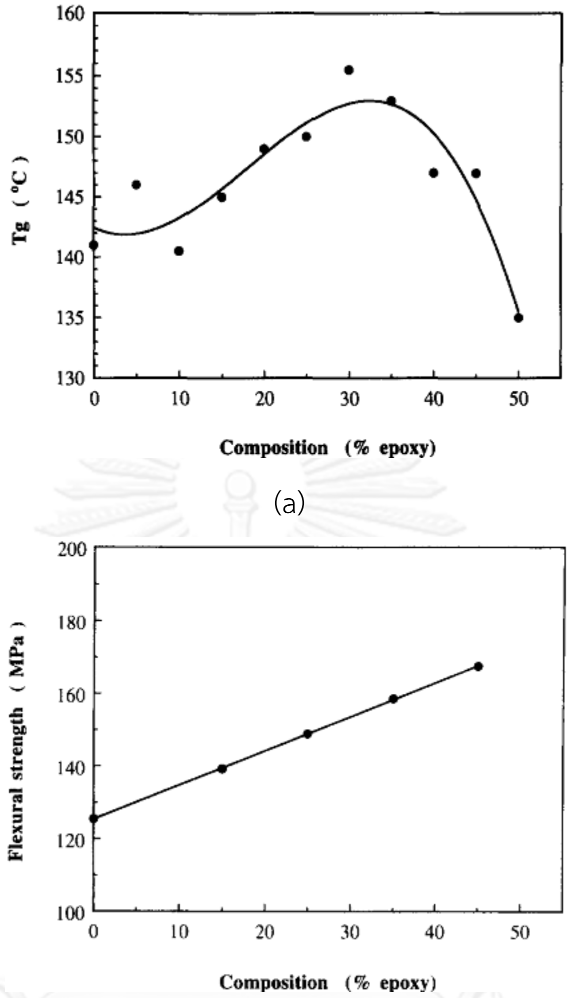


Figure 3.1 Infra-red spectrum over the region from 1000-800 cm^{-1} of the 40% epoxy copolymer after the (a) 25 °C, (b) 100 °C, (c) 140 °C, (d) 160 °C and (e) 205 °C stage of cure.



(a)

(b)

Figure 3.2 (a) The glass transition temperature and (b) the flexural strength of copolymer.

Rimdusit and Ishida (2000) [13] 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 as shown in Figure 3.3. The synergistic behavior is observed, with the maximum T_g, DMA of 180 °C belonging to BEP541. The T_g of the polybenzoxazine used in this study has been reported to be about 160 –170 °C, and that of phenolic novolac is about 170 °C. The T_g of EPON825 depends strongly on the type of curing agent used, with the value ranging from 100 to 170 °C. Because synergistic behavior was observed in both the binary [33] and ternary systems, phenolic resin should not play a role in this behavior. Two main factors, crosslink density and molecular rigidity, are believed to contribute to the synergistic behavior of our binary and ternary systems, and the source of the behavior should come from the contribution of both benzoxazine and epoxy resins.

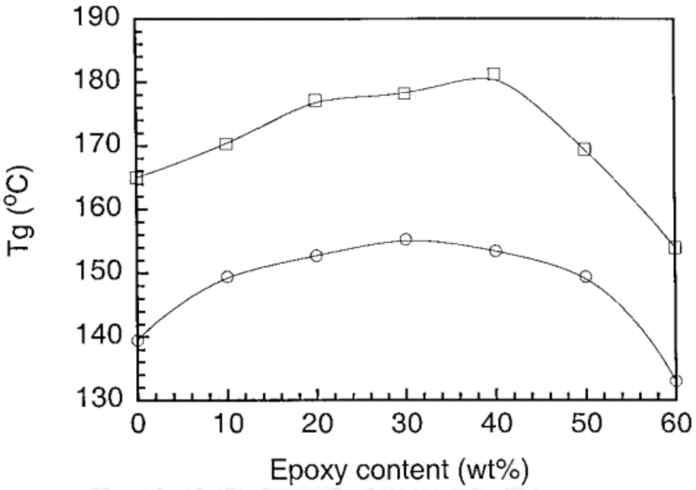


Figure 3.3 Synergism in the T_g's of the ternary system: (○) DSC T_g's and (□) DMA T_g's.

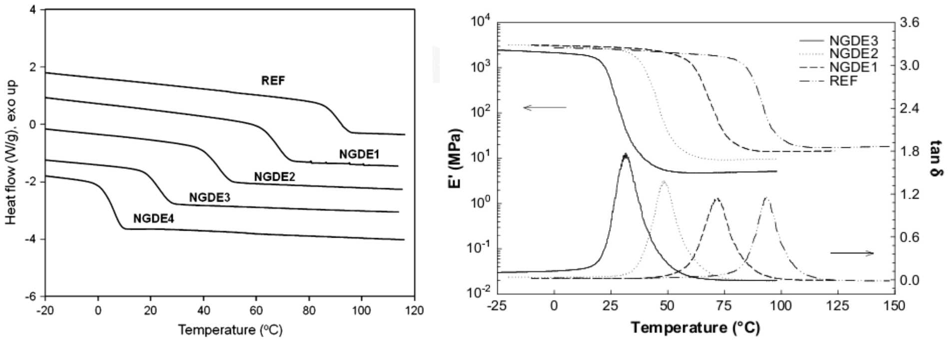
Xie and Rousseau (2009) [10] have developed methods to tailor T_g of shape memory epoxy polymer. Starting with an amine (Jeffamine D230) cured aromatic epoxy (EPON 826) system, epoxy polymers were synthesized by either reducing the crosslink density by substituting the diamine curing agent with a monoamine such as decylamine (DA) or introducing flexible by replacing the EPON 826 with a flexible aliphatic epoxy (NGDE). The molar compositions for all epoxy synthesized are summarized in Table 3.1.

All the other epoxy polymers in Table 3.1 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 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 decrease in the average molecular weight between crosslink points (Mc), as reflected in the increase of Mc in Table 3.1

Table 3.1 Compositions, shape fixity, and shape recovery of the epoxy samples

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

In NGDE series, replacing the rigid aromatic epoxide with the flexible aliphatic epoxy increases the chain flexibility of the material, thereby reducing its T_g. The results shown in Figure 3.4(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. The result correspond to the decreasing of Mc, as present in Table 3.1



(a) (b)

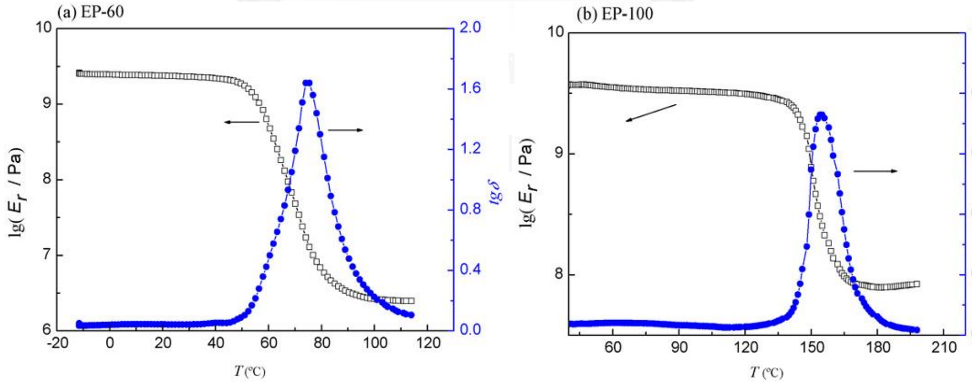
Figure 3.4 (a) DSC curves for the NGDE epoxy series. (b) DMA curves for the NGDE epoxy series.

Liu et al. (2010) [34] have investigated the effect of crosslink density, recovery temperature and consecutive cycles on the shape memory polymer properties. A series of shape memory epoxy resins 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 3.2 The results show an increasing in T_g values with the addition of curing agent. As the results, more curing agent brings higher cross-linking density and closer structure, which can hinder the movement of segment.

Table 3.2 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 3.2 EP-50 shows relatively low strength to be used as an SMP and is abandoned in the subsequent experiments. Therefore EP-60 and EP-100 samples are further characterized by DMA. The spectra and data obtained are shown in Figure 3.5. According to the results, EP-60 has a decrease of 3 orders on storage modulus between glassy and rubbery plateau, while EP-100 has a decrease of only 1.5 orders. Usually, a good SMP should have a change of storage modulus for more than 2 order. Thus EP-60 meets the requirements but EP-100 is abandoned for shape recovery tests.



(a) (b)

Figure 3.5 Storage modulus and loss tangent (tanδ) as a function of temperature of (a) EP-60, (b) EP-100.

The shape recovery ratio vs. temperature curves for SMEPs are presented in Figure 3.6 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.

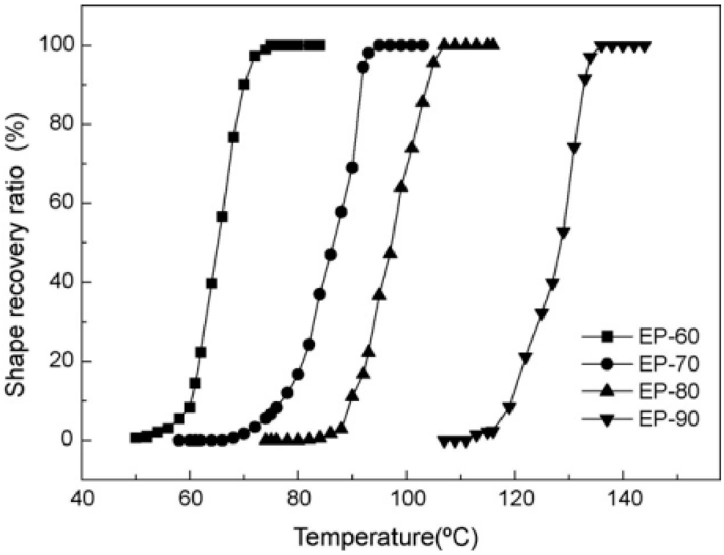


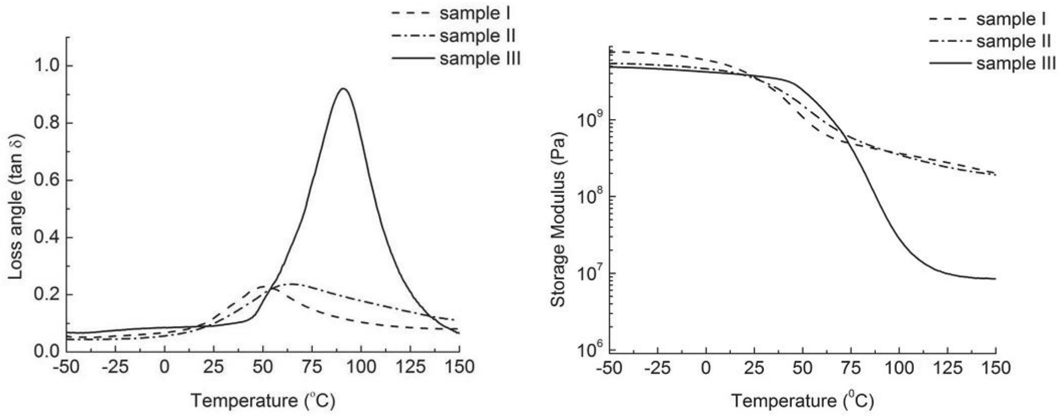
Figure 3.6 Shape recovery ratios of prepared epoxy resins vs. temperature

Erden and Jana (2013) [15] examined the properties of polyurethane-polybenzoxazine based shape memory polymers by using DSC, DMA, Universal testing machine (tensile mode) etc. SMP was synthesized form 4,4’-methylenebis phenyl isocyanate (MDI), polytetramethylene glycol (PTMG), 1,4-butanediol (BD) and benzoxazine (BA-a). Molar ratio of ingredients and weight percent hard segment (HS) are shown in Table 3.3.

Table 3.3 Corresponding molar ratio of raw materials

Sample	MDI mole	PTMG mole	BD mole	BA-a mole	HS [wt%]
I	5	1	4.0	0	71.2
II	5	1	3.5	0.5	73.4
III	5	1	3.0	1.0	75.3

The results from DMA are shown in Figure 3.7(a) and (b) It is evident that all three materials exhibited a single peak of tanδ, indicating a single value of T_g, respectively, 51, 65, and 91 °C for sample I to III, respectively. Also the increasing of T_g is due to the increasing amount of benzoxazine in the samples. The values of storage modulus in glassy state were found to be 7.5, 5.3, and 4.7 GPa respectively for samples I to III. The larger ratio of storage modulus at 20 °C below and 20 °C above, indicating that samples II and III would exhibit much better shape memory properties than sample I.



(a) (b)

Figure 3.7 Loss tangent (a) and storage modulus (b) as a function of temperature heating rate 4 °C min-1, frequency 1 Hz.

Furthermore, the recovery stress and shape recovery ratio had been observed. As the results in Figure 3.8 the recovery stress increased with the addition of benzoxazine. The lowest recovery stress of 6.8 MPa was found with sample I. The recovery stress increased substantially to 11.2 MPa (65% increase) and 13 MPa (91% increase), respectively. Figure 3.9 implied the shape recovery ratio of each sample. Sample I can recover only 72% at 150 °C on the other hands, sample II and III can recover up to 93% of their shapes.

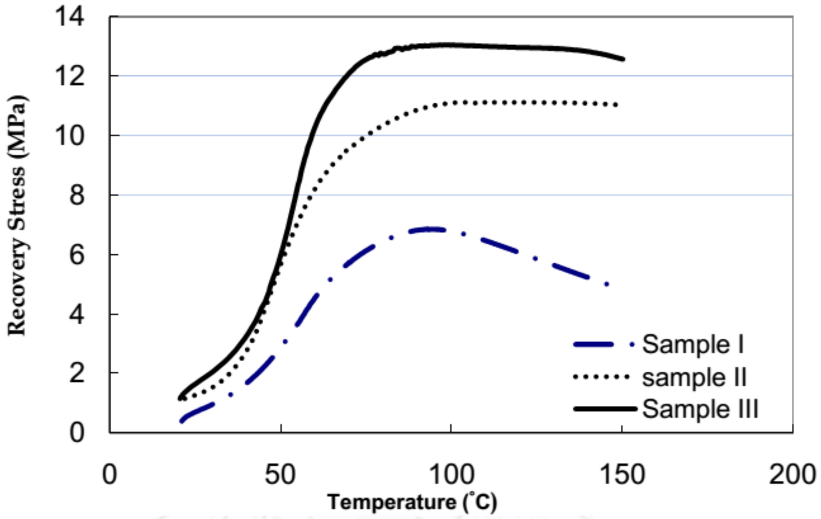


Figure 3.8 Recovery stress behaviors of 100% strained samples. Heating rate was 4 °C/min and stretching rate was 50 mm/min.

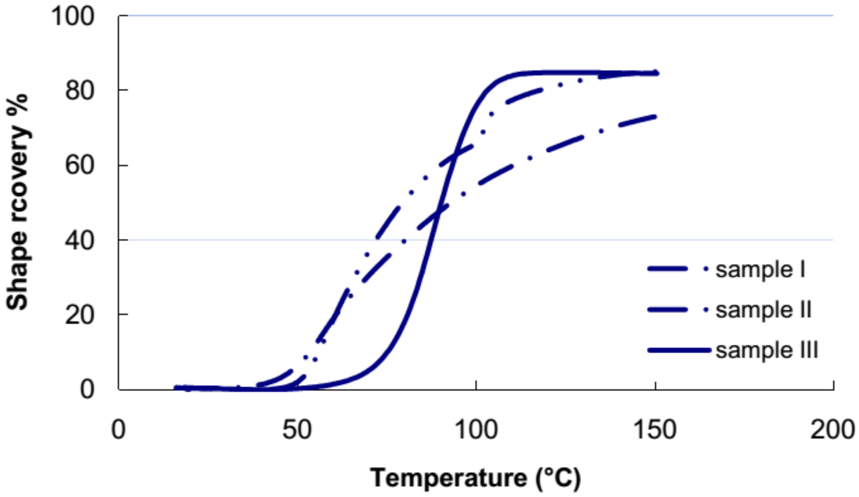


Figure 3.9 Shape recovery ratio of 100% strained samples. Heating rate was 4 °C/min and stretching rate was 50 mm/min.

Rimdusit et al. (2013) [35] have studied the effects of benzoxazine resin and Jeffamine D230 mol ratios on thermal stability, mechanical and shape memory properties. As displayed in table 3.4, The notation E, N, D, B stand for EPON 826, NGDE, Jeffamine D230 and BA-a, respectively. The digits after the notation give the molar ratio of the monomer in the same order. It was found that the storage modulus and crosslink density tended to increase with increasing BA-a content in the alloys as a result of the more rigid characteristics of the BA-a resin. Furthermore, the glass transition temperature also increases with increasing of BA-a content.

Table 3.4 Properties of benzoxazine-modified epoxy SMP samples from DMA analysis

Sample	**Storage modulus, E' (GPa) at 35 °C**	**Crosslink density (mol cm^{-3})**	**Glass transition temperature, T_g (°C)**
ENDB 1/1/1/0	3.18	2.90×10^{-3}	47
ENDB 1/1/0.8/0.2	3.90	3.25×10^{-3}	72
ENDB 1/1/0.6/0.4	4.34	3.62×10^{-3}	80
ENDB 1/1/0.4/0.6	4.44	3.79×10^{-3}	85
ENDB 1/1/0.2/0.8	4.62	3.81×10^{-3}	92
ENDB 1/1/0/1	4.70	4.29×10^{-3}	120

The shape recovery speeds of the benzoxazine-modified epoxy SMP are presented in Figure 3.10. All of the sample took only a few minutes to completely recover to their original shape. At high temperature, the shape recovery time decreased because the movement of chain segments became intense, which caused an increase in the recovery force on the samples.

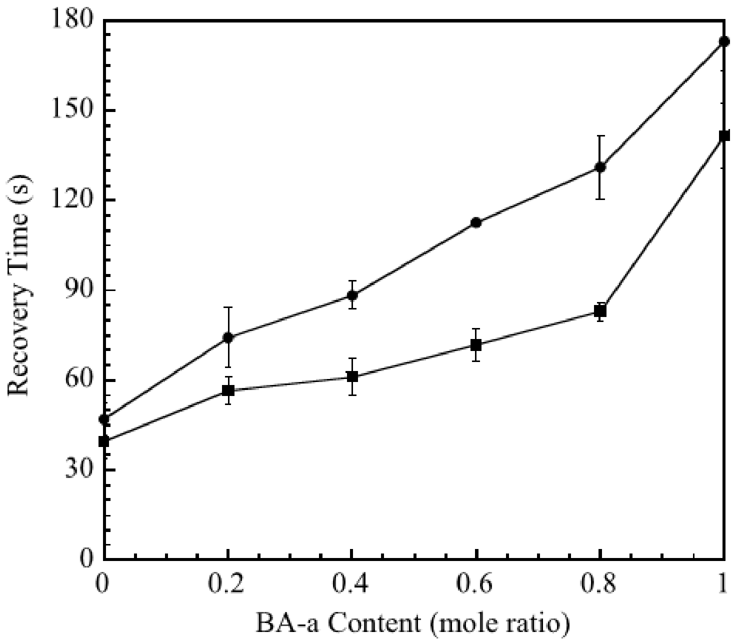


Figure 3.10 Recovery time as a function of BA-a content of the benzoxazine-modified epoxy SMP samples at various composition: (●) T_g, (■) T_g+20 °C

CHAPTER IV

EXPERIMENTAL

4.1 Raw Materials

The materials used in this research are benzoxazine resin and aliphatic epoxy. Benzoxazine resin is based on bisphenol-A, aniline and for formaldehyde. The bisphenol-A (polycarbonate grade) was provided 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 neopentyl glycol diglycidyl ether (NGDE) was available from Aditya Birla Chemical (Thailand). All chemicals were used as received.

4.2 Resin Preparation

4.2.1 Benzoxazine Resin Preparation

Benzoxazine resin (BA-a) was synthesized using bisphenol-A, formaldehyde and aniline at the stoichiometric mole ratio of 1:4:2. The mixture was heated to 110 °C in an aluminum pan and was mixed until a homogeneous mixture was obtained for approximately 30 minutes to yield a light yellow liquid monomer product, according to the patented solventless method in the U.S. Patent 5,543,516. 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 Aliphatic Epoxy/Benzoxazine SMP Samples

The BA-a resin was mixed with aliphatic epoxy (NGDE) at different mole percent of BA-a, which was varied between 30-50 mol%. The mixture was heated at 70-80 °C in an aluminum pan and stirred for about 10-20 minutes to yield a homogeneous mixture. The molten resin was poured into an aluminum mold and was thermally cured at 80 °C for 2 h in vacuum oven and 130 °C/ 12 h, 140 °C/ 4 h, 150 °C/ 4 h, 160 °C/ 2 h, respectively in an air circulated oven. The cured specimens were cut into various shapes for each specific test.

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 sample 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 320 °C under nitrogen purging. The purge nitrogen gas flow rate was maintained to be constant at 50 ml/min.

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

$$\%\text{conversion} = 1 - \frac{H_{rxn}}{H_0} \times 100 \qquad (4.1)$$

Where: H_{rxn} = is the heat of reaction of the partially cured samples

H_0 = is the heat of reaction of the uncured resin mixture

4.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

The chemical structure and network formation behavior of sample was studied by a Fourier transform infrared spectroscopy (FTIR). Fourier transform infrared spectra of all samples were acquired by using a Spectrum GX FT-IR spectometer from Perkin Elmer with an ATR accessory. All spectra were taken as a function of time with 64 scans at a resolution of 4 cm^{-1} and a spectral range of 4000-650 cm^{-1}. For aliphatic epoxy/benzoxazine mixture, a small amount of a viscous liquid sample was casted as thin film on a potassium bromide (KBr) window.

4.3.3 Dynamic Mechanical Analysis (DMA)

A dynamic mechanical analyzer (NATZSH, model DMA 242) was used to obtain a storage modulus (E′) and loss tangent (tanδ) of the SMP samples. The sample, with a dimension of 10×50×3 mm^3, was tested using a three-point bending mode at the frequency of 1 Hz and heating rate of 2 °C/min from room temperature to the temperature beyond the glass transition temperatures (T_g) of each sample.

The glass transition temperature was taken as the maximum peak on the loss tangent.

4.3.4 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 10×50×2 mm^3. Flexural properties were determined based on ASTM D 790M. The flexural strength and the modulus were calculated by the following equations:

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

$$\sigma_f = \frac{3FL}{2bd^2} \tag{4.3}$$

Where E_f = Flexural modulus, GPa

σ_f = Flexural strength, MPa

L = Support span, mm

m = The slope of the initial straight-line portion of the load deflection

b = Width of test beam, mm

d = Depth of tested beam, mm

F = Load at a given point on the load deflection curve, N

4.3.5 Shape Recovery Performance

The shape recovery performance is an essentially important characteristic of SMPs. Therefore, a systematic shape recovery test of aliphatic epoxy/benzoxazine SMP samples under bending load was performed. The procedure for the thermo-mechanical bending cycling of the SMPs includes the following steps (see Figure 3): First, the sample in its permanent shape was kept in an oven for 20 min at T_g+20 °C; then the SMPs was 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 was kept at room temperature with the external constraint to freeze the elastic deformation energy for 20 min. The SMP sample fixed on the apparatus was immersed into air circulated oven at an elevated temperature, and then it recovered to an angle θ_N. The method used to quantify the precision of deployment is illustrated in Figure 4.1

The value of the shape recovery ratio (R_N) is calculated by equation (4.4)

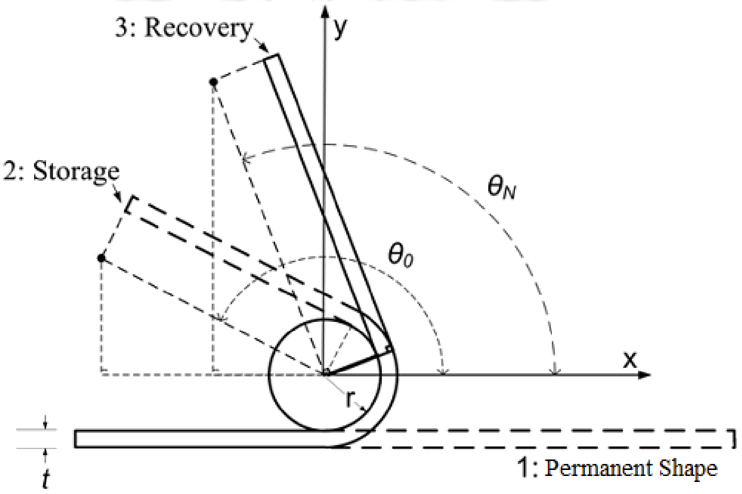


Figure 4.1 Schematic illustration of the setup for the shape recovery performance test [36].

$$R_N = \frac{\theta_0 - \theta_N}{\theta_0} \times 100 \tag{4.4}$$

4.3.6 Shape Fixity and Recovery Stress Test

The shape fixity and recovery stress of aliphatic epoxy/benzoxazine SMPs were investigated by Universal testing machine under three point bending mode. The experimental procedure for the shape fixity and recovery stress is schematically shown in Figure 4.2. Firstly, a fixed shape was formed by applying the force to a sample (10×50×2 mm^3) at T_g+20 °C and left to cool down to room temperature. The force was then removed perfectly to obtain a temporary shape. The deflection after unloading was measured, and rate of shape fixity (R_f) was determined. The sample was heated up to T_g+20 °C by keeping the fixed deflection content afterwards. Force during heating was measured and the recovery stress was obtained.

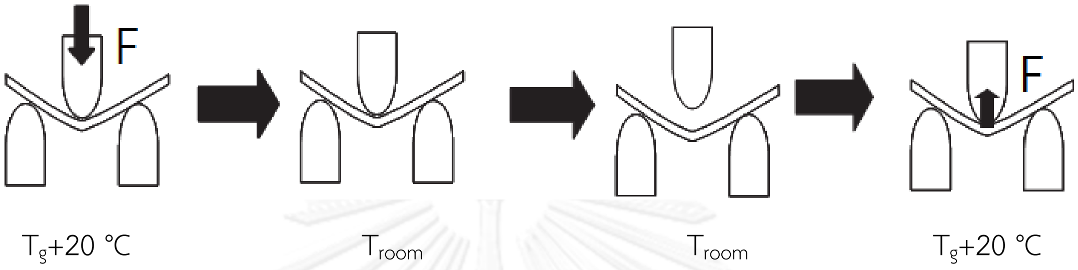


Figure 4.2 Experimental procedure in the shape fixity and recovery stress process [37].

CHAPTER V

RESULTS AND DISSCUSSION

5.1 Effect of Benzoxazine Resin Contents on Curing Behavior

Curing mechanisms of benzoxazine/aliphatic epoxy mixtures were investigated by a differential scanning calorimeter (DSC) in a temperature range of 30 °C to 320 °C with a heating rate of 10 °C/min as shown in Figure 5.1. From the graph, the thermograms revealed a maximum exothermic peak of all these resin mixtures to be about 245 °C-255 °C. The slightly changed exothermic peak position of the resins with an addition of the benzoxazine content implies that the benzoxazine resin has negligible effect on curing reaction of the resin mixtures and the curing reaction of these binary systems can proceed without the need of a catalyst or a curing agent for the polymerization process. Moreover, the reactions between the benzoxazine and the aliphatic epoxy were expected to comprise of at least two reactions; the first reaction at exothermic peak about 250 °C is the polymerization reaction between the monomers of the benzoxazine, whereas the second exothermic peak at a higher temperature, i.e. $T \sim 285$ °C as observed in the Figure is the reaction between the phenolic hydroxyl group on the polybenzoxazine and the epoxide group on the aliphatic epoxy.

Furthermore, this phenomenon was reported that the reaction between the phenolic hydroxyl group and the epoxide group was expected to proceed after the phenolic hydroxyl group from ring opening of the benzoxazine monomer occurred [13, 14, 38]. In addition, area under exothermic peak indicated the heat of reaction of the polymerization processes. From the Figure 5.1, the area under the exothermic peaks was found to increase with increasing the benzoxazine content. Those value increased from 147.7 J/g for BA-a = 30 mol% to 272 J/g for BA-a = 50 mol%. The results indicated that the increase in the number of moles of the reacted functional groups of each component in the aliphatic epoxy mixtures/benzoxazine mixtures, such as between the aliphatic epoxy and the benzoxazine monomer as well as the benzoxazine monomer and the benzoxazine monomer itself.

To further study the curing conditions of the mixture systems, the curing conditions of the aliphatic epoxy/benzoxazine mixtures were determined from the partial disappearance of the area under the curve of the exothermic peak in DSC experiment. Figure 5.2 illustrated the DSC thermograms of the aliphatic epoxy/benzoxazine at 50 mol% of the BA-a content at various curing conditions. The heat of reaction of the uncured sample was 272 J/g and the value decreased to 245.6, 236.7, 231.7 and 101.4 J/g, which corresponded to the degree of conversions estimated by Equation 5.1 of 9.7, 12.9, 14.8 and 62.7% after a step-by-step curing at 130 °C for 12 hours, 140 °C for 4 hours, 150 °C for 4 hours and 160 °C for 2 hours, respectively. The results indicated that the degree of conversion about 62.7% can be useful to prepare the shape memory materials as report by Liu et al. [34]. Therefore, the curing process under this condition was used to cure all aliphatic epoxy/benzoxazine mixtures to prepare the samples for further characterization.

$$\%\text{conversion} = 1 - \frac{H_{rxn}}{H_0} \times 100 \qquad (4.1)$$

Where: H_{rxn} = is the heat of reaction of the partially cured samples

H_0 = is the heat of reaction of the uncured resin mixture

5.2 Fourier Transform Infrared Spectroscopy Investigation

The chemical structure of benzoxazine resin (BA-a), aliphatic epoxy and their network formation reactions were studied by Fourier transform infrared spectroscopy (FTIR). Figure 5.3 showed the FTIR spectrum taken from the benzoxazine resin, the aliphatic epoxy and the aliphatic epoxy/benzoxazine mixture at 50 mol% of BA-a. The characteristic IR absorption bands of the BA-a resin were found at 1230 cm^{-1} assigned to C-O-C stretching mode of benzene ring and 1496 and 936 cm^{-1} assigned to tri-substituted benzene ring as shown in Figure 5.3a. The IR absorption bands of the aliphatic epoxy were observed at 1098 cm^{-1} assigned to C-O-C stretching mode of ethers as well as 1254, 909 and 850 cm^{-1} assigned to epoxide ring mode as shown in Figure 5.3b. In Figure 5.3c, it was evidently confirmed by FTIR that the aliphatic epoxy/benzoxazine mixture contained both benzoxazine resin and aliphatic epoxy characteristic absorptions, such as those at 1496 and 936 cm^{-1} from benzoxazine species and that of 1254, 909 and 850 cm^{-1} from epoxide ring of aliphatic epoxy.

The network formation between the benzoxazine resin and the aliphatic epoxy after thermal cure were also monitored by FTIR spectroscopy. Figures 5.4a and 5.4b showed the FTIR spectrum taken from the benzoxazine resin before and after its polymerization to polybenzoxazine. According to the polymerization mechanism reported by Dunkers and Ishida [39], the oxazine ring is opened by breakage of a C-O bond of the oxazine ring. Then the benzoxazine molecule transformed from a ring structure to a network structure. During this process, the tri-substituted benzene ring, backbone of benzoxazine ring, became tetra-substituted benzene ring. The ring-opening polymerization of the BA-a was observed from the decrease of the absorption bands at 1496 and 936 cm^{-1} and the appearance of the new absorption band at 1477 cm^{-1} which was tetra-substituted benzene ring. In addition, a broad intensive IR absorption band appeared at 3400 cm^{-1} was assigned to O-H groups of the phenolic hydroxyl group that can react with epoxide group for ring opening polymerization [13, 14, 33]. The FTIR spectrum of the aliphatic epoxy/benzoxazine mixture at 50 mol% of the BA-a before and after polymerization were shown in Figures 5.4c and 5.4d. After being step cured at 160 °C for 2 hours. The absorption band at 1477 cm^{-1} of the polybenzoxazine also found in the aliphatic epoxy/benzoxazine alloys and the absorption bands at 1254, 909 and 850 cm^{-1} assigned to the epoxide group disappeared. The disappearance of epoxide group indicated that it reacted with hydrogen bonding of phenolic hydroxyl group to form ether link and a new hydroxyl group [40] which appeared as the absorption bands at 1036 and 3400 cm^{-1}, respectively. It was realized that the benzoxazine and aliphatic epoxy ring opened, and the curing reaction proceeded quantitatively without curing agents. These results were in good agreement with the previous report by Rimdusit et al. [13] and Kimura et al. [41].

5.3 Dynamic Mechanical Analysis (DMA) of Aliphatic Epoxy/Benzoxazine SMPs

Dynamic mechanical properties of aliphatic epoxy/benzoxazine SMPs were shown in Figure 5.5-5.6. Viscoelastic properties of the samples were investigated by DMA in 3 point bending mode. Several parameters such as storage modulus and loss tangent were obtained as a function of temperature from room temperature up to 200 °C based on a heating rate of 2 °C/min.

Figure 5.1 presents the value of storage modulus as a function of temperature of aliphatic epoxy/benzoxazine SMPs. The storage moduli at the glassy state (35 °C) were measured to be 2.8, 3.7, 3.8, 4.2 and 4.5 GPa at BA-a contents of

30, 35, 40, 45 and 50 mol% respectively. As seen in this figure, the storage moduli tended to increase with increasing BA-a content in the alloys. The phenomena is contributted to the addition of the more rigid molecular segment of the poly(BA-a) in the aliphatic epoxy/benzoxazine SMPs [42].

The addition of BA-a resin also resulted in a systematic increase of the modulus in rubbery plateau region from 40 to 172 MPa with an increase of the BA-a from 30 to 50 mol%. This result suggested that the presence of the BA-a resulted in a substantial enhancement in crosslink density of aliphatic epoxy/benzoxazine SMPs which was determined directly from the measured rubbery plateau modulus based on theory of rubber elasticity. For highly cross-linked materials that provide storage modulus in rubbery plateau higher than 10^7 Pa such as in our case,the polymer network will exhibit a more pronounced non-Gaussian character and the equation from theory of rubber elasticity is no longer applicable. Nielsen [43] has proposed an empirical equation that agrees much better than other equations especially for predicting elastic properties of dense network (equation 5.2).

$$\log\left[\frac{E_e^{'}}{3}\right] = 6.0 + 293(\rho_x) \tag{5.2}$$

Where $E_e^{'}$ (Pa) is an equilibrium storage modulus in rubbery plateau, ρ_x (mol/cm^3) is crosslink density which is the molar number of network chains per unit volume of the polymers.

The crosslink density values of aliphatic epoxy/benzoxazine SMPs at BA-a content of 30, 35, 40, 45 and 50 mol% were determined to be 3.8×10^{-3}, 4.1×10^{-3}, 4.9×10^{-3}, $5.2\times10^{-3}$and 6.0×10^{-3} mol/cm^3 respectively. It was observed that the crosslink density clearly increased with an increase in BA-a fraction in the alloys. In theory, higher crosslink density of the polymer network can lead to higher storage modulus and glass transition temperature (T_g). As a consequence, benzoxazine resin affects the aliphatic epoxy/benzoxazine SMPs in such a way to enhance their crosslink density as well as their network rigidity thus the obtained higher T_g.

Tanδ curves, obtained from the ratio of energy loss (E”) to storage energy (E’) in sinusoidal deformation, are shown in Figure 5.6. The peak positions of the tanδ

were used to also indicate the T_g of the specimens. As can be seen from Figure 5.6, the T_g of aliphatic epoxy/benzoxazine SMPs were 51 °C at BA-a = 30 mol%, 70 °C at BA-a = 35 mol%, 88 °C at BA-a = 40 mol%, 121 °C at 45 mol% and 140 °C at BA-a = 50 mol%. An incorporation of BA-a resin in aliphatic epoxy/benzoxazine SMPs, therefore, resulted in an increase in the T_g of the hybrid polymer. This is attributed to the more rigid molecular structure and possibly much higher intramolecular and intermolecular forces in the polybenzoxazine compared to the epoxy [44]. In addition, the observed increase of the T_g directly reflects the reduction of segmental mobility of polymer chains and the increase in stiffness of the alloys. with increasing crosslinked density as benzoxazine fraction in the alloy increases.

Moreover, the peak height of the tanδ was observed to decrease with increasing mole percent of the benzoxazine resin which suggested the elastic behavior of the alloys to increase with the amount of the benzoxazine. We also observed a broader of the width at half height of tanδ when the amount of benzoxazine increased. This behavior implied network heterogeneity to be more pronounced with the presence of resin mixtures. However, the transparency and the single peak of tanδ of each samples confirmed the single microscopic domain of these alloys, i.e. no sign of phase separation. In some special cases of shape memory polymers such as in multiple shape memory polymers (MSMPs), single broad switching transition is necessary to provide the multiple shape memory effects [45]. The effects are highly useful in various applications such as in packaging and robot.

5.4 Effect of BA-a Contents on Mechanical Properties of Aliphatic Epoxy/Benzoxazine SMPs

5.4.1 Flexural Properties of Aliphatic Epoxy/Benzoxazine SMPs at Room Temperature (Glassy State)

Mechanical properites via flexure testing at room temperature (glassy state), i.e. flexural strength (σ_f) and modulus (E_f) of the aliphaic epoxy/benzoxazine SMP samples were examined. Figures 5.7 and 5.8 show the plots of the flexural strength and flexural modulus at the room temperature of aliphatic epoxy/benzoxazine SMPs as a function of the BA-a content, respectively. In the Figure 5.7, we can observe that the flexural strength of the aliphatic epoxy/benzoxazine SMPs increased with an increasing in the amount of the BA-a. The flexural strength of the samples were measured to be 52 MPa for BA-a = 30 mol%, 78 MPa for BA-a = 35 mol%, 108 MPa for BA-a = 40 mol%, 124 MPa for BA-a = 45 mol% and 132 MPa for BA-a = 50 mol%. This characteristic is due to the addition of high flexural strength polybenzoxazine, i.e. $\sigma_f \sim$ 126-139 MPa [46, 47]. Interesting, the aliphaic epoxy/benzoxazine SMP samples show the flexural strength values higher than that of cyanate ester-epoxy shape memory polymer, i.e. 14-100 MPa [48]. Moreover, an addition of the BA-a into the aliphatic epoxy was also found to improve the flexural modulus of the aliphatic epoxy/benzoxazine SMPs samples as seen in Figure 5.8. From the figure, the flexural modulus of the aliphatic epoxy/benzoxazine SMPs samples was in the rang of 1.6 GPa for BA-a = 30 mol% to 4.0 GPa for BA-a = 50 mol%. This could be due to the addition of the more rigid polybenzoxazine, i.e. E_f ~ 4.5-5.8 GPa [46, 47] into the more flexible aliphatic epoxy. Furthermore, the enhanced crosslink density results in decreased free volume that can improve the stiffness as well as the strength of the resulting polymer alloys [14] as well as the reaction formation between the activated phenolic hydroxyl groups in the polybenzoxazine and the epoxide groups in the epoxy [49] that can adequately support stress transfer in these alloy systems.

5.4.2 Flexural Properties of Aliphatic Epoxy/Benzoxazine SMPs at Rubbery State

The potential applications in deployable structure of the aliphatic epoxy/benzoxazine SMPs were investigated by flexural testing in the rubbery state (T_g+20 °C). In general, the improvement of flexural properties in the rubbery state can specify the SMPs to resist external loading. In this work, the flexural testing was carried out on the Universal testing machine (Instron model 5567) equippd with the environmental chamber at a T_g+20 °C. Figure 5.9 depicts the plot of the flexural strength at theirs T_g+20 °C of the aliphatic epoxy/benzoxazine SMPs at different BA-a contents (mole percents). The flexural strength values at the rubbery state of the aliphatic epoxy/benzoxazine SMS samples composed of the BA-a resin content of 30, 35, 40, 45 and 50 mol% were measured to be 0.4, 0.6, 0.9, 1.5 and 2.3 MPa, respectively. From the results, the flexual strength at the rubbery state of the aliphatic epoxy/benzoxazine SMPs increased with increasing of the BA-a resin content from 30 to 50 mol% as similarly tended to the flexural strength at the room temperature. The increasing of flexural strength at the rubbery state of the samples was due to the enhancement of crosslink density of the aliphatic epoxy/benzoxazine SMP samples as observed in DMA results. This result suggests that the flexural strength at the rubbery state of the samples was suitable for the shape memory material compared with commercial SMPs based on styrene resin (Veriflex®) with the flexural strength in the rubbery state about 0.23±0.03 MPa [50].

Furthermore, the relationship between the BA-a mole percent and flexural modulus at rubbery state of the aliphatic epoxy/benzoxazine SMP samples was illustrated in Figure 5.10. The flexural modulus values of the SMP samples were 2.5 MPa for BA-a = 30 mol%, 3.5 MPa for BA-a = 35 mol%, 7.2 MPa for BA-a = 40 mol%, 8.5 MPa for BA-a = 45 mol%, and 10.4 MPa for BA-a = 50 mol%. As seen in this figure, the flexural modulus tended to increase with increasing of the BA-a resin content in the alloys. This observation indicated that the addition of the BA-a resin can help improve the flexural modulus at the rubbery state of the samples. Additionally, the value is also higher than that of a commercial thermoset SMP epoxy system (DP7AR) as previously reported by Liu el al. [51] i.e. E_f at T_g+20 °C = 8.51 MPa. This could be related to more benzene ring in polybenzoxazine molecular structure which enhanced rigidity of the aliphatic epoxy/benzoxazine SMPs [35].

5.5 Shape Memory Properties

5.5.1 Effect of BA-a Contents on Shape Fixity of Aliphatic Epoxy/Benzoxazine SMPs.

Shape fixity (R_f) issued to indicate the ability to memorize the temporary shape of the shape memory polymer (SMP). When the SMP sample is heated to a temperature above glass transition temperature (T_g), the sample can develop large deformations which can be fixed by cooling to a temperature below T_g or room temperature (25 °C). To investigate the effect of benzoxazine contents on the shape fixity at various fixing temperature, the shape fixity values of the aliphatic epoxy/benzoxazine SMPs at various BA-a contents as displayed in Figure 5.11 were in a range of 84.5% to 83.1% at T_g-10 °C, 97.4% to 96.5% at T_g-20 °C and 99.3% to 98.1% at the room temperature. From the results, all of the shape fixity values of the aliphatic epoxy/benzoxazine SMP samples with varying fixing temperature tended to be lowered by an increase the BA-a resin contents from 30 to 50 mol%. The slightly decrease in the shape fixity values implied that the fixed temporary shape of the aliphatic epoxy that works as reversible switching phase decreased with the increase of the BA-a that works as stable polymer network or hard-segment. This reduction of the shape fixity has been similarly reported by Ji et al [52] that the shape fixity of the polyurethanes decreased from 96% to 84% with the increase of hard-segment content from 30 to 50%. Consequently, the shape fixity values of our aliphatic epoxy/benzoxazine SMPs were found to lower decrease than that system of polyurethane SMPs.

Moreover, it was found that the shape fixity of the SMP samples increased from about 84% to 99% when the fixing temperature was decreased from T_g-10 °C to room temperature. The results suggest that at T_g-10 °C, some molecular chain segments were unfixed. This characteristic results in the SMP samples can partially restore to permanent shape. This behavior make the SMP samples uncontrolled of its temporary shape. The higher shape fixity at T_g-20 °C and room temperature (25 °C) were close to 100% due to the temperature range of Tg-20 °C and room temperature are suitable for freeze the motion of the molecular segments. Comparing at the same fixing temperature, i.e. T_g-10 °C and T_g-20 °C, the shape fixities of our aliphatic epoxy/benzoxazine SMPs, i.e. about 83.1-84.5% and 96.5-97.4%, respectively, were found to be higher than the values of commercial polyurethane SMPs (about 77%) [53] due to the present of high thermal stability of polybenzoxazine in the alloys. Therefore, the aliphatic epoxy/benzoxazine SMPs can be fixed in a temporary shape in wide range between T_g-20 °C and room temperature. This advantage of the SMP samples fixed in the wide temperature range can be useful for wide-range temperature applications or in various environments.

5.5.2 Effect of BA-a Contents on Shape Recovery Time of Aliphatic Epoxy/Benzoxazine SMPs.

To investigate the shape memory performances of the aliphatic epoxy/benzoxazine SMPs, a fold-deploy shape memory was performed. Bending deformation was widely employed for evaluating shape memory properties of polymer materials due to a large deflection being easily obtained in the range of small strain through bending [54].

First of all, the mandrel with a flat sample (permanent shape) fixed on it was put into an environmental chamber at transition temperature ($T \geq T_g$). Then, the flat sample became elastic and was bent into U-shape (temporary shape). This shape was held until the sample was cooled back to room temperature, and the temporary shape was fixed for 20 min to confirm that the sample did not deform. After that, the bent sample was heated up to transition temperature and recovered to its permanent shape. The recovery behavior of the bent sample was recorded by a digital video camera. The recovering angles of SMP sample was determined by measuring the angle between the straight ends of the bent samples. In experimental, snapshots of the shape recovery sequence at T_g+20 °C of the aliphatic epoxy/benzoxazine SMP sample at BA-a = 40 mol% is illustrated in Figure 5.12. It can be seen that the SMP sample can fully recover its permanent shape with 100% shape recovery or recovery angle with 180°. All of our SMP samples, i.e. with benzoxazine contents from 30-50 mol% also showed fully shape recovery performance of 100% at T_g+20 °C. This characteristic maybe imply that, in the aliphatic epoxy/benzoxazine SMP systems, the macromolecules are covalently cross-linked to form the three-dimensional network structures which the alloys becomes reversibly rubbery at T_g above [22].

The effect of BA-a contents on shape recovery times of the aliphatic epoxy/benzoxazine SMPs by bending test at different active temperatures, i.e. a T_g and a T_g+20 °C, are depicted in Figures 5.13 and 5.14, respectively. From the figures, all SMP samples need only few minutes to recover to their permanent shape which indicate a relatively good shape memory behavior. This result is consistent with the shape memory composites of epoxy and activity polyurethane as report by Liu et al. [55]. Figures 5.13 and 5.14 show the curves of recovery angle against recovery time for the aliphatic epoxy/benzoxazine SMPs at their T_gs and T_gs+20 °C. The curve from the plot of the recovering angle and time can be divided into three zones. The start stage (at a recovery angle of 0° to 50°), transition stage (at a recovery angle of 50° to 150°) and terminal stage (a recovery angle of 150° to 180°). This phenomenon suggested that the aliphatic epoxy/benzoxazine SMPs has a relative low recovery rate at the start and terminal stage. At the start stage between 0°-50°, the release of constrained force was followed by heavy friction among molecules, thus the recovery angle slowly increased. After that, fraction force reduced under the gradual adjustment of segments results in the slopes of recovery angle is sharply as named the transition stage. At the terminal stage, the shape recovery rate becomes slower than the transition stage because the constrained force of all samples had been released result in a little of it remaining [34, 35, 56].

In addition, the plot of the shape recovery time of the aliphatic epoxy/benzoxazine SMP samples with various contents of 30 to 50 mol% of the BA-a is also depicted in Figure 5.15. From the figure, we can observe the shape recovery time of the SMPs is in the ranging of 76 to 148 s at a T_g and 64 to 120 s at a T_g+20 °C. From the results, the shape recovery time decreased with increasing the active temperature. This phenomenon might be explained that, at the higher temperature, the activated molecular chain segments can move more intensely. Moreover, the shape recovery time of the SMP samples increased with an increasing amount of BA-a contents. In general, for the chemically cross-linked glassy polymers, this result implied that the movement of the molecular chain segment of the SMPs could be more restricted with increasing BA-a content because of an increasing of crosslink density that results in the high modulus at T_g and excellent rubber elasticity above T_g as previously discussed in DMA results. Additionally, the recovery times of the aliphatic epoxy/benzoxazine SMPs were also faster than that of the shape memory polymer of epoxy resin E-51 (WSR 618) cured by aromatic amine curing agent as reported by Liu et al. [34]. Interestingly, the incorporation of the BA-a into the SMP samples can control the shape recovery time, therefore broadening the application of the resulting aliphatic epoxy/benzoxazine SMPs.

Furthermore, in order to observe the performance of the shape memory behavior over period of time for fixed temporary shape. The aliphatic epoxy/benzoxazine SMP sample at BA-a = 40 mol% was used as representative sample to demonstrate the shape memory behavior after the time period of 20 min, 7 days, 15 days, 30 days for fixed temporary shape as shown in Figure 5.16. From the figure, we could see that the SMP samples showed negligible change in its temporary shape after 20 min, 7 days, 15 days and 30 days. That is the times of full recovery of these samples were 84 s, 85 s, 85s, and 86 s, respectively. Then, the SMP samples can fully recover to their permanent shape after heated up to T_g+20 °C. This result implied that the performance of SMP based on aliphatic epoxy/benzoxazine can maintain over a period of time.

5.5.3 Effect of BA-a Contents on Recovery Stress of Aliphatic Epoxy/Benzoxazine SMPs

The recovery stress is essential property for smart actuators which is a device that is used to apply a specific motion or force to a product or process. The recovery stress of SMPs determined from the elastic stress in deformation process. When the SMPs were heated above T_g, the SMPs were deformed and generated the elastic stress. This elastic stress was stored when the SMPs were cooled below T_g. Then, the SMPs were reheated above T_g again, the stress stored in the SMPs was released as recovery stress [28].

The experimental procedure of the recovery stress test of aliphatic epoxy/benzoxazine SMP samples was observed from Figure 5.17. Firstly, permanent state of the SMP sample was applied at 20 °C above T_g (T_g+20 °C) as seen in Figure 5.17(a). After that the SMP sample was applied load during heating at T_g+20 °C until its maximum deflection (y_{max} = 10 mm) as shown in Figure 5.17(b). Then, the sample was held at room temperature under unloaded condition for 20 minute as depicted in Figure 5.17(c). Finally, the SMP sample was heated to Tg+20 °C by maintaining the fixed deflection constant. Recovery stress during heating was masured from the transition stage of the shape-fixed stage to the recovery shape stage, as can be seen in Figure 5.17(d).

The recovery stress versus time of the aliphatic epoxy/benzoxazine SMPs were shown in Figure 5.18. The maximum recovery stress of each samples were observed to be 0.25, 0.39, 0.62, 0.98, 1.59 MPa at BA-a contents 30, 35, 40, 45, 50 mol%, respectively. As the result, it could be seen that the BA-a resin help improve the recovery stress of the aliphatic epoxy/benzoxazine SMPs. The increasing of the recovery stress of the SMPs since the presence of the BA-a resin in the alloys results in increasing crosslink density, which improved storage modulus at rubbery state the alloys [22]. As previous reported by Liu et al. [51], the increase of the recovery stress value was observed in shape memory epoxy nanocomposites. It was found that at maximum filler loading (20wt%), the recovery stress was observed to be 1.5 MPa, i.e. 1 time greater than that of the neat epoxy SMP with the recovery stress value about 0.8 MPa. Interestingly, compared to our aliphatic epoxy/benzoxazine SMPs found that our systems can be improved the recovery stress about 6 times from 0.25 MPa at 30 mol% of BA-a to 1.59 MPa at 50 mol% of BA-a, which is more than that of the epoxy SMPs nanocomposites. Thus, the SMPs based on the polybenzoxazine is suitable to use in deployable structures, such as hinge [57].

5.3.4 Mechanical Properties of the SMP Samples after Repeated Recovery Cycles

The cycling capability of SMPs based on aliphatic epoxy/benzoxazine investigated with the flexural strength as a function of number of recovery cycles that was able to reflect the fatigue of the SMP materials was depicted in Figure 5.19. The repeated bending cycle test of the SMPs with various the BA-a contents was performed at T_g+20 °C in condition test at crosshead speed 1.0 mm/min and maximum deflection at 10 mm. From the figure, we can see that the aliphatic epoxy/benzoxazine SMP samples containing of 30, 35, 40, 45 and 50 mol% of BA-a showed averaged flexural strengths at all 100th cycle of about 0.42 ± 0.01, 0.64 ± 0.02, 0.93 ± 0.02, 1.55 ± 0.03 and 2.35 ± 0.04 MPa, respectively. Interestingly, as seen the figure, the slightly difference of the flexural strength value between the first and subsequent cycles was clearly observed which corresponded to our results of the flexural strength values of the samples at T_g+20 °C (rubbery state) as previously discussed. Therefore, the maintained flexural strength values with increase repeated cycles were also observed as previously reported by Rimdusit et al. [22]. This characteristic can imply that the SMP samples are the resistant to fatigue during repeated shape recovery process at T_g+20 °C because of the excellent thermal stability of the aliphatic epoxy/benzoxazine alloys and its chemical crosslink nature. Consequently, the aliphatic epoxy/benzoxazine SMPs can be useful in various application that have multiple recovery cycles.

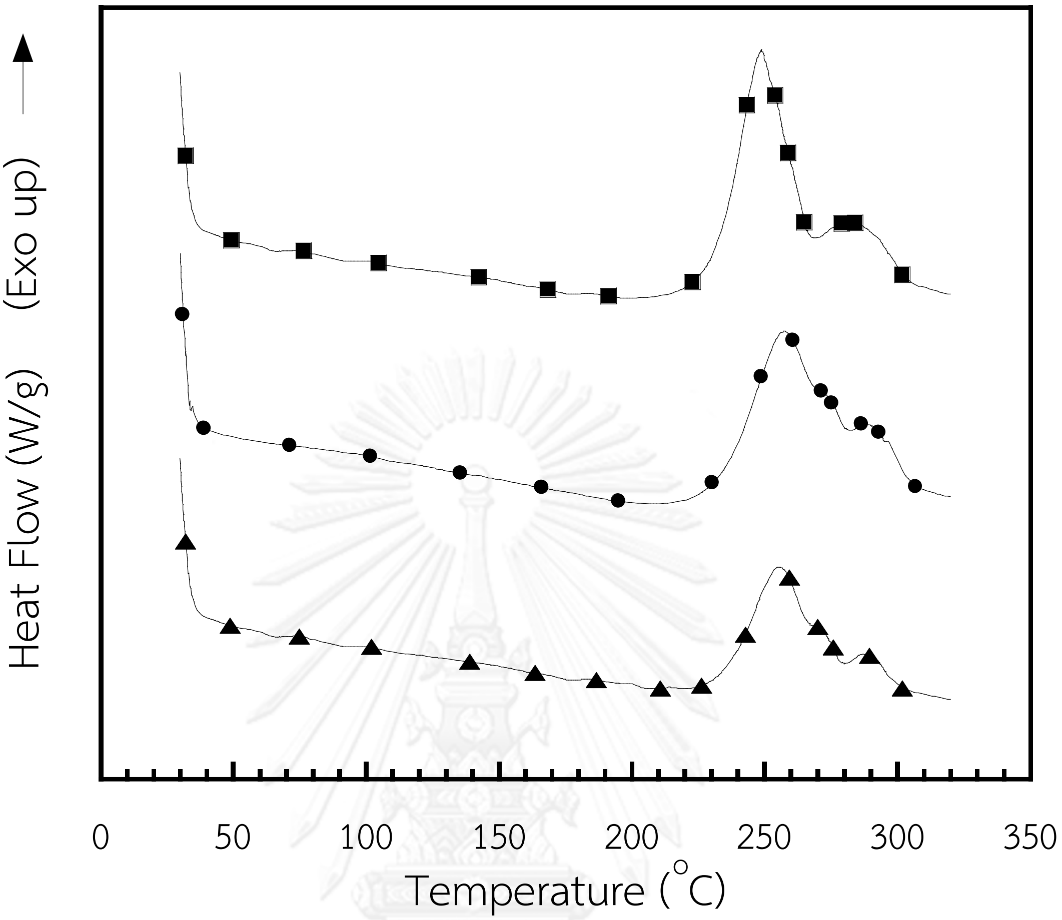


Figure 5.1 DSC thermograms of aliphatic epoxy/benzoxazine mixtures at various mole percents of the BA-a: (▲) 30 mol%, (●) 40 mol% and (■) 50mol%.

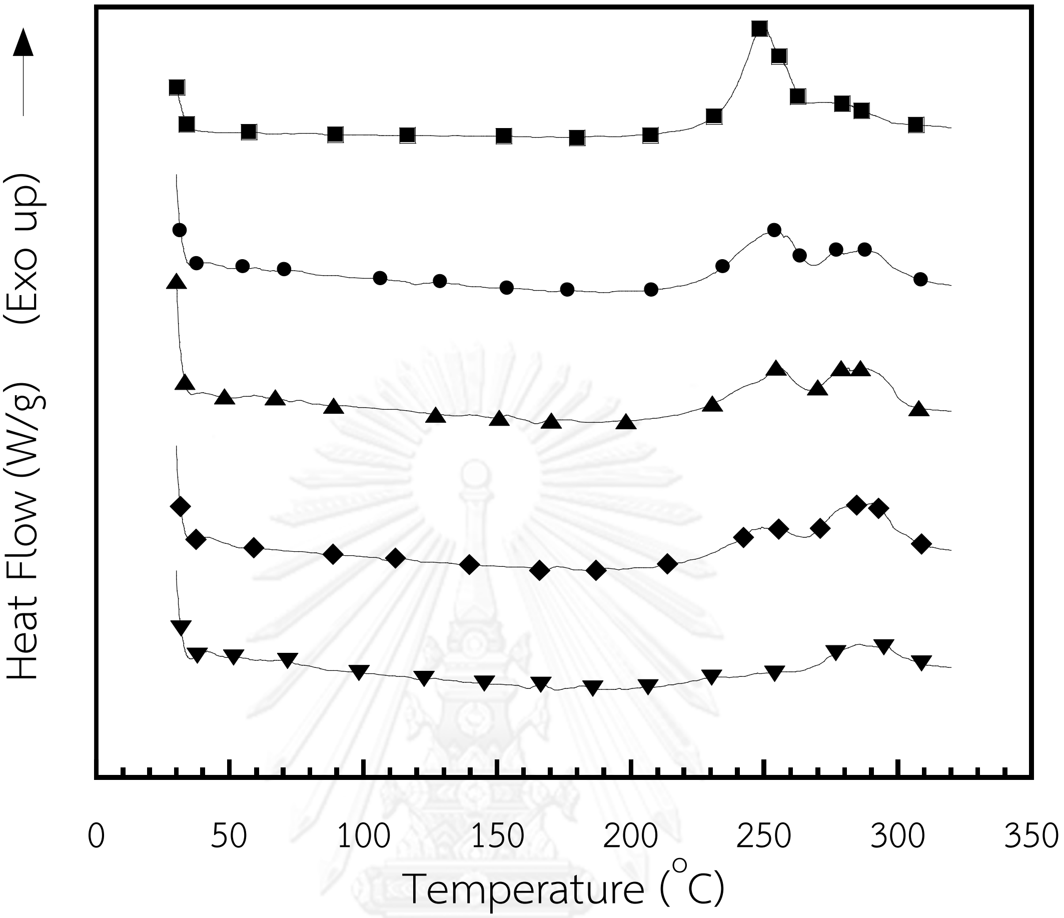


Figure 5.2 DSC thermograms of aliphatic epoxy/benzoxazine SMP samples at 50 mol% of the BA-a at various curing conditions: (■) uncured, (●) 130 °C/12 hrs, (▲) 130 °C/12 hrs + 140 °C/4 hrs, (◆) 130 °C/12 hrs + 140 °C/4 hrs + 150 °C/4 hrs and (▼) 130 °C/12 hrs + 140 °C/4 hrs + 150 °C/4 hrs + 160 °C/2 hrs.

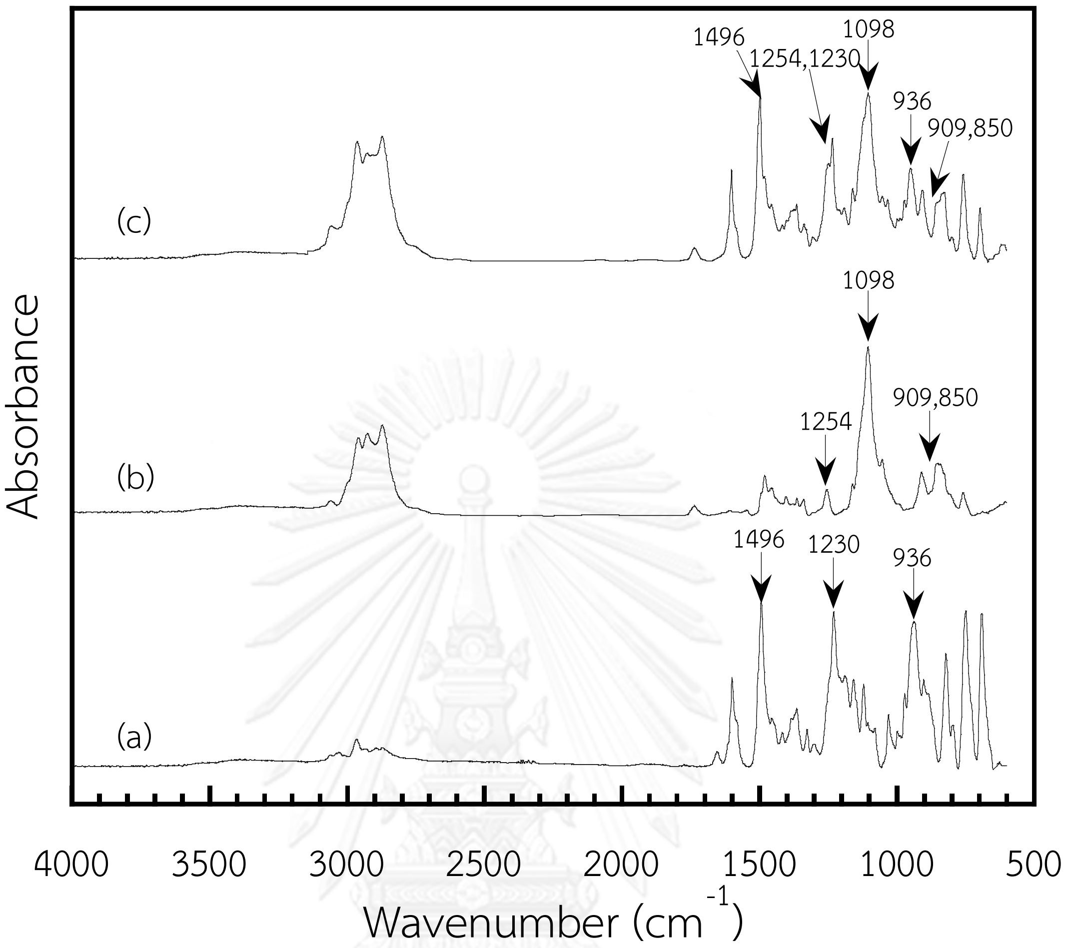


Figure 5.3 FTIR spectra of benzoxazine resin and aliphatic epoxy: (a) benzoxazine resin, (b) aliphatic epoxy and (c) the aliphatic epoxy/benzoxazine resin mixture at the BA-a 50 mol%.

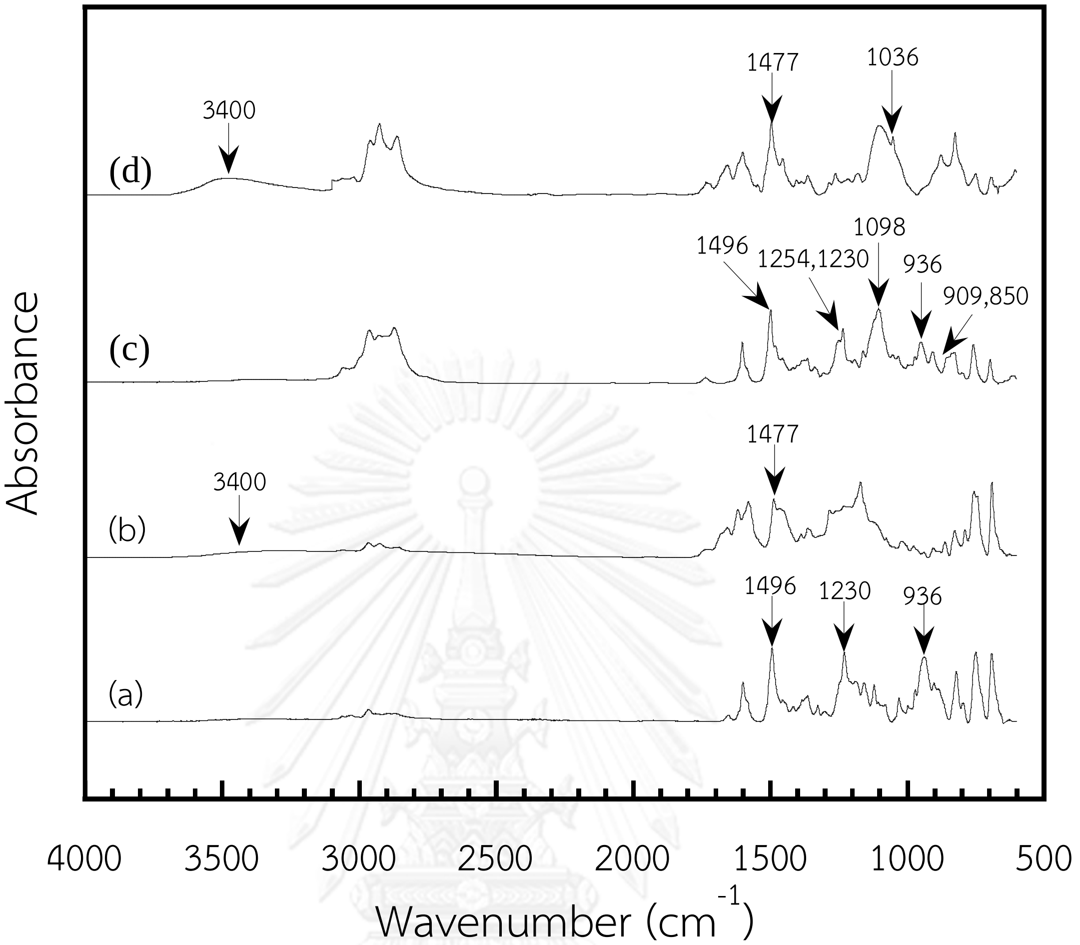


Figure 5.4 FTIR spectra of aliphatic epoxy and benzoxazine resin before and after curing: (a) benzoxazine resin, (b) polybenzoxazine, (c) aliphatic epoxy/benzoxazine resin mixture at the BA-a 50 mol% (d) aliphatic epoxy/benzoxazine alloy at the BA-a 50 mol%.

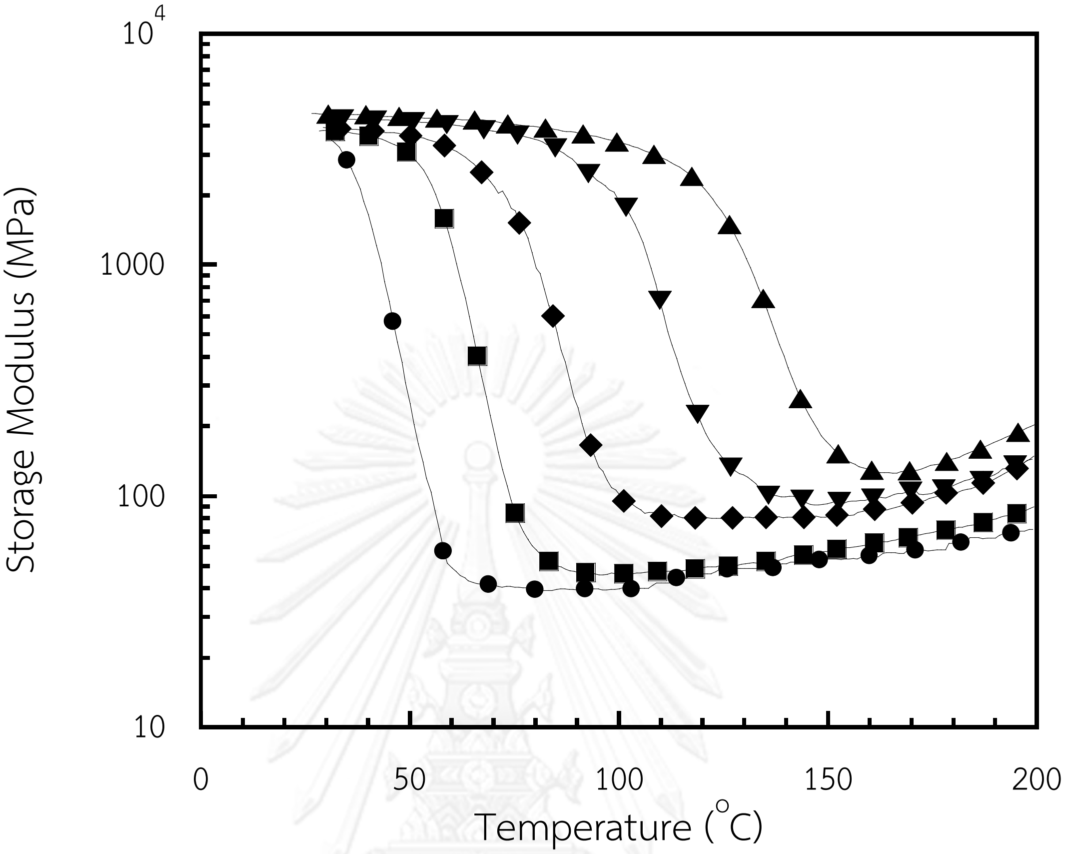


Figure 5.5 Storage modulus versus temperature of aliphatic epoxy/benzoxazine SMPs at various mole percents of the BA-a: (●) 30 mol%, (■) 35 mol%, (◆) 40 mol%, (▼) 45 mol% and (▲) 50 mol%.

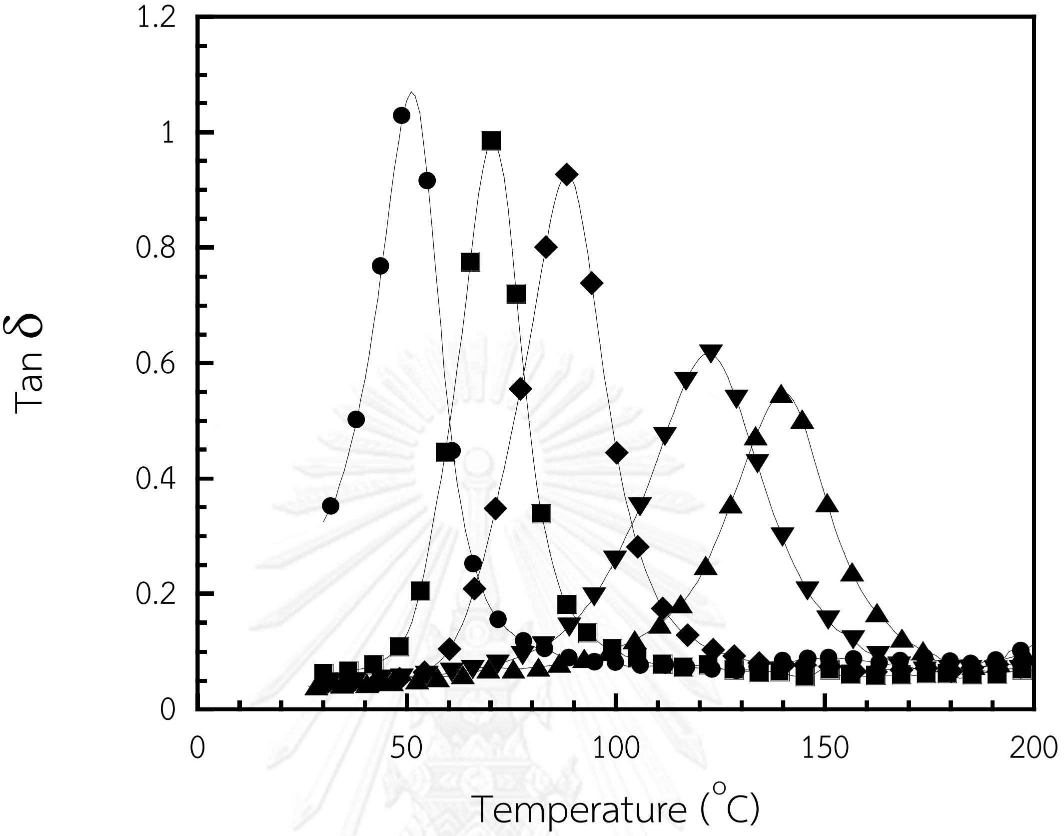


Figure 5.6 Loss tangent versus temperature of aliphatic epoxy/benzoxazine SMPs at various mole percent of the BA-a: (●) 30 mol%, (■) 35 mol%, (◆) 40 mol%, (▼) 45 mol% and (▲) 50 mol%.

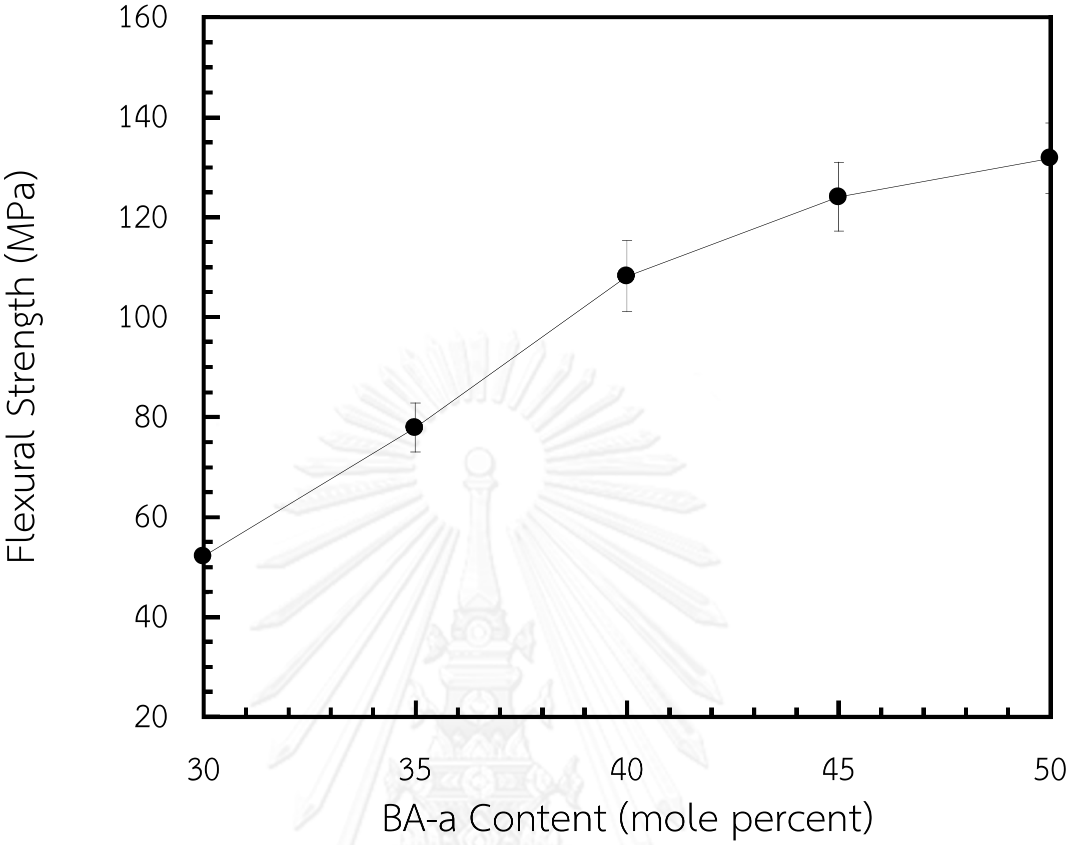


Figure 5.7 Flexural strength at room temperature of the aliphatic epoxy/benzoxazine SMP samples at various mole percents of the BA-a.

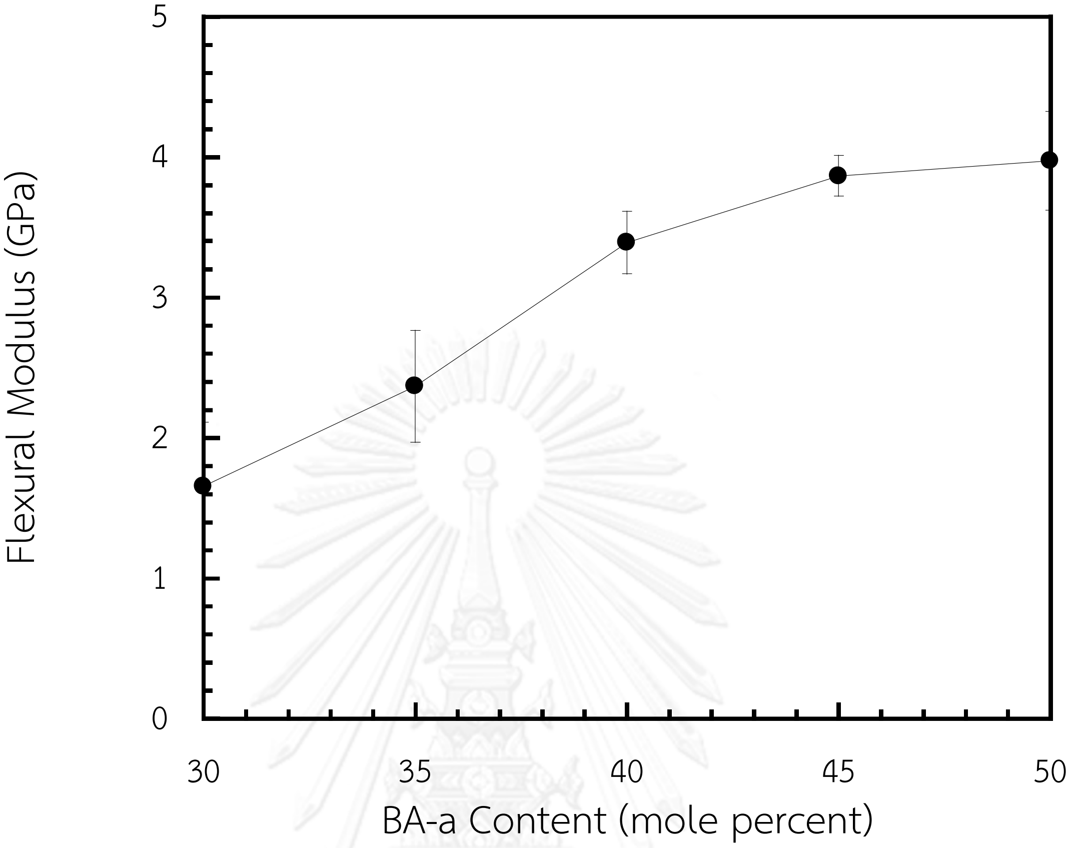


Figure 5.8 Flexural modulus at room temperature of the aliphatic epoxy/benzoxazine SMP samples at various mole percents of the BA-a.

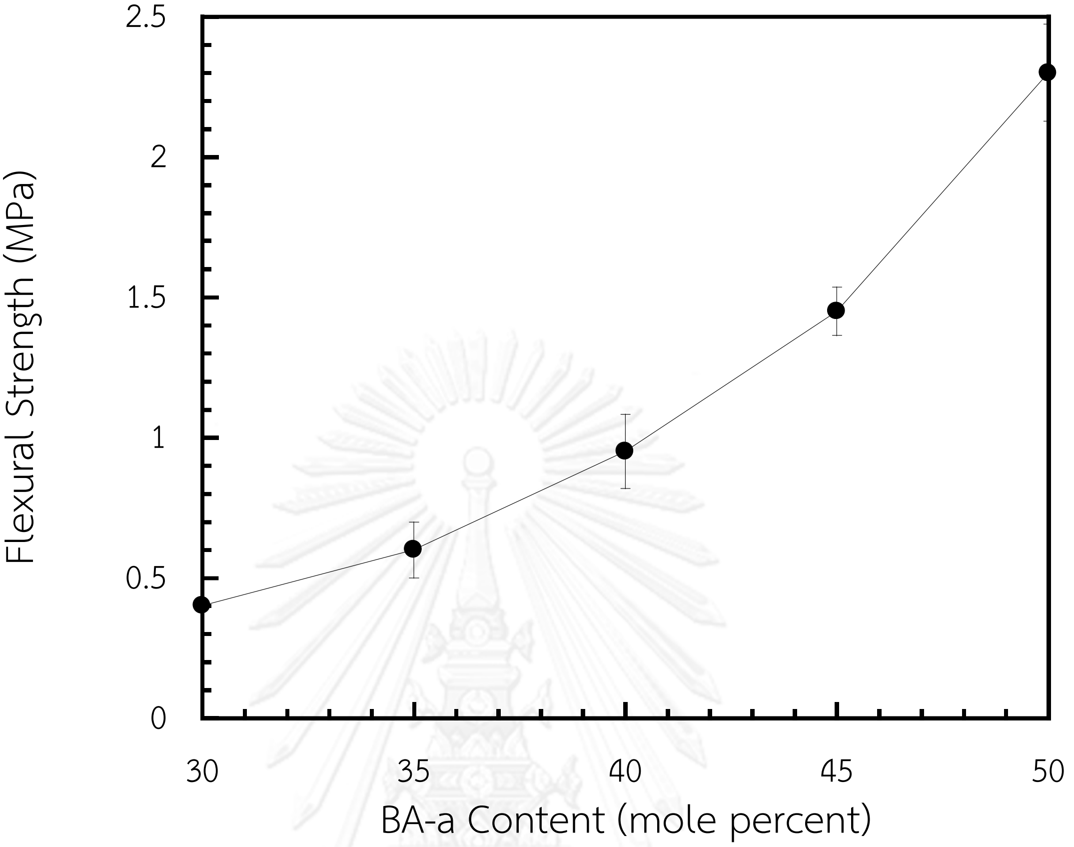


Figure 5.9 Flexural strength at T_g+20 °C of the aliphatic epoxy/benzoxazine SMP samples at various mole percents of the BA-a.

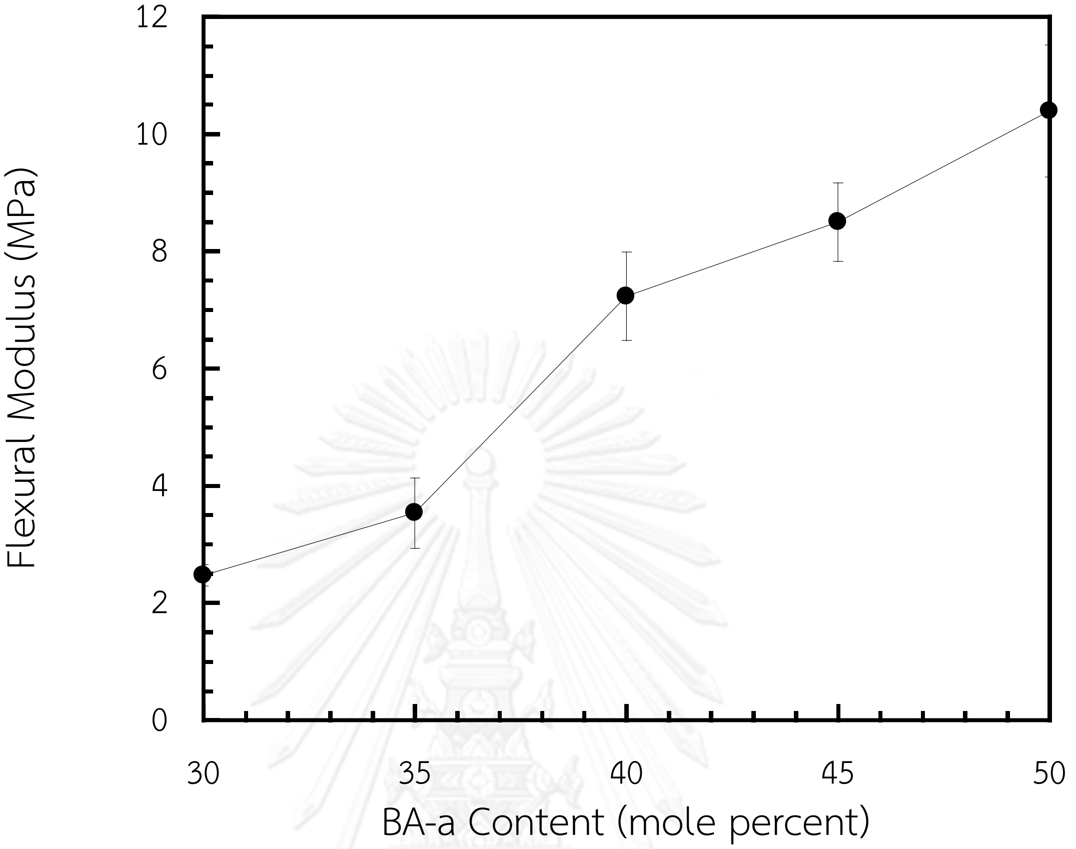


Figure 5.10 Flexural modulus at T_g+20 °C of the aliphatic epoxy/benzoxazine SMP samples at various mole percents of the BA-a.

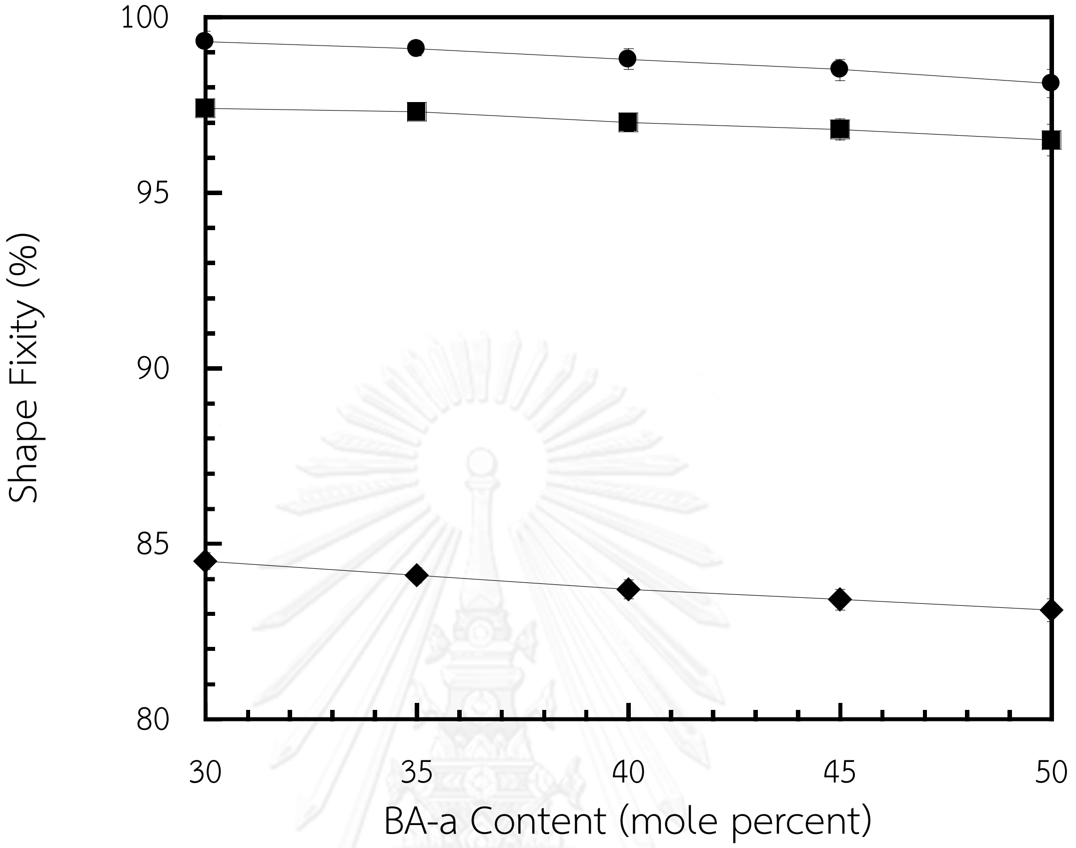


Figure 5.11 Effect of BA-a contents on shape fixity at different fixing temperature: (●) Room temperature, (■) Tg-20 °C and (◆) Tg-10 °C.

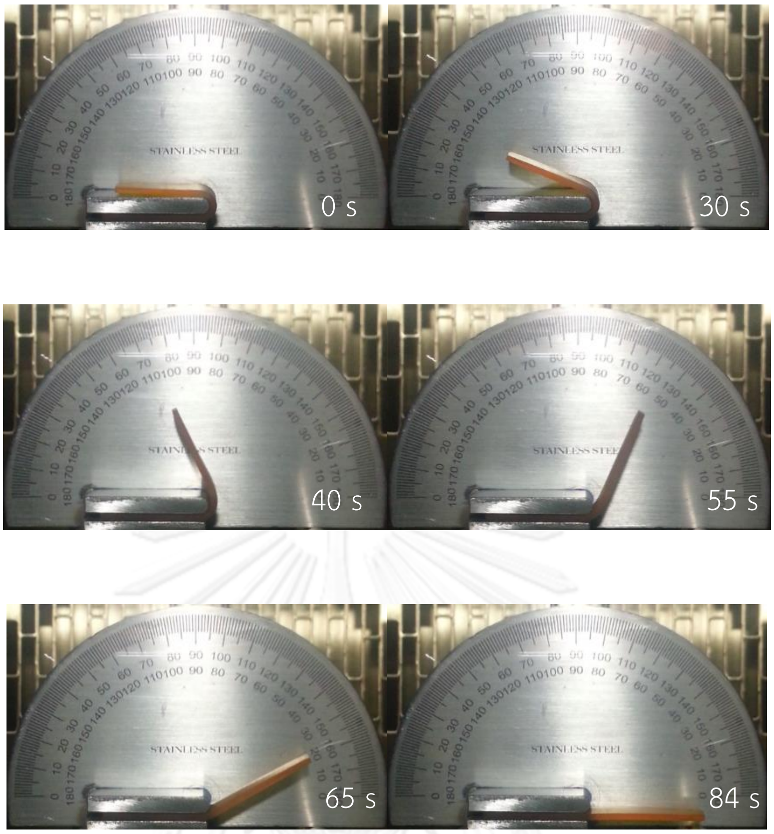


Figure 5.12 Series of images showed the shape recovery of the aliphatic epoxy-benzoxazine SMP sample with BA-a 40 mol% at a T_g+20 °C (108 °C). The permanent and temporary shapes are rectangular and U-shape, respectively.

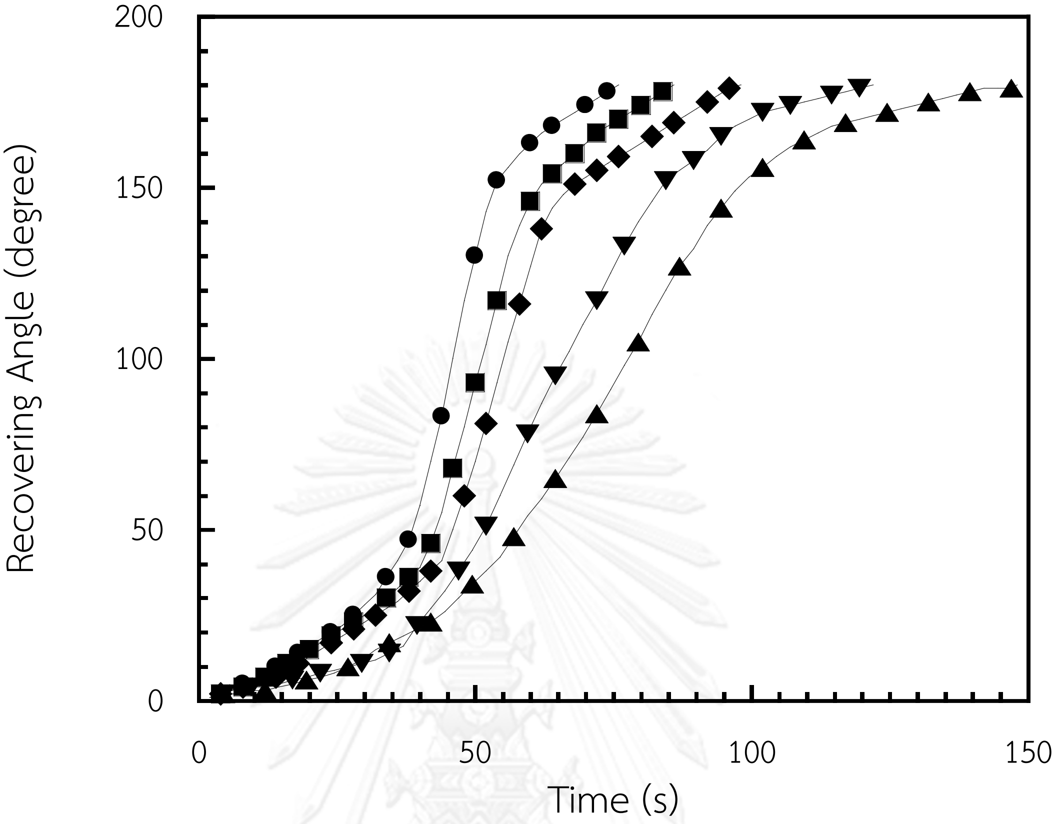


Figure 5.13 Recovery angle as a function of recovery time during the shape recovery process at a T_g of the aliphatic epoxy/benzoxazine SMP samples at various mole percents of the BA-a: (●) 30 mol%, (■) 35 mol%, (◆) 40 mol%, (▼) 45 mol% and (▲) 50 mol%.

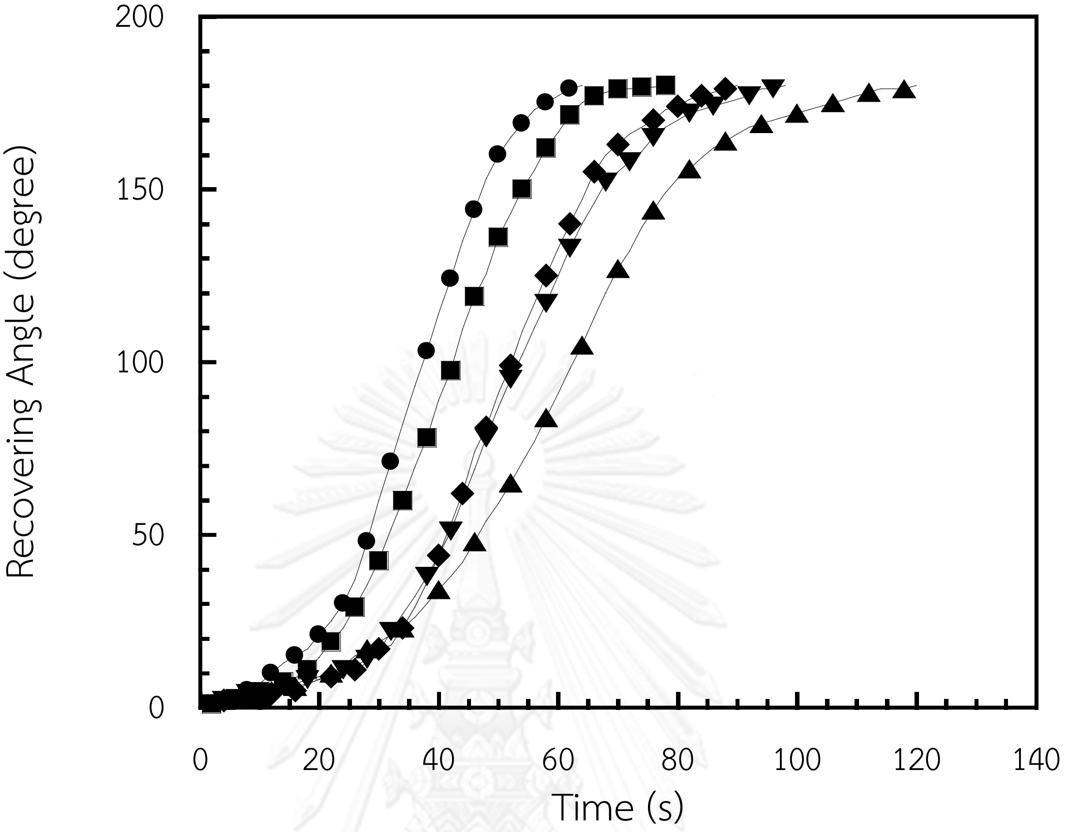


Figure 5.14 Recovery angle as a function of recovery time during the shape recovery process at a T_g+20 °C of the aliphatic epoxy/benzoxazine SMP samples at various mole percents of the BA-a: (●) 30 mol%, (■) 35 mol%, (◆) 40 mol%, (▼) 45 mol% and (▲) 50 mol%.

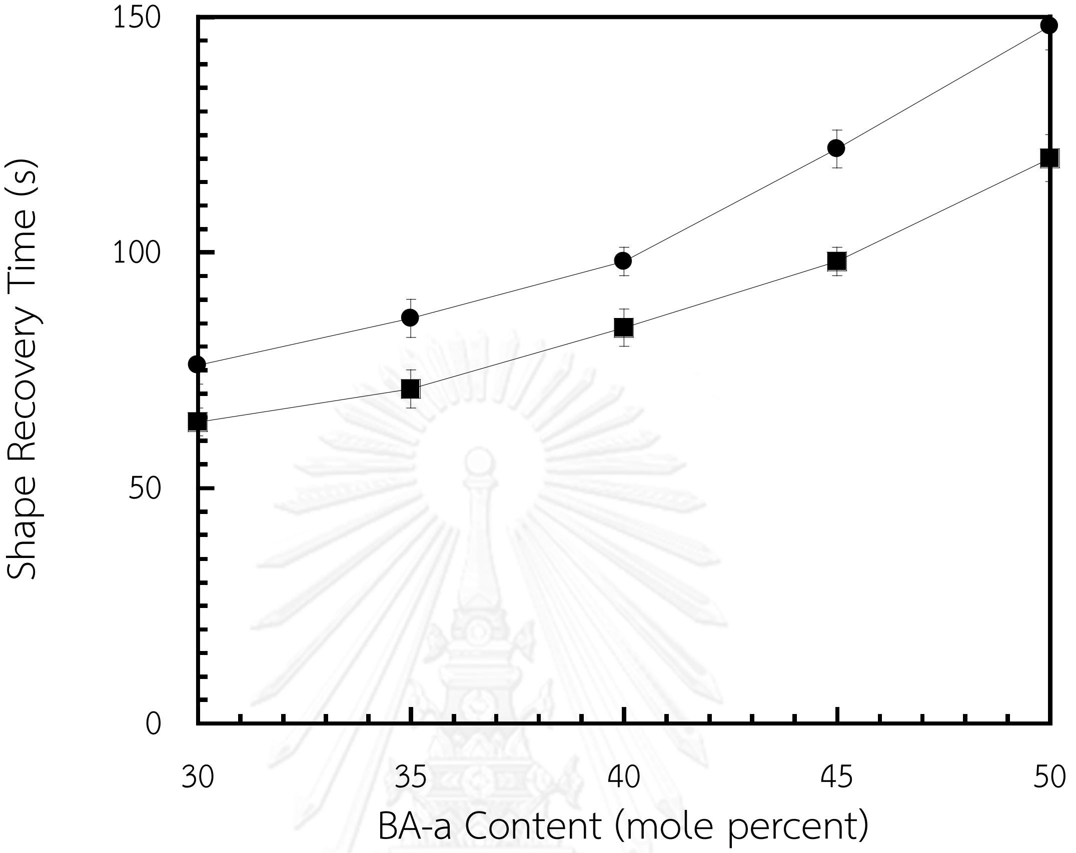
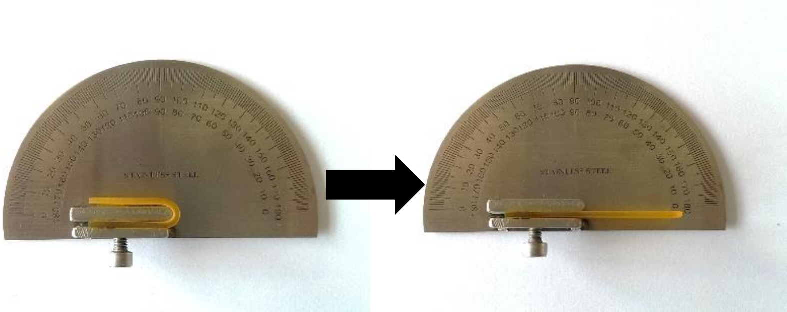
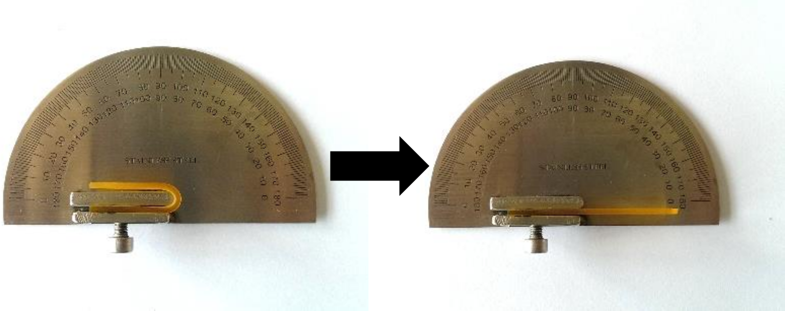


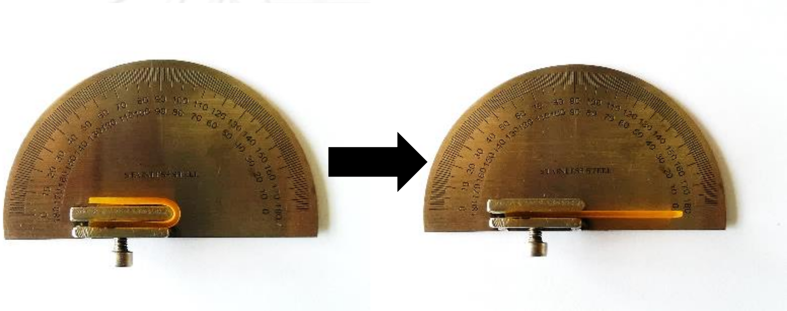
Figure 5.15 Recovery time as a function of BA-a contents of the aliphatic epoxy/benzoxazine SMP samples at various temperatures: (●) T_g and (■) T_g+20 °C.



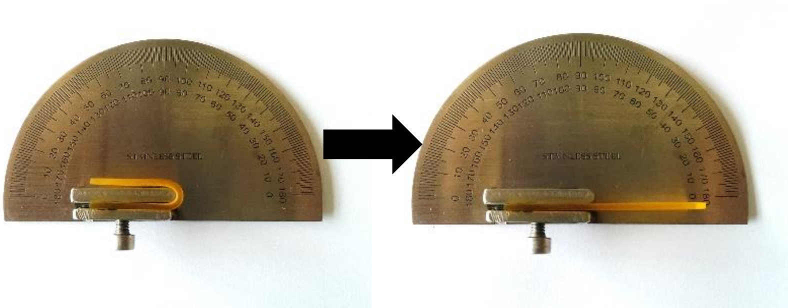
(a) Time of full recovery = 84 seconds.



(b) Time of full recovery = 85 seconds.



(c) Time of full recovery = 85 seconds.



(d) Time of full recovery = 86 seconds.

Figure 5.16 Performance of the aliphatic epoxy/benzoxazine SMPs at the BA-a 40 mol% at different time of fixed temporary shape: (a) 20 min, (b) 7 days, (c) 15 days and (d) 30 days.

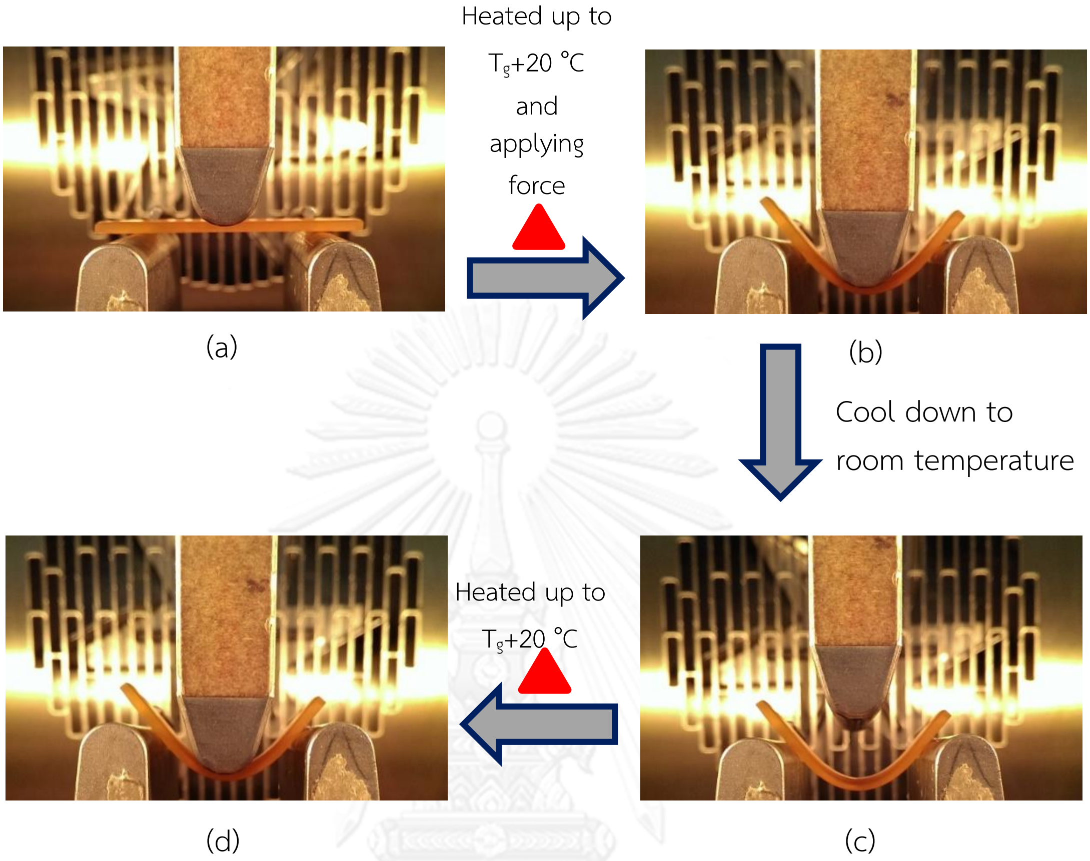


Figure 5.17 Photographs showing various states of bending in the recovery stress process for the aliphatic epoxy/benzoxazine SMP sample: (a) permanent state of the sample, (b) deformed state with y_{max} = 10 mm, (c) shape-fixed state after cooling and (d) shape-recovered state and stress during reheating was measured.

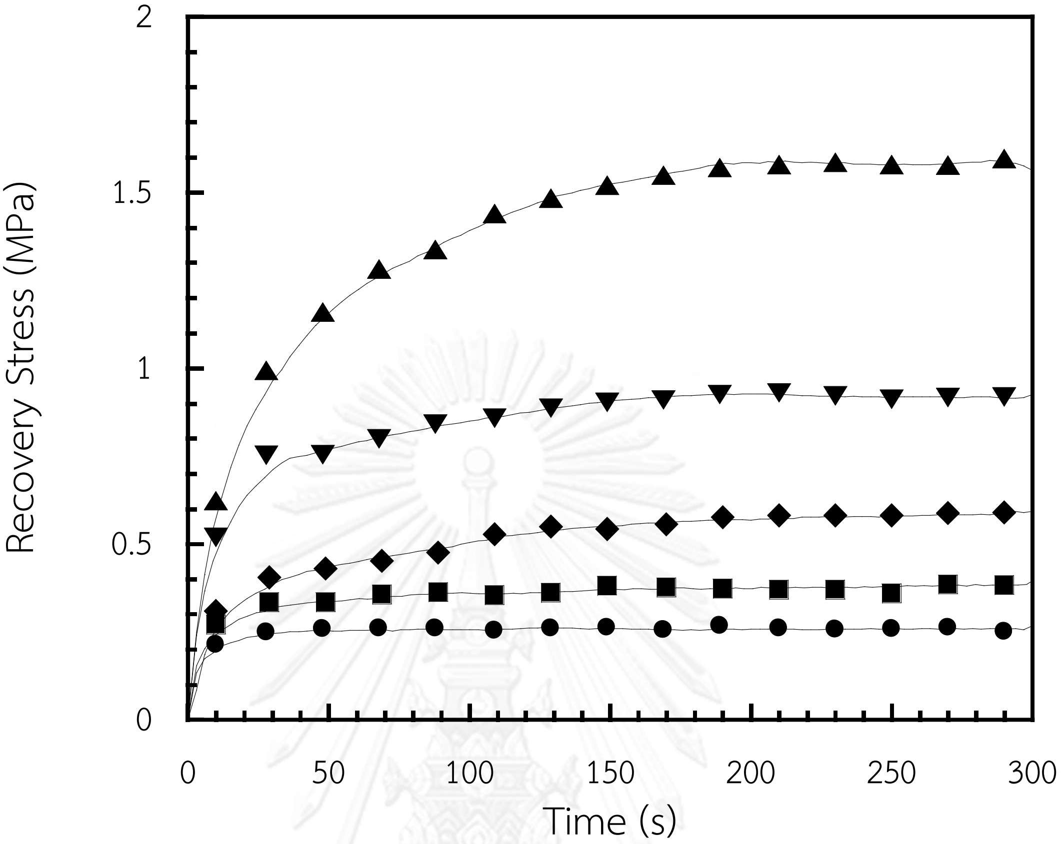


Figure 5.18 Recovery stress versus time of aliphatic epoxy/benzoxazine SMPs at various mole percents of the BA-a: (●) 30 mol%, (■) 35 mol%, (◆) 40 mol%, (▼) 45 mol% and (▲) 50 mol%.

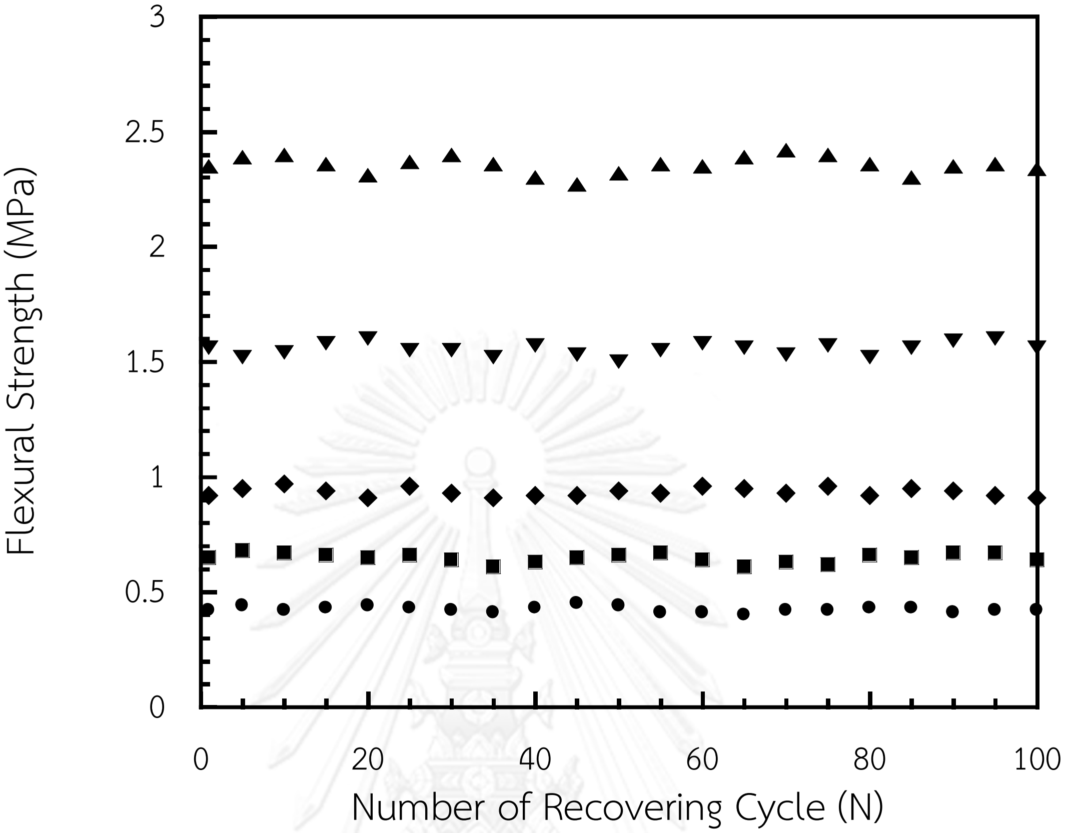


Figure 5.19 Flexural strength versus number of recovery cycles from consecutive shape memory cycle of the aliphatic epoxy/benzoxazine SMP samples at various mole percents of the BA-a: (●) 30 mol%, (■) 35 mol%, (◆) 40 mol%, (▼) 45 mol% and (▲) 50 mol%.

CHAPTER VI

CONCLUSIONS

The binary system of Polybenzoxazine alloying with aliphatic epoxy based shape memory polymer (SMP) was developed to be used in a wider range of shape memory application. In this thesis, effect of BA-a content ranging from 30-50 mol% in aliphatic epoxy based SMP on thermal stability, mechanical properties and shape memory properties were characterized.

In DSC experiment, a heat treatment at 130 °C for 12 hours, 140 °C for 4 hours, 150 °C for 4 hours and 160 °C for 2 hours was chosen as optimum curing condition of all aliphatic epoxy/benzoxazine SMP. FTIR experiment revealed the network formation of PBA-a and the ether link between aliphatic epoxy and PBA-a, after thermal curing program. An incorporation of the BA-a resin in the aliphatic epoxy based SMP resulted in an increase of glass transition temperature with increasing BA-a mole percent in the alloys. Additionally, storage modulus, crosslink density and recovery stress of aliphatic epoxy/benzoxazine SMPs were found to increase with the increasing amount of the benzoxazine resin in the alloys. The same trend was also observed in their flexural strength and flexural modulus at room temperature and rubbery state.

For shape memory properties, the obtained SMPs provided an outstanding shape fixity value up to 99% at room temperature. At different active temperatures i.e. T_g and T_g+20 °C, all samples needed only 1-3 minutes to fully recover to their permanent shape. Furthermore, the addition of the BA-a fraction was able to prolong the shape recovery time of the resulting shape memory polymers. Moreover, after reformed to temporary shape up to 100 cycles, all of the SMP samples fully recovered to their permanent shape with slightly change on their flexural strength. From those results, the obtained aliphatic epoxy/benzoxazine SMPs are attractive as a good candidate for shape memory materials to be used in a broad range of applications such as hinge or deployable structure.

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APPENDIX

APPENDIX

Characterization of Aliphatic Epoxy/Benzoxazine SMP Samples

Appendix A Glass transition temperature of aliphatic epoxy/benzoxazine SMP samples at various mole percents of BA-a from loss tangent of DMA analysis.

Sample	T_g from loss tangent (°C)
BA-a 30 mol%	51
BA-a 35 mol%	70
BA-a 40 mol%	88
BA-a 45 mol%	121
BA-a 50 mol%	140

Appendix B Storage modulus and rubbery plateau modulus of aliphatic epoxy/benzoxazine SMP samples at various mole percents of BA-a.

Sample	Storage modulus (E') at 35 °C (GPa)	Rubbery Plateau Modulus at T_g+50 °C (MPa)
BA-a 30 mol%	2.82	39.04
BA-a 35 mol%	3.73	49.05
BA-a 40 mol%	3.85	80.76
BA-a 45 mol%	4.23	120.58
BA-a 50 mol%	4.50	171.97

Appendix C Flexural strength and flexural modulus of aliphatic epoxy/benzoxazine SMP samples at various mole percents of BA-a at room temperature and T_g+20 °C.

Sample	At glassy state (room temperature)		At rubbery state (T_g+20 °C)	
	Flexural strength (MPa)	Flexural modulus (GPa)	Flexural strength (GPa)	Flexural modulus (MPa)
BA-a 30 mol%	52.12±3.78	1.65±0.23	0.40±0.05	2.47±0.10
BA-a 35 mol%	77.84±2.44	2.36±0.20	0.61±0.05	3.53±0.31
BA-a 40 mol%	108.14±3.56	3.39±0.11	0.95±0.08	7.23±0.38
BA-a 45 mol%	124.01±3.14	3.86±0.08	1.45±0.04	8.49±0.39
BA-a 50 mol%	131.72±3.51	3.97±0.17	2.30±0.08	10.39±0.57

Appendix D Shape fixity of aliphatic epoxy/benzoxazine SMP samples at various mole percents of BA-a at different fixing temperature.

Sample	Tg-10 °C	Tg-20 °C	Room temperature
BA-a 30 mol%	84.5±0.12	97.4±0.11	99.3±0.15
BA-a 35 mol%	84.1±0.11	97.3±0.10	99.1±0.10
BA-a 40 mol%	83.7±0.14	97.0±0.12	98.8±0.15
BA-a 45 mol%	83.4±0.15	96.8±0.15	98.5±0.12
BA-a 50 mol%	83.1±0.16	96.5±0.27	98.1±0.20

VITA

Mr. Thachanat Tanpitaksit was born in Chonburi, Thailand on September 30, 1988. He graduated at high school level from Princess Chulabhorn's College Chonburi, Thailand in 2006. In 2010, he received Bachelor's Degree in Chemical Engineering from the Faculty of Engineering, Srinakharinwirot University, Thailand. After graduation, he continued his study for a Master's Degree in Chemical Engineering at the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University Bangkok, Thailand.

Based on this study, he had given an oral presentation at the Pure and Applied Chemical International Conference (PACCON 2014). This conference was held during 8-10 January, 2014 at the Centara Hotel, Khon Kaen, Thailand. Moreover, he had also participated in Asian Polymer Association International Conference on Polymer: Vision & Innovations (APA 2014) and given an oral presentation based on this shape memory polymer research. This conference was held during 19-21 February, 2014 at India Habitat Centre, New Delhi, India.