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CHARACTERIZATION OF MULTIPLE-SHAPE MEMORY POLYMER FROM BENZOXAZINE-
URETHANE COPOLYMERS

Mr. Peerawat Prathumrat



A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering

Department of Chemical Engineering

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Multiple-shape memory polymers (multiple-SMPs) are highly class of smart materials that can memorize more than one temporary shape and can be recovered to their original shape in a single deformation cycle upon external stimuli such as heat. In this research, novel series of multiple-SMPs were prepared from urethane prepolymer (which acts as reversible switching unit) and benzoxazine resin (BA-a) (which also acts as net-point networks). The BA-a mass fraction in BA-a:PU multiple SMPs was in the range of 55% to 80% . The multiple-SMPs properties including shape fixity and shape recovery were investigated by universal testing machine (UTM) in three-points bending mode. The results revealed that BA-a:PU multiple-SMPs showed excellent shape fixity values of 70-96% for first temporary shape and 83-99% for second temporary shape. In terms of shape recovery, the multiple-SMPs also provided outstanding values of 88-96% for first temporary shape and 97-99% for original shape by increasing the amount of BA-a resin from 55% to 80% of BA-a mass content. In addition, the flexural strength and flexural modulus were also characterized by UTM. The results showed the increase of both flexural strength and flexural modulus with increasing of BA-a mass fraction. However, these values were decreased with increasing of temperature from room temperature to $T_g - 10^\circ\text{C}$ and $T_g + 10^\circ\text{C}$, respectively. The glass transition temperature was systematically increased with the increase in BA-a content; it was reported to be in the range of 130°C to 180°C . Interestingly, the glass transition temperatures for each composition of BA-a/PU were in a board range (ca. 100°C). Furthermore, all BA-a/PU samples could be greatly recovered to the original shape for 5 cycles.

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CHAPTER I

INTRODUCTION

1.1 General introduction

Shape memory polymers (SMPs) are known as smart polymer materials changing their shapes upon an external stimulus condition such as temperature [1], electric and magnetic field [2], water [3], solvents [4], and light [5]. They have an ability to memorize the temporary shape and subsequently, recover to the original shape when stimulated [6, 7]. Most of engineering applications are relevant to smart actuators, sensors, medical devices, which play important role in the aerospace and electronics industries [8, 9].

In general, SMPs are formed by two active phases. One is the fixity phase and the other one acts as the switch phase. The fixity phase memorizes the initial shape of the polymer while the switch phase allows fixing the temporary shape. In addition, the switch phase has a transition temperature, which enables the recovery of the primary shape. This temperature can be the melt temperature (T_m) or the glass transition temperature (T_g) of the polymer depending on the crystalline or amorphous nature of the switch phase. In typical applications, the SMPs are capable to fix one temporary shape when the SMPs is heated over the T_g . In general, load is applied to the sample at higher temperature than its transition temperature before it is cooled down [8, 10].

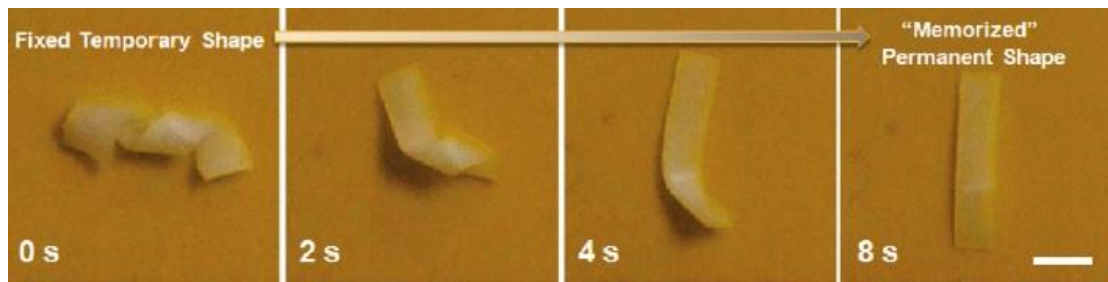


Figure 1.1 Photographs of Sylgard/PCL composite showing the recovery from a fixed temporary shape to its “memorized” permanent shape on a temperature-controlled plate at 80 °C (the scale bar represents 5 mm) [6].

Current research efforts have attempted to increase the number of temporary shapes that a SMP can memorize in a shape memory cycle. The multiple-SMPs are able to fix many temporary shapes related to broad glass transitions in the application temperature range and eventually recovered to initial shape by the closing shape-fixed temperature each. For example, in a previous study, Hoeher *et al.* achieved a tunable multiple-shape memory polyethylene blends, which had broad glass transition temperature ranging from 35 to 150 °C [11]. In order to study the effect of triple-SMPs, the samples were fixed to temporary shapes at temperature levels of 115 and 60 °C and recovered to the initial shape at temperature levels of 48 and 118 °C, respectively. In terms of multiple-SMPs or quadruple-SMPs, the samples were fixed at 122, 78, and 42 °C and recovered at the same trigger temperature each. Therefore, the broad glass transition temperature was an important factor in the study of multiple-SMPs behaviors. Applications of the multiple-SMPs could have potential to be used as raw materials for different applications including intelligent fasteners and removable stents [12].

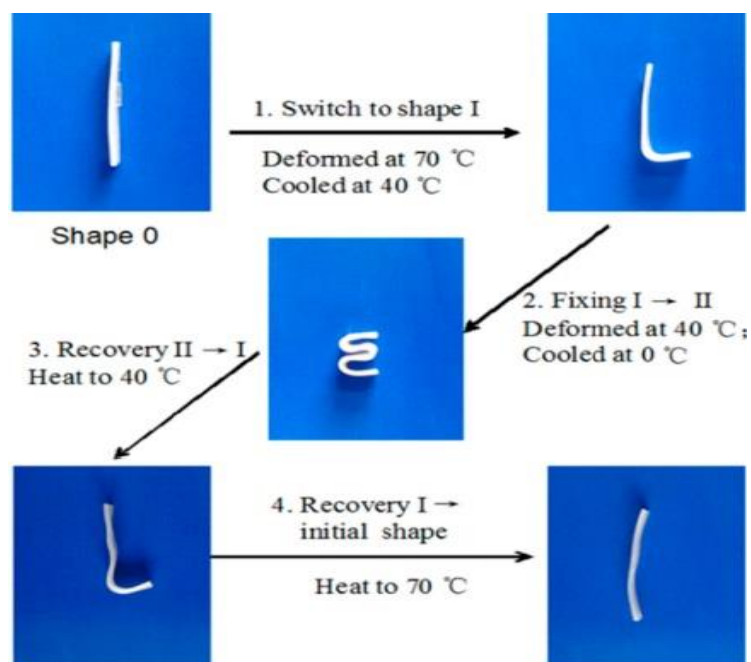


Figure 1.2 Qualitative process of triple shape memory polyurethane fixing and recover [13].

In the recent study of Wang *et al.*, shape memory polyurethane as shown in figure 1.2 was heated to 70 °C, all segments have a good motion performance. When the polymer was cooled to 40 °C, the hard segment with the crosslinking network would be slowly frozen, whereas the PCL-diols chains were still motived, corresponding to the stage that the initial shape was fixed to the shape I. The crosslinking structure acts as the reversible phase, and the rest of hard segments of shape-memory polyurethanes (SMPUs) act as the fixed phase. When the polymer was cooled to 0 °C the shape I was fixed to the shape II. In the shape recovery process, the polymer has the same role as the shape-fixed process [13]. In addition, Gu and Jana have studied SMPUs appeal particular interest because of their biodegradability, inexpensive raw materials, and high potential for commercialization. SMPUs have

certain disadvantages such as slow recovery rate, low values of shape fixity. Therefore, the optimization of SMPUs with the introduction of nano-fillers such as carbon nanotubes, organic components, and silicon carbide would enhance their overall utilization with higher effectiveness. This study investigated polymeric chemical additive polybenzoxazine (PBA-a) for improve properties of SMPs properties. It was predicted that PBA-a would deliver physical interactions via hydrogen bonds, form covalent bonds with PU chains [14]. While, Erden and Jana studied SMPs between benzoxazine resins (BA-a) and SMPUs, they reported that both recovery stress (RS) and shape recovery (SR) increased with the addition of BA-a. A specimen at 17 wt% BA-a produced the highest values of RS and SR with 13 MPa and 93%, respectively in comparison to RS of 6.8 MPa and SR of 72% for polyurethane. The researchers suggested that BA-a could be either chemically bonded with SMPU chains by copolymerization or grafting reactions or blended with SMPU as a separation phase. In addition, PBA-a can act as an additional hard phase for SMPU due to its higher glass transition temperature and much higher storage modulus than the soft phase of SMPU [15].

Polybenzoxazine (PBA-a) is a thermosetting polymer which has excellent properties such as high glass transition temperature, high thermal stability, easy processability, creating no by-product, and almost near zero shrinkage. Benzoxazine resins (BA-a) can be synthesized by a solventless method from bisphenol A, paraformaldehyde, and aniline [16]. Moreover, PBA-a can be polymerized by thermal-induced ring opening polymerization by cationic bond dividing at high temperature without using any catalyst or curing agent. In the system of benzoxazine-urethane alloy, it could be noted that the addition of PBA-a could broaden the observed glass

transition of the resulting alloys at varied urethane contents [14, 16]. In the recent study of our research group, similar behaviors of the transition temperature have also been observed in the SMPs of BA-a-modified epoxy with lower extent of BA-a [17, 18].

Consequently, the purpose of this research is to investigate feasibility of benzoxazine-urethane copolymers as multiple-shape memory polymers and major characteristics of multiple-shape memory polymers from benzoxazine-urethane copolymers such as shape fixity, shape recovery, thermal and mechanical properties.

1.2 OBJECTIVES

1. To investigate feasibility of benzoxazine-urethane copolymers as multiple-shape memory polymers.
2. To examine major characteristics of multiple-shape memory polymers from benzoxazine-urethane copolymers such as shape fixity, shape recovery, thermal and mechanical properties.

1.3 SCOPES OF THE STUDY

1. Synthesis of BA-a typed benzoxazine resin by solventless synthesis technology.
2. Synthesis of urethane prepolymer by diol and toluene diisocyanate (TDI).
3. Determination of the optimum composition of benzoxazine-urethane copolymers on multiple-shape memory characteristics with varied 10-50% by weight of urethane prepolymer content.
4. Properties evaluation of benzoxazine-urethane as follows.

4.1 Thermal properties

- Curing behaviors and glass transition temperature (Differential scanning calorimeter and Dynamic mechanical analyzer)
- Thermal degradation temperature and thermal stability (Thermogravimetric analyzer)

4.2 Mechanical properties

- Dynamic mechanical properties (Dynamic mechanical analyzer)
- Flexural properties (Universal testing machine)

4.3 Shape memory properties

- Multiple-shape fixity ratio
- Multiple-shape recovery ratio
- Deformation temperature
- Cycle of multiple-shape memory ratio

1.4 PROCEDURES OF THE STUDY

1. Reviewing related literature.
2. Preparation of chemicals and equipment for using in this research.
3. Synthesis of benzoxazine resins (BA-a) and urethane prepolymers.
4. Preparation of poly(benzoxazine-urethane).
5. Determination of thermal, mechanical and multiple-shape memory properties of poly(benzoxazine-urethane) as follows:
 - Transition temperature
 - Degradation temperature
 - Flexural strength and flexural modulus
 - Multiple-shape fixity ratio

- Multiple-shape recovery ratio
 - Cycle of multiple-shape memory ratio
6. Analysis of the experimental results.
 7. Preparation of the final report.



CHAPTER II

THEORY

2.1 Shape memory polymers (SMPs)

Shape memory polymers (SMPs) represent a specific class of the smart materials which can fix the temporary shape and recover to their original configuration depend on external stimulus such as temperature, electric and magnetic field, light, humidity, water contact, and organic solvent [7, 8] as illustrated in Figure 2.1. In general, SMPs have some unique properties, first of all they are biodegradable, as well as they can be soft to hard. Their further physical properties could change from rigid to elastic depending on being thermoplastic and thermosetting (covalently cross-linked) polymeric materials. The SMPs can also store up to three different shapes in memory. SMPs are widely used in several applications such as cable, packaging industry, medicine, and automotive [12]. One of major disadvantages of SMP devices is their missing reversibility of the shape change which should be corrected by the user [19].

2.1.1 Class of shape memory polymers

The following sections will provide a detailed overview on the engineering properties of different classes of SMPs namely the two thermal transitions of a distinct block/component of the SMPs and the melting temperature as well as the glass transition temperature. The melting transition can be applied in chemical-crosslinked rubbers, in semicrystalline polymer networks as well as in physical-crosslinked polymers. Similarly, the glass transition temperature can be applied in chemical-crosslinked thermosets and physical-crosslinked thermoplastics [19]. The viscoelastic

property of SMPs is an important factor that enables the polymer network recovery to the original shape due to of different physical and chemical stimulus [20].

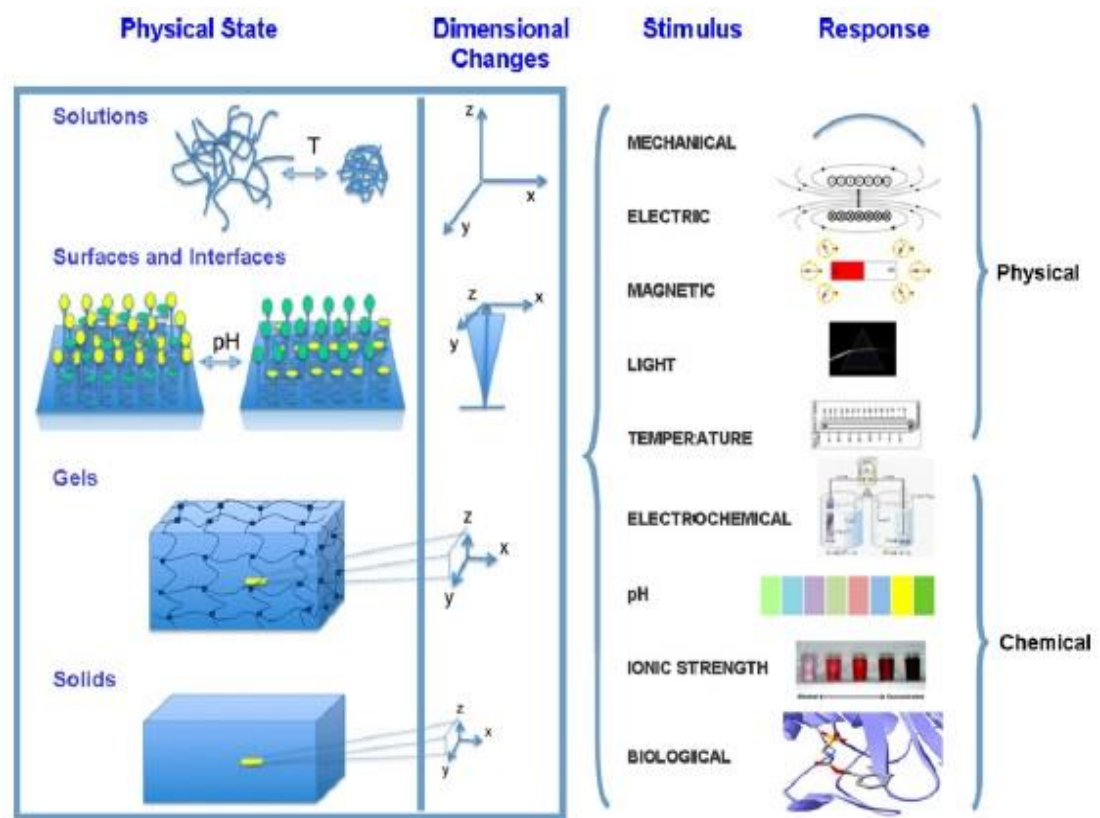


Figure 2.1 Schematic representations of dimensional changes in polymeric solutions, at surfaces and interfaces, in polymeric gels, and polymer solids resulting from physical or chemical stimuli [21].

2.1.1.1 Shape memory polymers based on a melting transition

One potential of the fixation of the second phase SMPs is their crystallization. The melting of this phase will lead to the shape recovery of the SMPs. Often based on crosslinked semicrystalline networks or (multi)block copolymer systems have higher stiffness than those of other SMP materials [22]. Most of the studied materials of T_m -type SMPs are based on polyesters, polyethers, or polyolefins such as polyethylene.

All these soft phases present a low melting temperature, which will still have the existence of a crystalline hard phase with increasing the switching temperature. Attractively, a similar behavior of SMP could be observed in an ethylene-1-octene copolymer (EOC) which shows the short chain branches, for example, Hoehner *et al.* observed the switching temperature of the crosslinked polyethylene blends such as EOC, LDPE, and HDPE found that the switching temperature ranging from 35 to 150 °C depending on the degree of branching as well as the crosslinking density [11, 17].

2.1.1.2 Shape memory polymers based on a glass transition

Polymeric materials with a glass transition temperature (T_g) above room temperature can be classified for T_g -based SMPs. Within this context a large variety of different materials have been investigated. In comparison to the T_m -based SMPs, the T_g -based SMPs reveal a slower shape recovery due to the broad glass transition [19]. Accordingly, these SMPs are not appropriate for immediate shape recovery but the slow recovery gets attention for biomedical applications [23]. PUs are composed of a soft block with a glass transition instead of a semicrystalline soft block can also feature a shape memory effect (SME). In contrast to the T_m -based shape memory PUs, these systems are obvious and are more trends to biodegradation due to the missing crystallinity of the switch segment.

2.1.2 Parameters for characterization of SMPs [24]

To characterize the properties of shape memory polymers, a group of parameters is needed. First, the parameters should be able to indicate the nature of polymers. Second, to discriminate them from other materials properties, shape memory properties are shown through a series of thermo-mechanical cyclic processes. Therefore the parameters should be able to define the whole shape memory

processes as well. At last, the design of the parameters should consider the potential applications. The parameters are introduced in the following [24].

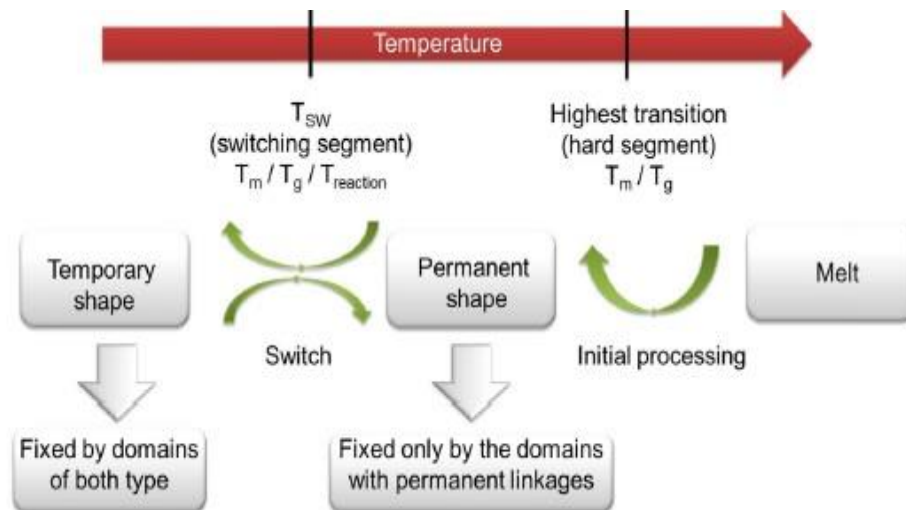


Figure 2.2 Schematic representation of the basic principle of the shape memory effect in polymers [19].

2.1.2.1 Shape fixity (R_f)

The parameter which described when a shape memory polymer is heated to a temperature above the transition temperature for triggering shape memory behaviors (T_g), it can develop large deformations which can be mostly fixed by cooling to a temperature below T_g . This parameter was proposed to describe the extent of a temporary shape being fixed in one cycle of shape memorization. Shape fixity is equal to the amplitude ratio of the fixed deformation to the total deformation, 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.

2.1.2.2 Shape recovery (R_r)

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

2.1.2.3 Recovery stress

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

The dilemma for the characterization of recovery stress of SMPs is chiefly caused by viscoelasticity of polymers, especially for the thermoplastic SMPs. Owing to the limitations of equipment and efficiency of heat transfer, it is practically impossible to heat or cool an SMP to a certain temperature in a sufficiently short time in experiments. Therefore the stress relaxation is inevitable by all means if only the SMP is in a constrained state. As a consequent, the stress generated in deformation must be lost more or less in the shape fixing and shape recovery processes. Additionally, the rate of stress relaxation alters with the temperature change in the whole shape

memory process, which means that its influence on the recovery stress is unknown. In the other words, the recovery stress may change all the time with the stress relaxation, but the exact nature of the change is uncertain. Therefore it is difficult to calculate the recovery stress in quantitative terms.

2.1.2.4 Recovery rate

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

2.2 Multiple-shape memory polymers (Multiple -SMPs)

Multiple -SMPs such triple-SMPs feature two temporary states (A and A') as well as the permanent shape. The sample will change from shape A' to shape A induced by one trigger, whereas a second trigger induces the change back to the permanent shape. The concept can also be expanded to multiple shapes. There are two foremost procedures for the design of triple SMPs: (a) a very broad thermal transition, especially a glass transition temperature and (b) multiphase design that each phase provides a separate transition, which is responsible for one part of the SME [19]. Especially, the latter strategy is rather complicated due to the required complex design of the new polymeric material. However, a better operate over the SME and the imposed switching temperature is possible. Since the former strategy requires a broad glass transition temperature also commercial polymers have been investigated in this context [19]. The broad thermal transition factor to the tunable multi-SME has also

been found responsible for the so-called temperature memory effect, which refers to the capability of an SMP system to memorize a temperature [25]. Moreover, the triple or quadruple-SMP is based on a broad glass transition temperature.

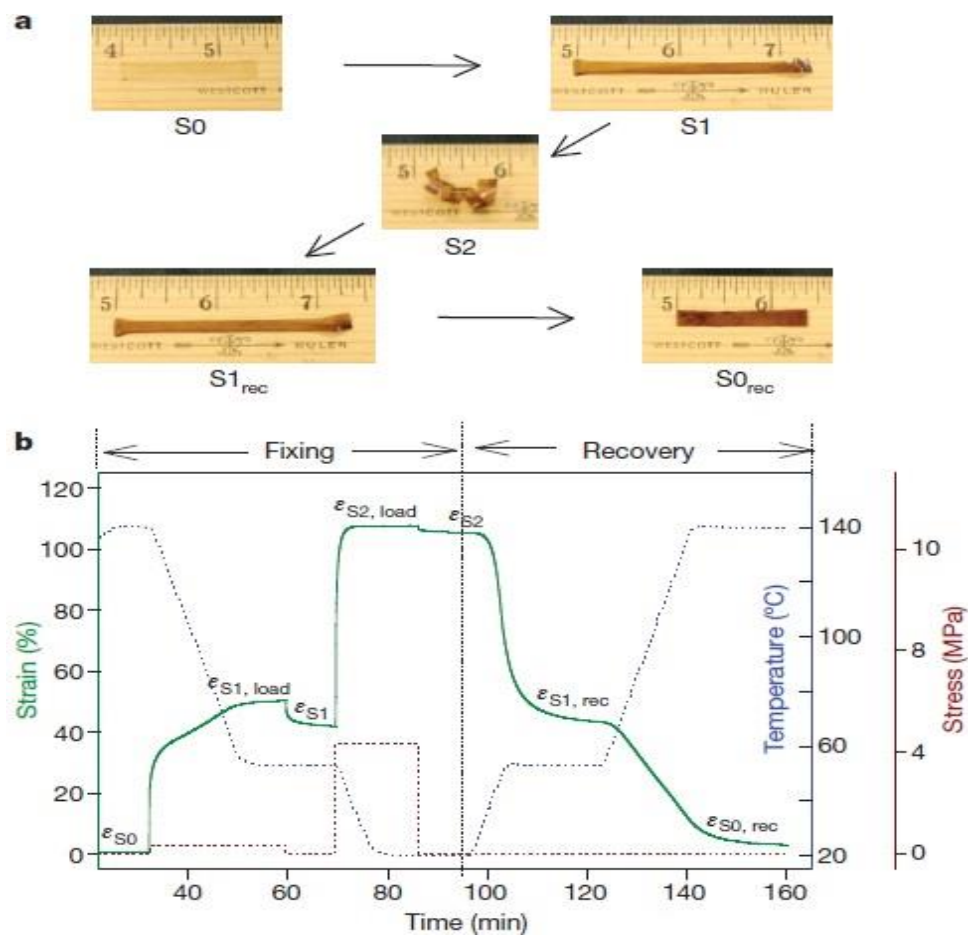


Figure 2.3 Triple-shape memory properties of PFSA. (a), Visual demonstration. (b), Quantitative thermal mechanical cycle ($T_{d1}=T_{r2}=140\text{ }^{\circ}\text{C}$, $T_{d2}=T_{r1}=53\text{ }^{\circ}\text{C}$) [26].

In previous study, the examinations of triple-SMPs, Xie *et al.* used the broad glass transition of T_g -type polymers to describe multiple SMEs [26], which can remember more than one temporary shape. The triple SMEs have been successfully created through only one broad glass transition (from ~ 55 to $\sim 130\text{ }^{\circ}\text{C}$) of commercial perfluorosulphonic acid ionomer (PFSA). The triple-shape memory effect for PFSA is

demonstrated in Figure 2.3(a). The permanent shape S_0 was deformed at 140 °C and fixed at 68 °C to yield the first temporary shape S_1 , which was further deformed at 68 °C and fixed at 20 °C to yield the second temporary shape S_2 . Upon reheating to 68 °C, the recovered first temporary shape S_{1rec} was obtained. Further heating to 140 °C yielded the recovered permanent shape S_{0rec} . Quantitatively, two triple-shape memory cycles are illustrated in Figure 2.3(b) (with two deformation temperatures of 140 °C and 53 °C) [26].

2.3 Benzoxazine resin

Benzoxazine is a phenolic resin is one of new thermosetting plastics that synthesized can be prepared by using solventless synthesis technology from bisphenol A, aniline, and paraformaldehyde at a 1 : 2 : 4 molar ratio [16]. The curing process of a benzoxazine resin into a polybenzoxazine occurs via a ring-opening polymerization by thermal cure without catalyst agent and does not produce byproducts during cure which results in no void in the products [27].

The polybenzoxazine offers many advantages, i.e. a variety of reactants can be used to design desired molecular structures. Furthermore, thermal polymerization is easy to carry out and is not dependent on the use of a strong acidic or basic catalyst. In addition, processing is easier compared to traditional resins because of low viscosity. Moreover, benzoxazine polymerization does not produce any by product. 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.

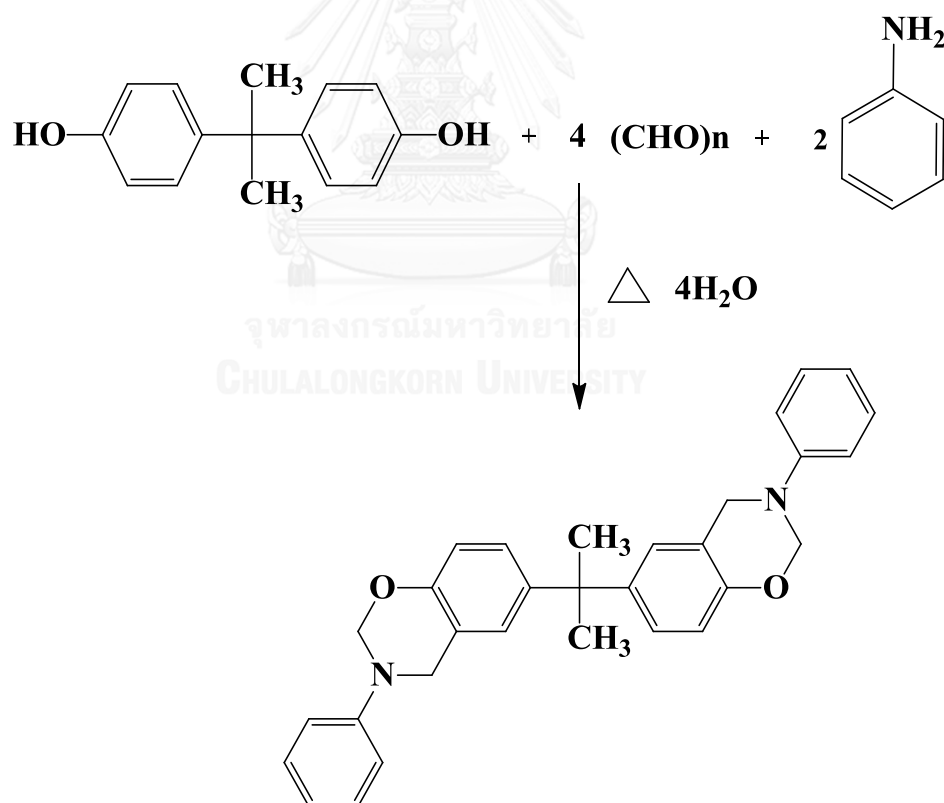


Figure 2.4 Synthesis of BA-a benzoxazine monomer.

2.3.1 The materials for the synthesis of bifunctional benzoxazine monomer based on bisphenol A.

2.3.1.1 Bisphenol A

Bisphenol A is produced by reacting phenol with acetone in the presence of an acid catalyst (shown in Figure 2.5). Common catalysts are aqueous acids or acid clays. Promoters such as thioglycolic acid and resorcinol are also used [28].

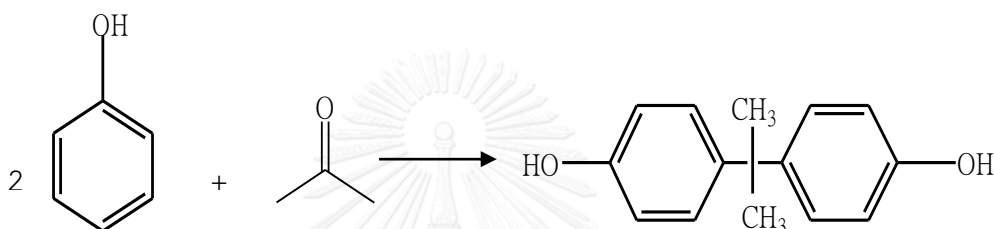
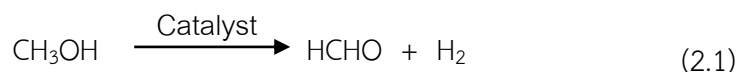


Figure 2.5 Synthesis of bisphenol A.

2.3.1.2 Formaldehyde

Formaldehyde is an unstable colorless gas, which is commercially supplied in 37% aqueous solution, as a solid cyclic trimer (trioxan), and as a solid polymer (paraformaldehyde) which is used in this work. Almost all formaldehyde produced is derived from methanol either by oxidative dehydrogenation using silver or copper catalyst (see Equation 2.1), or by oxidation in the presence of Fe₂O₃ and MoO₃ (see Equation 2.2) [28].



In the oxidative dehydrogenation, the generated hydrogen is oxidized to water upon addition of air.



2.3.1.3 Aniline

The classical method of synthesis of aniline is the reduction of nitrobenzene with hydrogen in the vapor phase using a copper/silica catalyst (shown in Figure 2.6). Nitrobenzene is produced in the nitration of benzene using a mixture of nitric acid and sulfuric acid [28].

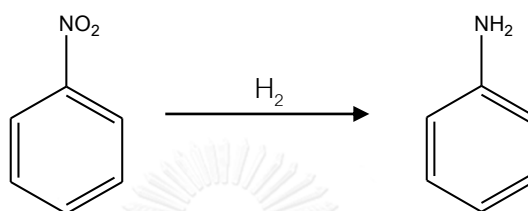


Figure 2.6 Synthesis of aniline by nitrobenzene.

Recently Aristech Chemical completed a 90,000-ton aniline plant using plant using phenol as the feedstock. This technology was developed by Halcon; it is also used by Mitsui Toatsu in Japan. The amination of phenol is conducted in the vapor phase using an alumina catalyst, and yields are very high.

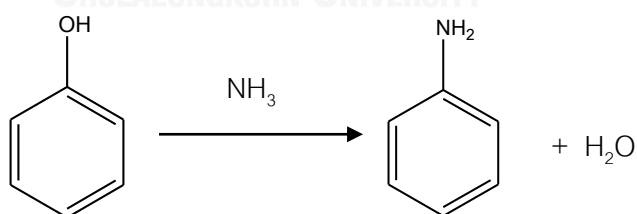


Figure 2.7 Synthesis of aniline by phenol.

2.4 Polyurethane

Polyurethanes (PUs) are a very large and varied family of incredibly versatile and useful engineering materials with a vast spectrum of physical, chemical, and mechanical properties. During the past years, the chemistry of PUs and related

intermediates has been exploited to develop many products in the form of coatings, adhesives, foams, and elastomers [29]. Polyurethanes can be either thermoplastics or thermosets.

A polyol (which means multiple alcohols or multiple OH groups) can have from two to many OH groups. Just as with a stepwise polymerization reaction, the polyol monomer must have at least two reactive groups in order to polymerize. If three or more reactive groups are present, crosslinks can form. The other monomer in the reaction to form a urethane bond is an isocyanate which is the NCO combination of atoms. The types of chemical compounds that have two isocyanate groups are called diisocyanates. When a polyol reacts with an isocyanate, a molecular rearrangement occurs that creates a more stable molecular structure. The hydrogen bond is formed from the hydrogen on the polyol with the carbon in the isocyanate. Some previous bonds in the polyol and in the isocyanate break to allow these new bonds to form.

A urethane elastomer can be regarded as a linear block copolymer of the type as shown in Figure 2.8. This segmented polymer structure can affect its properties over a very wide range of strength and stiffness by modification of its three basic building blocks: the polyol, diisocyanate, and chain extender. Essentially, the hardness range covered is that of soft jelly-like structures to hard rigid plastics. Properties are related to segmented flexibility, chain entanglement, interchain forces, and crosslinking.

Shape-memory polyurethane (SMPU) is basically consisted in soft and hard segments; thermodynamic immiscibility between these two segments leads to phase separation, which makes SMPU an outstanding candidate for a shape-memory material. Hard segments, which mean diisocyanate, act as essential points for shape recovery, whereas soft segments refer to polyol, are responsible for absorbing external stress

applied on the SMPU. At temperatures below glass transition temperature (T_g), the soft segments do not have enough kinetic energy to execute good mobility; thus, SMPUs are relatively difficult to be deformed in the glass state. Above T_g , SMPU transforms from a glass state to a rubber state and becomes easily deformed [30].

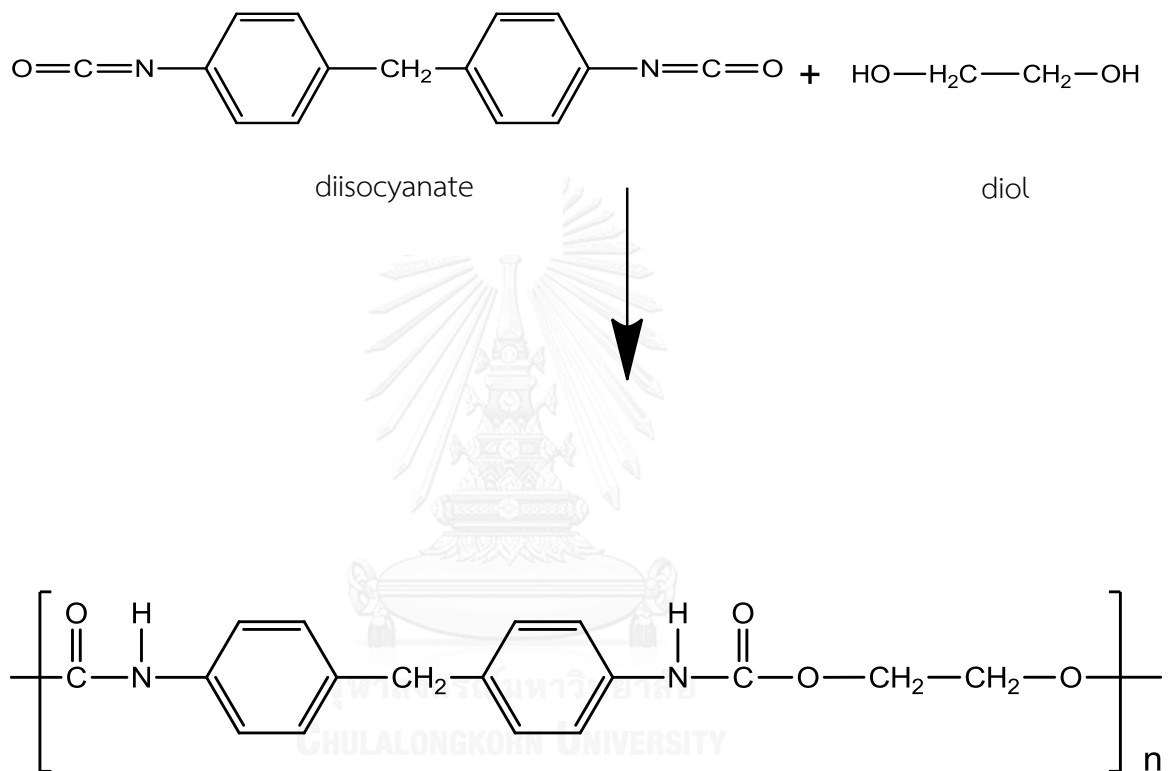


Figure 2.8 The basic units in a urethane block copolymer.

2.4 Network between benzoxazine resin and urethane prepolymer

From previous work, Takeichi studied about synthesis and characterization of poly(urethane-benzoxazine) films [31]. The poly(urethane-benzoxazine) films as novel polyurethane (PU)/phenolic resin composites were prepared by blending a benzoxazine monomer (BA) and TDI-polyethylene adipate polyol (MW 1000) based PU prepolymer. FT-IR spectroscopic technique was used to investigate the reaction between benzoxazine resin and urethane prepolymer. From the experiment, the mechanism of benzoxazine-urethane alloys was reported as the Figure 2.6.

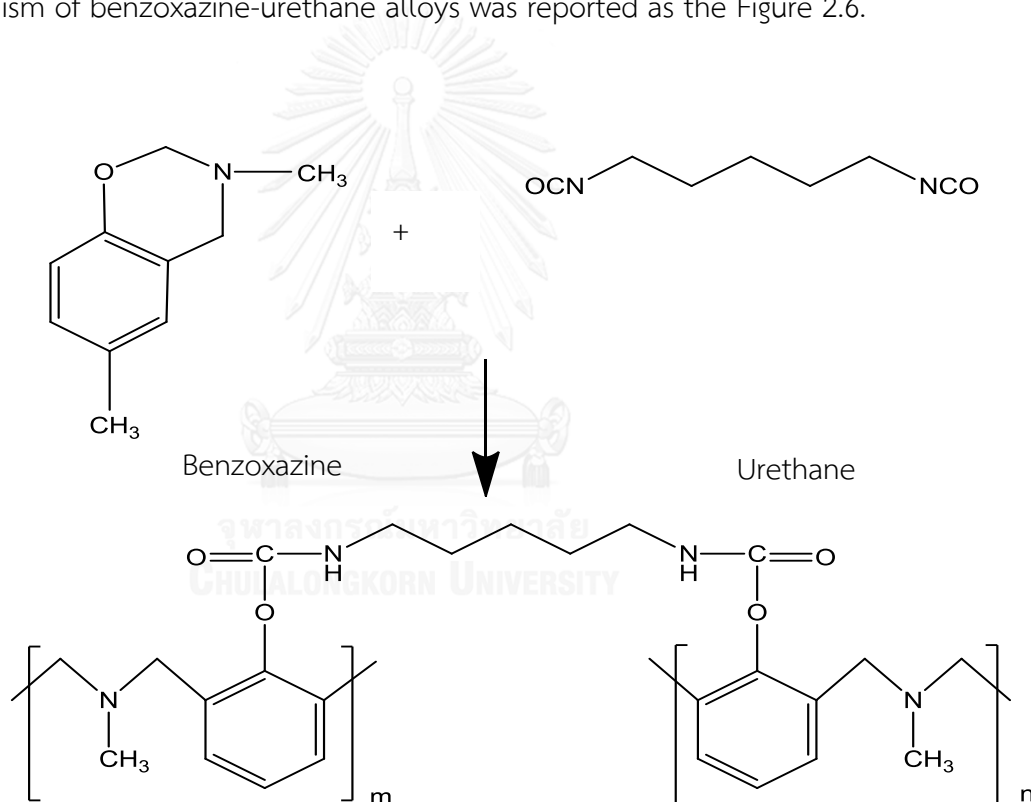


Figure 2.9 The reaction of benzoxazine-urethane alloys

CHAPTER III

LITERATURE REVIEW

Xie (2010) has studied multi-shape memory effect from perfluorosulphonic acid ionomer (PFSA) its possesses a broad glass transition temperature range from 55 to 130 °C shown by $\tan \delta$ curve in Figure 3.1. According to the results, the triple-shape memory effect for PFSA is demonstrated in Figures 3.2-3.3. The permanent shape S0 was deformed at 140 °C and fixed at 68 °C to yield the first temporary shape S1, which was further deformed at 68 °C and fixed at 20 °C to yield the second temporary shape S2. Upon reheating to 68 °C, the recovered first temporary shape S1rec was obtained. Further heating to 140 °C yielded the recovered permanent shape S0rec.

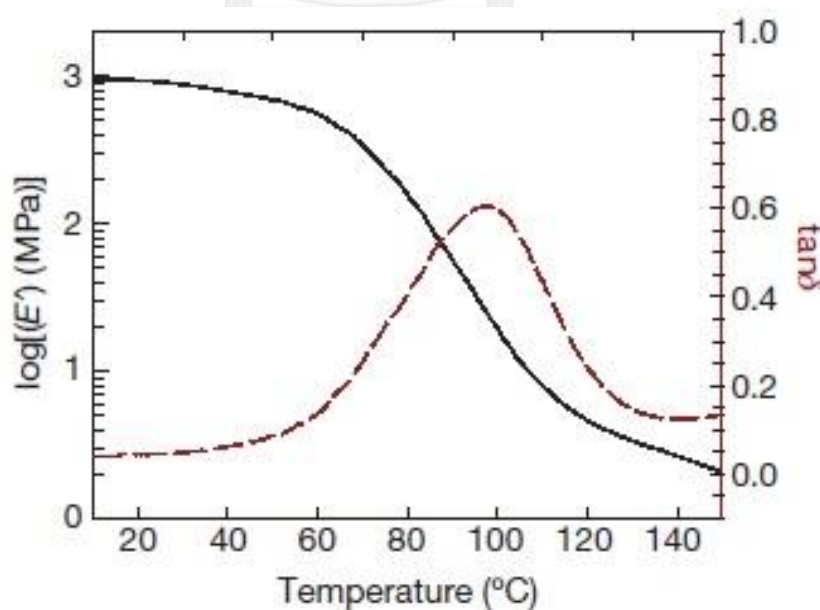


Figure 3.1 Dynamic mechanical analysis curve of PFSA. $\tan \delta$ is the ratio between the loss modulus E'' and the storage modulus E' [26].

In addition, shape recovery ratios are 97.4 and 94.6%, respectively. So it can be said that the multiple-shape memory of PFSA has excellent properties for use in various applications such as chloro-alkali cells, sensors and actuators.

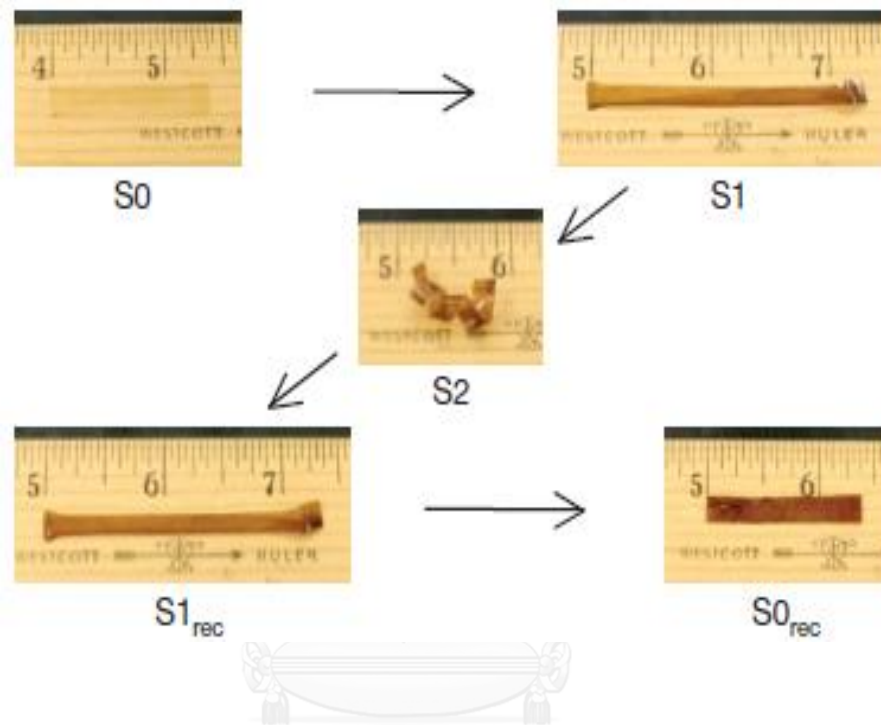


Figure 3.2 The visual demonstrates of triple-shape memory properties of PFSA [26].

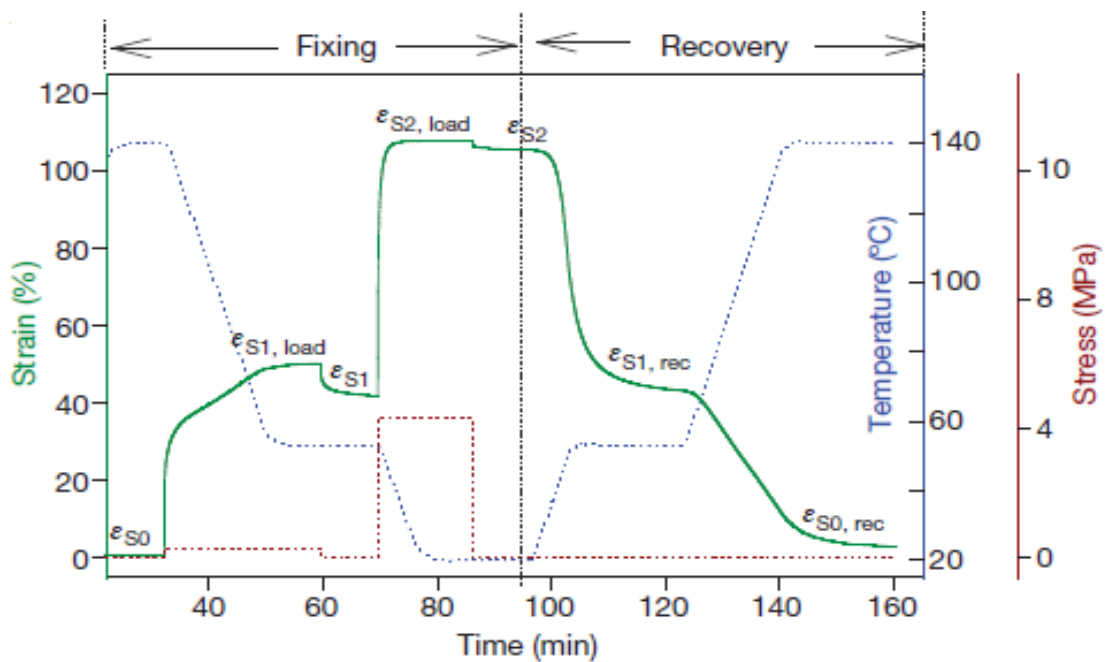


Figure 3.3 Quantitative thermal mechanical cycle ($T_{d1}=T_{r2}=140\text{ }^{\circ}\text{C}$, $T_{d2}=T_{r1}=53\text{ }^{\circ}\text{C}$). $R_r(S0 \rightarrow S1)$: 83.5%, $R_r(S1 \rightarrow S2)$: 96.7%, $R_r(S2 \rightarrow S1)$: 97.4%, $R_r(S1 \rightarrow S0)$: 94.6% [26].

Hoeher *et al.* (2013) have studied tunable multiple-shape memory polymer with high strain storage capacity. Multiple-SMP was synthesized by a lightly cross-linked polyethylene blend comprising 80 wt% ethylene-1-octene copolymers (EOC), 15 wt% Low density polyethylene (LDPE), and 5 wt% High density polyethylene (HDPE). The results are shown a trigger temperature for dual-shape memory effect to fix a temporary shape of 80 $^{\circ}\text{C}$. Furthermore, the programmed material showed an excellent recovery ratio of $R_r = 99.7 \pm 0.3\%$ is shown in Figure 3.4. In addition, the results are shown a broad trigger temperature of triple-shape memory from 35 to 150 $^{\circ}\text{C}$ in Figure 3.6.

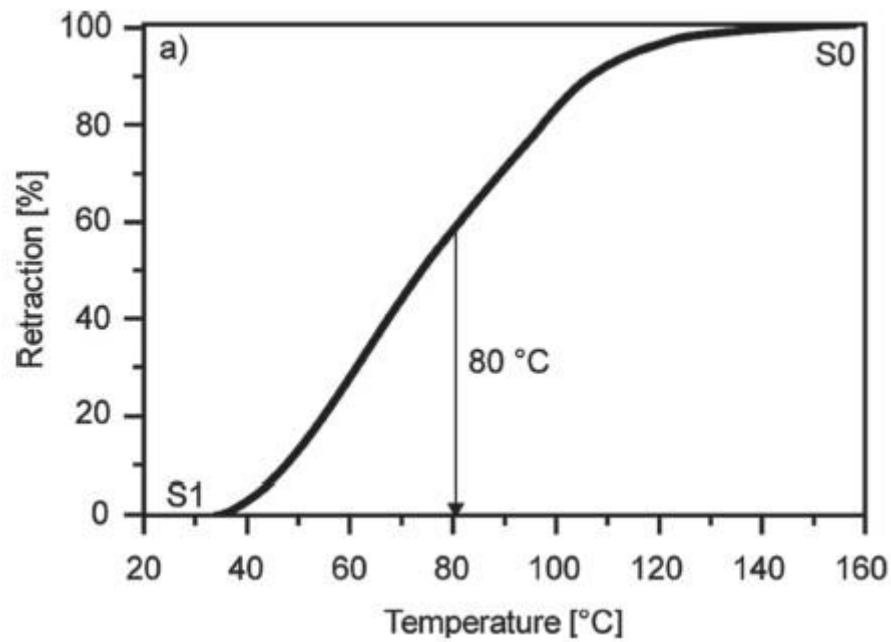


Figure 3.4 Retraction versus temperature diagram of a cross-linked E80/L15/H5 blend programmed to a dual-shape memory [11].

Whereas triggered the triple-shape memory polymer is more complicated than the dual-shape memory polymer. The temperature is fixed the first temporary shape of 115 °C and the sample was stretched of $421 \pm 8\%$. Then fixed to the secondary temporary shape at temperature of 60 °C and the strain of the sample was obtained as $1165 \pm 9\%$ as figure 3.5. For recover to the initial shape, temperatures used for recover are 48 and 118 °C and the recovered strains were $99.7 \pm 0.3\%$ as shown in Figure 3.6.

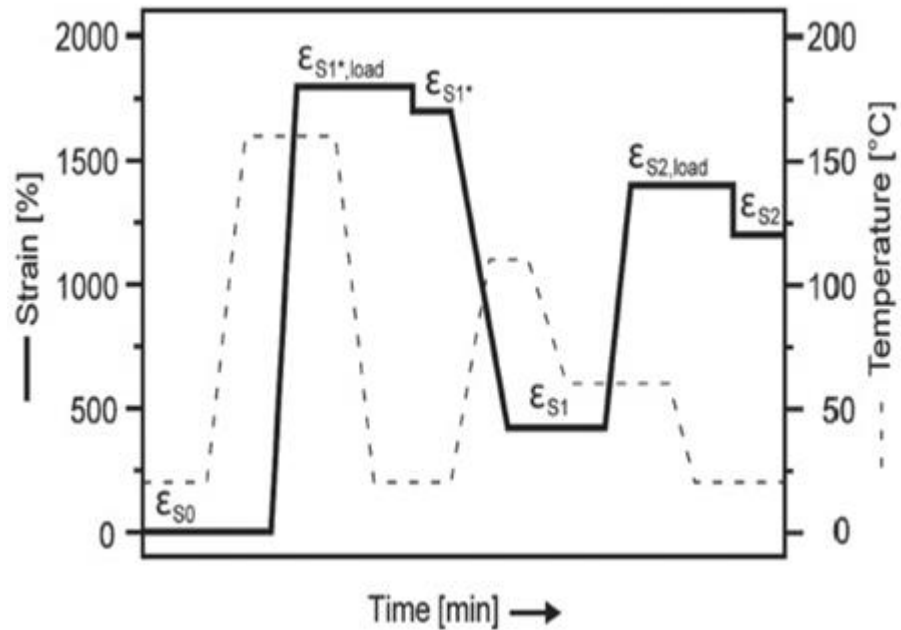


Figure 3.5 Strain/temperature versus time diagram showing programming steps for a triple-shape memory [11].

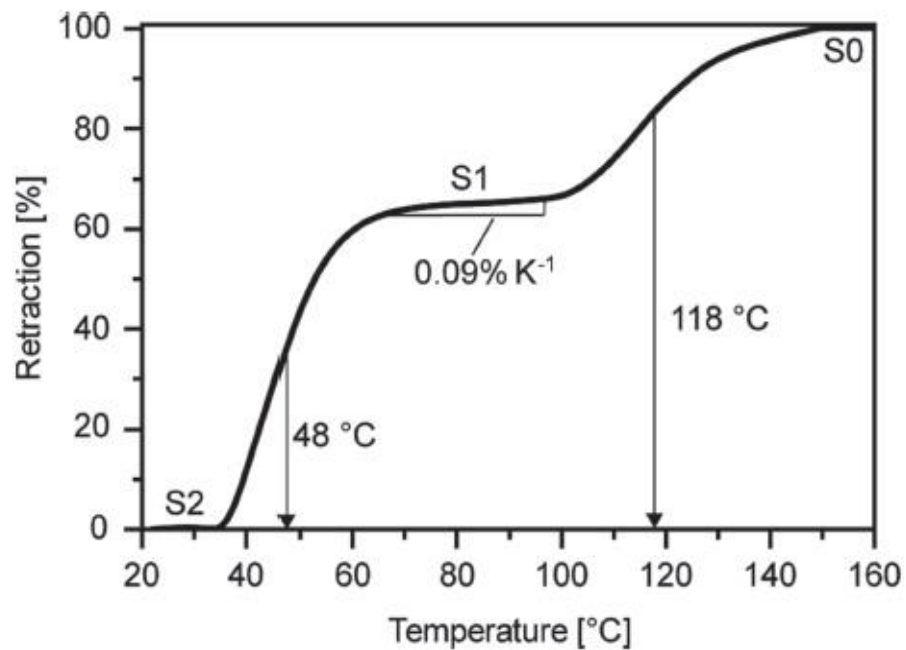


Figure 3.6 Retraction versus temperature diagram of a cross-linked E80/L15/H5 blend programmed to a triple-shape memory [11].

Samuel *et al.* (2014) have investigated miscible PLLA/PMMA blends with broad glass transitions temperature examined as an alternative platform to design multiple-SMPs. In addition, these transitions broadened significantly for miscible blends, and the symmetric 50% PLLA/50% PMMA presented the broadest glass transition temperature with a range of temperatures between approximately 60 and 100 °C as shown in Figure 3.7. Therefore, the use of miscible polymer blends could make a radical change in the design of multiple-SMP systems, and to the best of our knowledge, the use of such melt-blended miscible polymer pairs was only documented for dual-SMP purposes but multiple-SMPs have never been investigated.

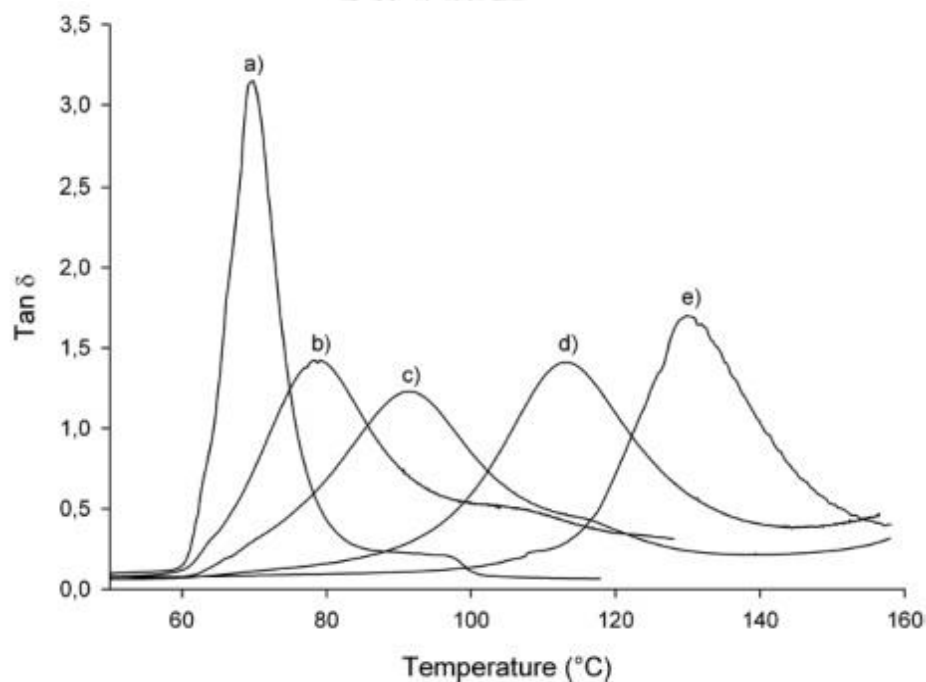


Figure 3.7 Tan δ profiles for 100% PLLA (a), 70% PLLA/30% PMMA (b), 50% PLLA/50% PMMA (c), 20% PLLA/80% PMMA (d), and 100% PMMA (e) thin films [8].

In triple-shape memory experiments, a programming step could be designed for the symmetric blend as shown in figure 3.8 displays a cycle with the two consecutive stretching steps at two temperatures at 94 and 65 °C. A first uniaxial stretching is

performed at 94 °C under a low stress (0.1 MPa), and the material is subsequently cooled to the second stretching temperature of 65 °C under a high stress (2 MPa). Two recovery events with well-defined switch temperatures could be programmed using a double stretching step, and triple-shape memory effects were subsequently attempted with a recovery step performed at staged temperatures of 70 and 94 °C.

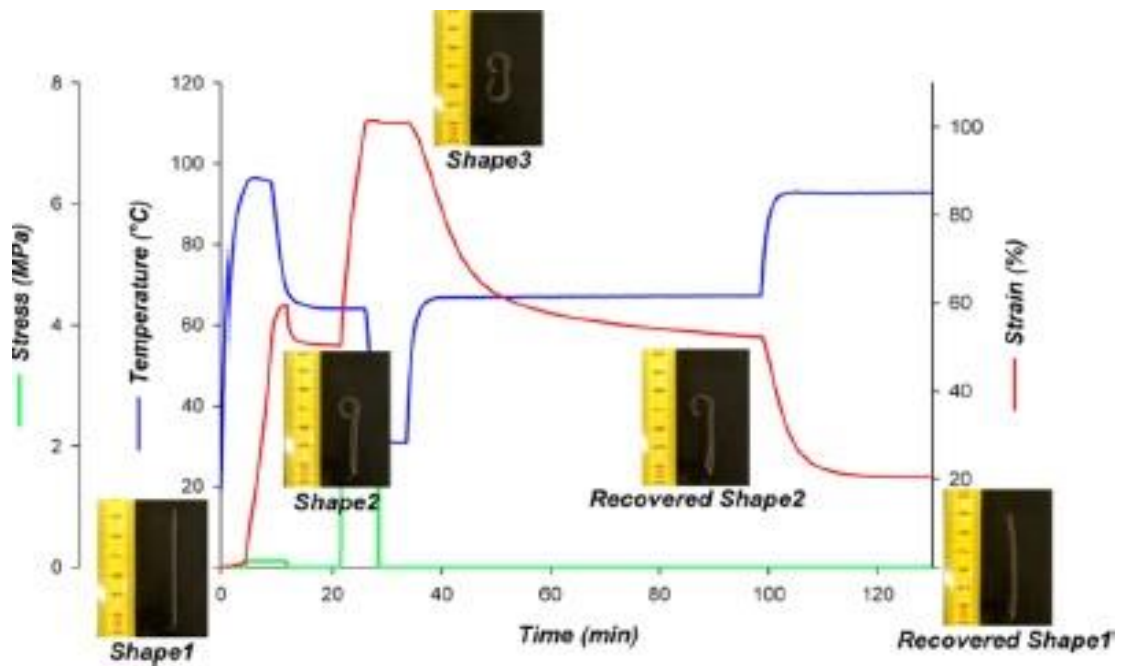


Figure 3.8 Triple-shape memory programming for the symmetric blend with two consecutive uniaxial stretchings at 94 and 65 °C and subsequent triple-shape recoveries at two staged temperatures of 70 and 94 °C [8].

Lee *et al.* (2001) have investigated thermomechanical properties of shape memory polyurethane (PU) block copolymers composed of 4,4'-methylenebis(phenylisocyanate), poly(tetramethylene glycol), and 1,4-butanediol as a chain extender were synthesized by a two-step process. It suggests that hard segments get more aggregated to form domains in the PU block copolymer as hard segment content increases. Such domain formation has a significant influence on the mechanical and

thermomechanical properties of PU, such as maximum stress, tensile modulus, and elongation at break. Especially, maximum stress, tensile modulus, and elongation at break increased significantly at 30 wt% of hard segment content, and the highest loss tangent was observed at the same composition.

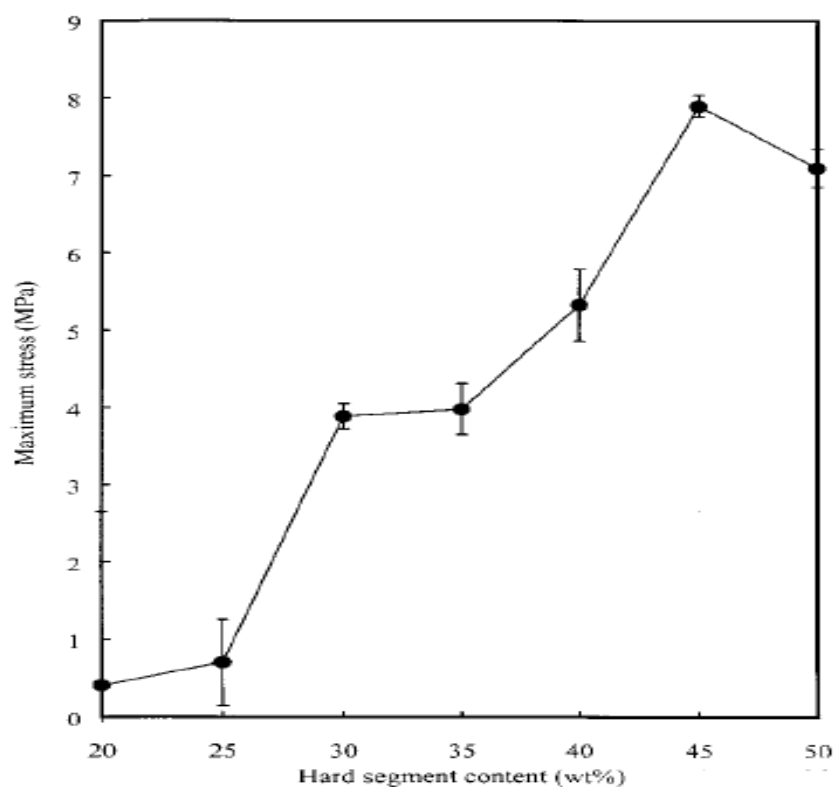


Figure 3.9 Maximum stress of polyurethane block copolymers with various wt% of hard segment (bar indicates 95% confidence limit) [32].

The shape fixity of the PUs with 30, 35, 40, and 45 wt% of hard segment was measured after it was deformed by 50%, kept for 5 min at 20 °C below T_g , and the load was removed. All of the PUs tested show more than 90% of shape retention at each hard segment contents. Shape recovery was measured after the PU was kept for 5 min at 20 °C above T_g with the load removed and ranged from 80 to 95% depending on the hard segments. But shape recovery was not observed at 20, 25, and 50 wt% of

hard segment content. The observation can be concluded that 80-95% of shape recovery was obtained at the 30-45 wt% of hard segment content where PU copolymers can make strong interaction among hard segments enough to restore the polymer back to the original shape.

Table 3. 1 Shape memory properties with various hard segments of polyurethane contents [32]

Hard segment content (%)	Glass transition temperature (°C)	Shape fixity (%)	Shape recovery (%)
30	-3.6	89	82
35	-2.5	90	90
40	-2.4	91	92
45	0.3	92	95

Erden and Jana (2013) examined the properties of polyurethane-polybenzoxazine based shape memory polymers by using DSC, DMA, Universal testing machine (tensile mode) etc. SMP was synthesized from 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 3.2.

The results from DMA are shown in Figure 3.10. It is evident that all three materials exhibited a single peak of $\tan \delta$, indicating a single value of T_g , respectively,

51, 65, and 91 °C for samples I, II and III, respectively. Also the increasing of T_g is due to the increasing amount of benzoxazine in the samples.

Table 3. 2 Corresponding molar ratio of raw materials [15]

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

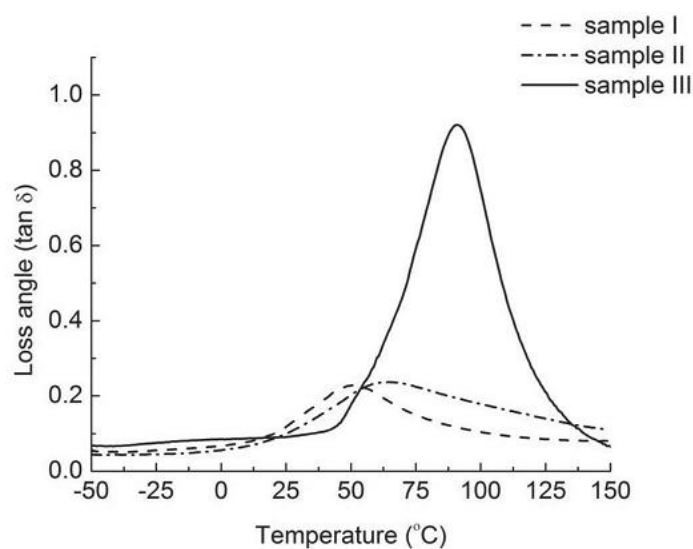


Figure 3.10 Loss tangent as a function of temperature heating rate $4\text{ }^{\circ}\text{C min}^{-1}$, frequency 1 Hz [15].

Furthermore, the recovery stress and shape recovery ratio had been observed as the results in Figure 3.11 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 3.12 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.

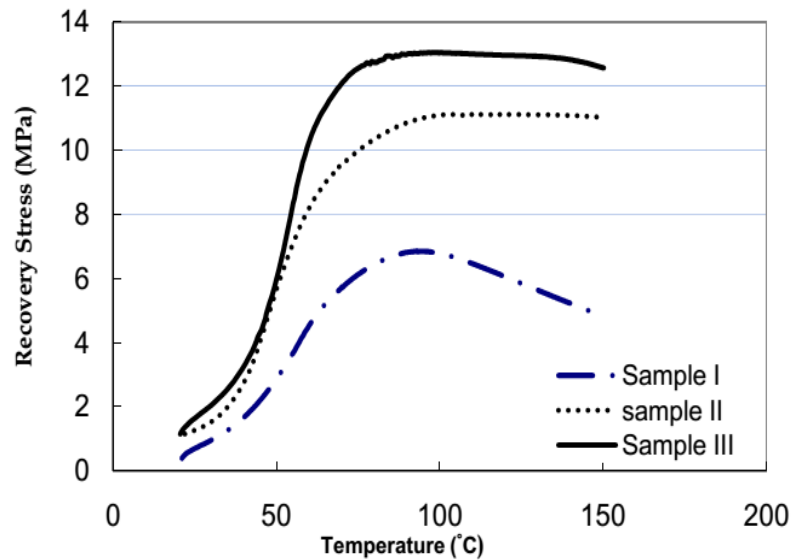


Figure 3.11 Recovery stress behaviors of 100% strained samples. Heating rate was 4°C/min and stretching rate was 50 mm/min [15].

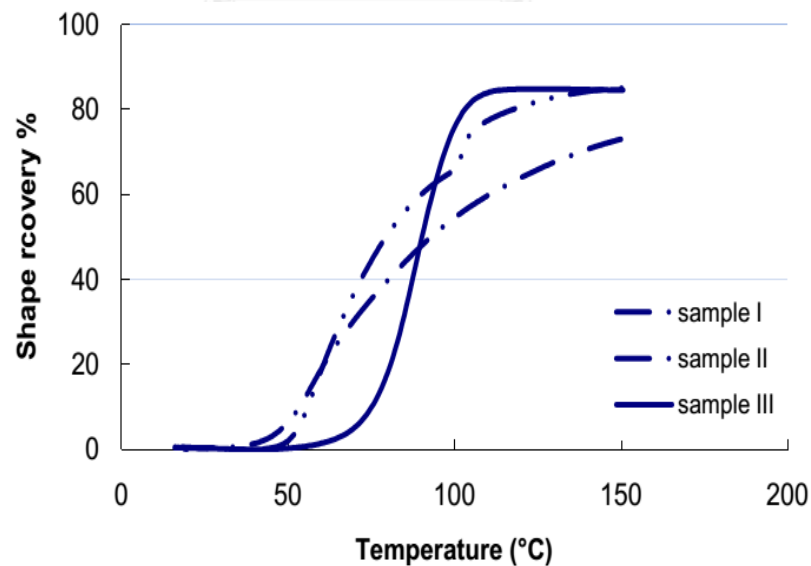


Figure 3.12 Shape recovery ratio of 100% strained samples. Heating rate was 4°C/min and stretching rate was 50 mm/min [15].

Rimduisit *et al.* (2011) have investigated thermomechanical characteristics of benzoxazine-urethane copolymers by using DSC, DMA. The urethane prepolymer was prepared by propylene glycol (MW = 2000) and 2,4-toluene diisocyanate (TDI). The copolymer was blended by benzoxazine (BA-a) and urethane prepolymers. The results from DMA are shown in Figures 3.13 (a) and (b)

The T_g of the alloys can be roughly estimated from the maximum peak temperature in the loss modulus curve of each sample. From the figure, we can see that the T_g of the neat polybenzoxazine was determined to be 165 °C of the polymer alloys were about 177, 192, 220, and 245 °C in BA-a/PU 90/10, 80/20, 70/30, and 60/40. Therefore, adding PU into the polybenzoxazine can substantially increase the T_g of the polymer alloys. T_g 's of all alloys were greater than those of the BA-a and the PU, i.e., 165 °C and -70 °C. On the part of storage modulus of the BA-a/PU alloys were reduced from 5.2 GPa to 1.8 GPa with the addition of the PU from 0 to 40% by weight.

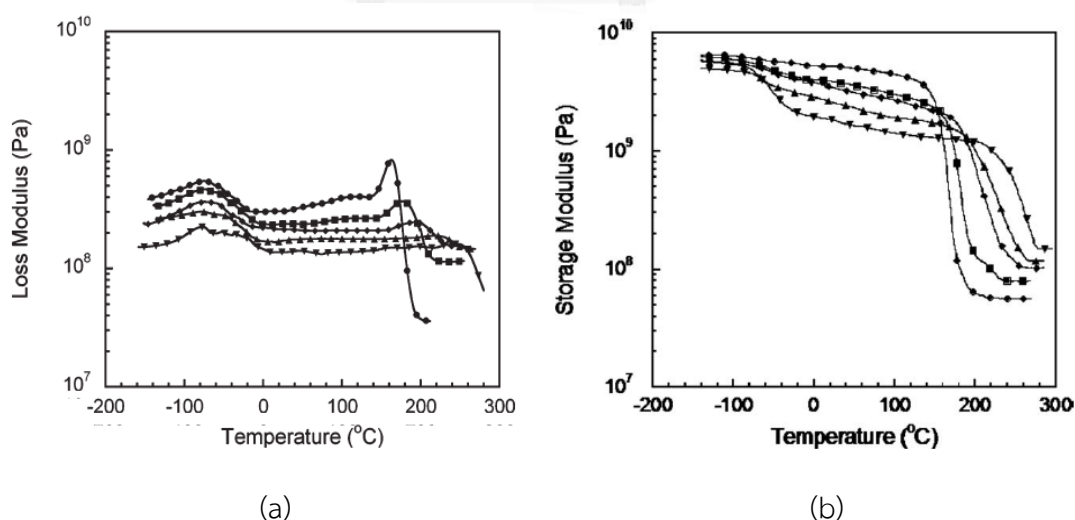


Figure 3.13 Loss modulus (a) and storage modulus (b) of BA-a/PU alloys at various compositions (●) 100/0, (■) 90/10, (◆) 80/20, (▲) 70/30, and (▼) 60/40 [17].

Furthermore, the broad glass transition temperature can also be determined from DMA on the $\tan \delta$ curve of each specimen. As shown in the Figure 3.13, broad glass transition temperatures were about 110, 100, 100, and 90 °C, respectively. The broadening glass transition temperature is an important factor for determine the amount of temporary shapes for multiple-shape memory system.

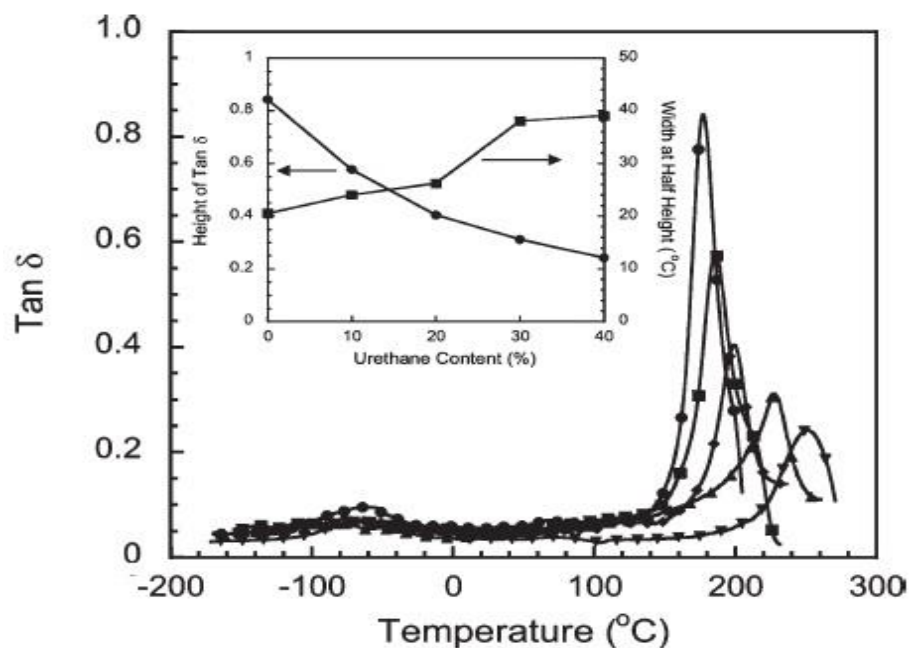


Figure 3.14 $\tan \delta$ of BA-a/PU alloys at various compositions: (●) 100/0, (■) 90/10, (◆) 80/20, (▲) 70/30, and (▼) 60/40 [17].

Tanpitaksit *et al.* (2015) have investigated effects of benzoxazine resin on property enhancement of shape memory epoxy. A suitable content of BA-a in the aliphatic epoxy (NGDE)/polybenzoxazine (PBA-a) samples for good shape memory performance is in a range of 30 to 50 mol%. The storage modulus of the obtained NGDE/PBA-a shape memory polymers (SMPs) was increased from 3.57 GPa for 30 mol% BA-a content to 4.50 GPa for 50 mol% BA-a content. Flexural modulus and flexural

strength at room temperature of the samples at 50 mol% BA-a were found to be as high as 3.97 GPa and 132 MPa compared to the maximum values of 2.54 GPa and 100 MPa of SMP based on cyanate ester-epoxy. All samples exhibited a high value of shape fixity close to 100%. A presence of the BA-a in the samples also discovered a greater recovery stress ranging from 0.25 to 1.59 MPa.

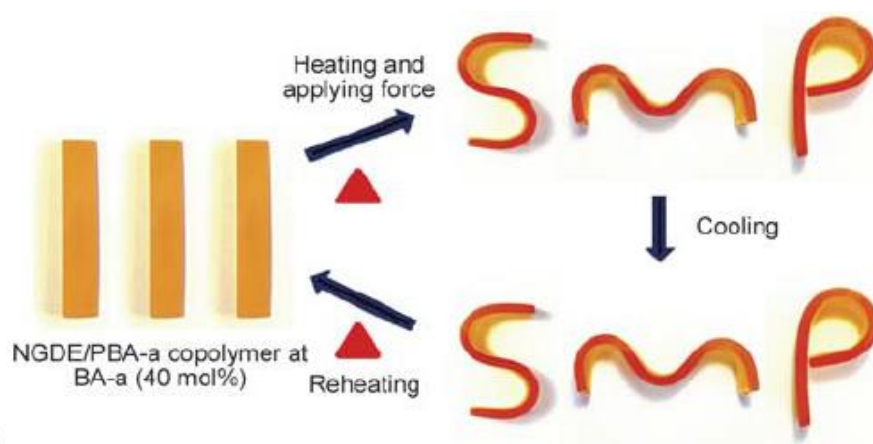


Figure 3.15 NGDE/PBA-a SMP at original shape, temporary shape and recovered shape at $T_g + 20^\circ\text{C}$ [18].

Table 3.3 Properties of NGDE/PBA-a SMP at various BA-a contents [18]

Sample	Flexural strength (MPa)	Flexural modulus (GPa)	Shape fixity at room temp. (%)
BA-a 30 mol%	52	1.6	99.30
BA-a 35 mol%	78	2.4	99.10
BA-a 40 mol%	108	3.4	98.80
BA-a 45 mol%	124	3.8	98.50
BA-a 50 mol%	132	4.0	98.10

The properties of this system are presented in table 3.3, which shows that the increase in the ratio of BA-a result, the flexural strength increased due to the effect of the addition of high flexural strength PBA-a which approximately 126-139 MPa and chemical linkage formation between PBA-a with the epoxy network as the flexural modulus is higher as well. Because of the addition of the more rigid PBA-a is approximately 4.5-5.8 GPa into the more flexible aliphatic epoxy as well as an enhanced crosslink density of the obtained polymer network described previously. In addition, the shape fixity of all ratios is similar values.

Kuang *et al.* (2016) have studied triple-shape memory epoxy with varying the molar ratio of the diamine adduct cross-linker (FM) from 33 to 67. The thermal reversible DA adduct was first evaluated as a molecular switch for shape memory by DMTA in a three-point bending deformation mode. The shape memory effect was quantified in terms of shape fixity, R_f , and shape recovery, R_r , as shown in Table 3.4.

Table 3.4 Calculated values of R_f and R_r for triple-shape memory epoxy

Sample	R_f (B) (%)	R_f (C) (%)	R_r (C-B) (%)	R_r (B-A) (%)
Control	0	100	100	-
FM33	38	100	100	80
FM50	54	100	99	61
FM67	75	100	100	32

The TSM cycle involves a two-step shape fixing process followed by a two-step recovery process. The sample was first heated to 140°C and deformed by ramping the strain rate at 5%/min to 10% strain ($\epsilon_{B,load}$). The sample was then cooled to 80°C at 5°C/min while holding the strain constant. The external load was released by unloading

and fixed the first temporary shape B, which corresponds to ϵ_B . In the second fixing step, shape B was further deformed using the same strain rate until a strain of 20% ($\epsilon_{C,load}$) at 80°C. The temperature was further cooled to 20°C followed by the second release of external force. For recovery, shape C was heated to 80°C yielding the recovered shape B ($\epsilon_{B,rec}$). After increasing the temperature to 150°C, the shape recovered to shape A ($\epsilon_{A,rec}$).



CHAPTER IV

EXPERIMENTAL

4.1 Raw Materials

The materials used in this research were benzoxazine resin, and urethane prepolymer. Benzoxazine resin was based on bisphenol-A, aniline and formaldehyde. The bisphenol-A (polycarbonate grade) was provided by PTT Phenol Co., Ltd. (Thailand). Para-formaldehyde (AR grade) was purchased from Merck Company and aniline (AR grade) was contributed by Loba Chemie Pvt. Ltd. Toluene diisocyanate (Mw = 2000) was provided by the South City Group (Thailand) while polypropylene glycol polyol was supplied by TPI Polyol Co., Ltd. (Thailand).

4.2 Specimen Preparation

4.2.1 Benzoxazine Resin Preparation

Benzoxazine resin (BA-a) synthesized by using bisphenol-A, formaldehyde and aniline at the molar ratio of 1:4:2. The mixture was heated to 110°C in an aluminum pan and was stirred 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 [16]. 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 Urethane Prepolymer Preparation

Urethane prepolymer was prepared by reacting propylene glycol with 2,4-tolulene diisocyanate (TDI) at a 1:2 molar ratio. Dibutyltin dilaurate (DBDT) (0.075 wt%) was used as a catalyst for the synthesis. The two reactants for urethane resin preparation were stirred under a nitrogen atmosphere at 70°C for 2 hours. After the completion of the reaction, the obtained clear and viscous urethane prepolymers were cooled down to room temperature and kept in a nitrogen-purged, closed container.

4.2.3 Preparation of Benzoxazine-Urethane Multiple-SMP Samples

The benzoxazine monomer (BA-a) was blended with the urethane prepolymers (PU) to provide BA-a/PU mixtures. Each resin mixture was measured at a desirable mass fraction. The mixture was then heated to about 115°C in aluminum pan and mixed until a homogeneous mixture was obtained. The molten resin mixture was poured into an aluminum mold and step-cured in an air-circulated oven at 150°C for 1 hour, 160°C and 170°C for 2 hours each. The specimen was finally left to cool down to room temperature and was then ready for material characterizations.

4.3 Characterization Methods

4.3.1 Differential Scanning Calorimetry (DSC)

Curing behaviors of BA-a/PU mixtures were studied by a differential scanning calorimeter (DSC) model DSC1 Module from Mettler-Toledo (Thailand). The samples were sealed with a mass in range of 5-10 mg in an aluminum pan with lid and they were systematically scanned under a nitrogen flow rate of 50 ml/min. The heating rate used was 10°C/min and the sample was scanned from room temperature to 300°C.

The degree of conversion of a sample was determined according to the relationship in Equation (4.1):

$$\text{Conversion (\%)} = \left(\frac{H_{\text{rxn}}}{H_0} \right) \times 100 \quad (4.1)$$

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

H_0 = heat of reaction of uncured resin mixture

4.3.2 Thermogravimetric Analysis (TGA)

Thermal stability of benzoxazine-urethane multiple-SMP samples was performed on a thermogravimetric analyzer (model TGA1 Module) from Mettler-Toledo (Thailand). The testing temperature program was ramped at a heating rate of 20°C/min from 30 to 850°C under nitrogen atmosphere with a constant N₂ purge gas flow rate of 50 ml/min. The sample mass used was approximately 5-10 mg. The degradation temperature (T_d) and char yield of the samples were reported at their 5% weight loss and at 800°C, respectively.

4.3.3 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical properties of benzoxazine-urethane copolymers were obtained by dynamic mechanical analyzer (DMA, model DMA242, Netzsch, Germany). The specimen, with a dimension of 10 mm × 50 mm × 2 mm, was tested using a three point bending mode at a heating rate of 2°C/min from 30°C to 300°C. A test frequency of 1 Hz and strain amplitude of 5 μm under nitrogen atmosphere was used in this experiment. Glass transition temperature (T_g) of the specimens was obtained from the maximum peak on the loss tangent curve. The broad glass transition temperature of the

benzoxazine-urethane copolymers used as switching temperature was determined from the width range of the loss tangent curve base.

4.3.4 Mechanical Property Test (Flexural Mode)

The mechanical properties of BA-a/PU multiple-shape memory samples such as flexural strength and flexural modulus were measured by a universal testing machine (Instron, model 5567) based on ASTM D 790 with a thermal chamber at room temperature for original shape, and at $T_g - 10^\circ\text{C}$ and $T_g + 10^\circ\text{C}$ for temporary shapes. The dimension of a rectangular specimen was 10 mm × 50 mm × 2 mm. The test method was a three-point bending mode with a supporting span of 32 mm. The test was performed using a crosshead speed of 1.0 mm/min.

The flexural strength and flexural modulus based on ASTM D 790 were calculated by the following equations:

$$E_f = \frac{L^3 m}{4bd^3} \quad (4.2)$$

$$\sigma_f = \frac{3PL}{2bd^2} \quad (4.3)$$

Where: E_f = Flexural modulus, GPa

σ_f = Flexural strength, MPa

L = Support span, mm

m = Slope of the initial straight-line portion of the load deflection

b = Width of test beam, mm

d = Depth of tested beam, mm

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

4.3.4 Shape Fixity and Shape Recovery Test

Shape fixity of BA-a/PU multiple-shape memory samples was studied by a universal testing machine with a thermal chamber under a three point bending mode. Firstly, the first temporary shape was formed by applying force for 5% bending to a sample (10 mm × 50 mm × 2 mm) at $T_g + 10^\circ\text{C}$, then the sample was cooled to $T_g - 10^\circ\text{C}$ and applying force again for 10% bending to a sample. After that, the sample was left to cool down to room temperature. The force was then removed completely to obtain a second temporary shape (10% bending). The deflection after unloading was then measured, and shape fixity at each temporary shape of each sample was then determined.

In shape recovery test, the sample was heated to temperature at $T_g - 10^\circ\text{C}$ to recover to first temporary shape and followed by heating to $T_g + 10^\circ\text{C}$. At this temperature, the sample gradually recovered to its original rectangular shape.

The shape fixity (R_f) and shape recovery (R_r) were calculated using Equations (4.4) and (4.5) for the dual-shape memory effect, according to a report by Xie [26].

$$R_f = \frac{\epsilon}{\epsilon_{\text{load}}} \times 100 \quad (4.4)$$

$$R_r = \frac{\epsilon - \epsilon_{\text{rec}}}{\epsilon} \times 100 \quad (4.5)$$

Where: ϵ_{load} = The maximum strain under load

ϵ = The fixed strain after cooling and load removal

ϵ_{rec} = The strain after recovery

Equations (4.4) and (4.5) are expanded to Equations (4.6) and (4.7) to calculate R_f and R_r for the triple-shape and quadruple-shape memory effects.

$$R_f = \frac{\epsilon_y - \epsilon_x}{\epsilon_{y,\text{load}} - \epsilon_x} \times 100 \quad (4.6)$$

$$R_r = \frac{\epsilon_y - \epsilon_{x,\text{rec}}}{\epsilon_y - \epsilon_x} \times 100 \quad (4.7)$$

Where: $\epsilon_{y,\text{load}}$ = The maximum strain under load

ϵ_y and ϵ_x = The fixed strains after cooling and load removal

$\epsilon_{x,\text{rec}}$ = The strain after recovery



CHAPTER V

RESULTS AND DISCUSSION

5.1 Curing Behaviors of Benzoxazine-Urethane Resin Mixtures

The curing reaction of the binary mixtures of BA-a and PU at 55:45, 60:40, 70:30, and 80:20 mass ratios were investigated by differential scanning calorimetry using a heating rate of 10°C/min at a temperature range of 30 to 300°C is depicted in Figure 5.1. From the thermograms, a single dominant exothermic peak of the curing reaction in each resin composition was observed. The exothermic peak of the neat benzoxazine resin was located at 228°C which attributed to ring-opening polymerization of oxazine ring. The exothermic peak was shifted to higher temperature when PU fraction was increased in the mixtures. As shown in this figure, the positions of exothermic peak at 90:10, 80:20, 70:30, 60:40, and 55:45 mass ratios were found to be 241°C, 246°C, 254°C, and 255°C, respectively.

Furthermore, an area under the exothermic peak was also noticed to be decreased with increasing PU fraction. The heat of reaction values of the BA-a:PU resin mixtures, which were determined from the area under the exothermic peak were 280 J/g, 215 J/g, 198 J/g, 179 J/g, and 173 J/g at BA-a:PU mass ratios of 100:0, 90:10, 80:20, 70:30, 60:40, and 55:45, respectively. The phenomenon was possibly because the reactions between BA-a and PU were expected to comprise at least two reactions. The first reaction is the exothermic curing peak among the benzoxazine monomers, while the second reaction should be the reaction should be the reaction between the

isocyanate group of the urethane prepolymer and phenolic hydroxyl group of the polybenzoxazine. The second reaction was expected to proceed after the phenolic hydroxyl group from ring opening of the benzoxazine monomer was produced. The thermograms also suggested that the decrease of the area under the curing reaction peaks the binary mixtures when the amount of all urethane prepolymers, this principle was explained by Rimdusit *et al.* [33]. This behavior is ascribed to the change from the BA-a:BA-a interaction to a more BA-a:PU interaction with increasing the PU fraction in the binary mixture. The systematic decrease of the exotherms with the PU implied that the BA-a:PU interaction possessed a lower heat of reaction per mole of the reactant compared to that of the BA:BA interaction.

Figure 5.2 exhibits the DSC thermograms of the mixtures of the benzoxazine resins and urethane prepolymer (MW = 2000 Dalton) at a mass ratio of 55:45 at various curing conditions. For determining the curing condition of every compositions were used in this work, the specific mixture i.e. BA-a:PU at 55:45 mass ratio was selected based on the ratio that required the highest curing temperature. The heat of reaction of the uncured resin mixtures determined from the area under the exothermic peak of 173 J/g. It was reduced to 154 J/g after curing at 150 °C for 1 hour and was decreased to 137 J/g and 49 J/g after more curing at 160 °C and post curing at 170 °C for 2 hours, respectively. After the post curing at 170 °C for 2 hours, the exothermic peak was disappeared corresponding to 71% conversion of the resin mixtures can be useful to prepare the shape memory materials as report by Erden and Jana [15]. In their results, they suggested that the degree of conversion about 70% of 17.5wt% of BA-a filled in shape memory polyurethane provided samples with good balance properties for

shape memory performance. The shape fixity and shape recovery of the 17.5wt% of BA-a filled in shape memory polyurethane were 99.3% and 93%, respectively. The degree of conversion of the sample was determined according to the following relationship by Equation 4.1. Consequently, the curing process under this condition was used to cure all benzoxazine-urethane mixtures to prepare the samples for further characterization.

$$\text{Conversion (\%)} = \left(\frac{H_{\text{rxn}}}{H_0} \right) \times 100 \quad (4.1)$$

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

H_0 = heat of reaction of the uncured resin mixture

5.2 Thermal Degradation and Thermal Stability of Benzoxazine-Urethane Multiple-Shape Memory Polymer.

The thermal degradation temperature at 5wt% loss and residue weight at 800 °C are important parameters used to determine the temperature stability of polymeric materials that investigated by thermogravimetric analyzer. Figure 5.3 illustrates TGA thermograms of the neat BA-a and BA-a:PU multiple-SMPs at various mass ratios of BA-a. The samples were scanned from room temperature to 850 °C with heating rate of 20 °C/min under nitrogen atmosphere. From the figure, the degradation temperatures of the multiple-SMP at 5wt% loss were found to be slightly lower than that of the neat polybenzoxazine. The TGA curves of the binary mixtures at various mass ratios of urethane prepolymer at 20wt%, 30wt%, 40wt%, and 45wt% suggested that an addition of the urethane resin into the benzoxazine resin gradually decreased the thermal degradation temperature of the obtained copolymers. The degradation temperature

of the polybenzoxazine homopolymer at 5 wt% loss was determined to be 337 °C. The degradation temperatures of BA-a:PU multiple-SMPs at the urethane mass ratio of 20wt%, 30wt%, 40wt%, and 45wt% were determined to be 332 °C, 323 °C, 296 °C and 268 °C, respectively. Therefore, one benefit of blending benzoxazine resin with PU prepolymer is the potential enhancement of thermal stability of the PU due to higher thermal properties of polybenzoxazine. In addition, the residue weight at 800 °C of the BA-a:PU multiple-SMPs was found to decrease with an increasing of the PU fraction in the binary polymeric system. As can be seen in this figure, the residue weight of BA-a:PU multiple-SMPs at mass ratios of 100:0, 90:10, 80:20, 70:30, 60:40, and 55:45 were determined to be 26.1%, 24.6%, 20.6%, 19.1%, and 16.2%, respectively. The reduction of the thermal stability of the BA-a:PU copolymers with the increasing of PU mass ratios is attributed to the fact that the structure of polyurethane composed of a less thermal stability aliphatic structure of the polyol compared to a greater aromatic rings in the polybenzoxazine used as previously reported by Rimdusit *et al.* [17].

5.3 Dynamic Mechanical Properties of Benzoxazine-Urethane Multiple-Shape Memory Polymer.

Dynamic mechanical properties of benzoxazine-urethane multiple-SMPs were exhibited in Figures 5.4 and 5.5. The viscoelastic properties of the samples were investigated by dynamic mechanical analyzer in the three-point bending mode. Several parameters such as storage modulus and loss tangent were obtained as a function of temperature range of room temperature up to 250°C with a heating rate of 2°C/min. In Figure 5.4, the storage modulus (E') curves at glassy state (30°C) of BA-a:PU multiple-SMPs at various mass contents was tended to decrease with increasing mass fraction

of the urethane prepolymer. This is attributed to the fact that PU is an elastomer providing higher flexibility than BA-a. This result clearly suggests that the addition of PU makes the polymer alloys more flexible and significantly broadens the mechanical properties of the polybenzoxazine. The reason of this behavior was reported by Rimdusit *et al.* [34]. The values of storage modulus of the BA-a:PU were measured to be 3.6 GPa, 1.8 GPa, 1.5 GPa, and 1.0 GPa with mass fraction of PU at 20wt%, 30wt%, 40wt% and 45wt%, respectively. Moreover, the higher mass fraction of the PU was found to improve the rubbery plateau modulus of the BA-a:PU copolymers.

Loss tangent ($\tan \delta$) curves was obtained from the ratio of loss energy (E'') to storage energy (E') are shown in Figure 5.5. The peak of various $\tan \delta$ curve were used to also indicate the glass transition temperature (T_g) of the samples. As can be seen from this figure, the T_g of BA-a:PU multiple-SMPs were determined to be 130°C, 135°C, 157°C, and 180°C with mass ratios of BA-a:PU at 55:45, 80:20, 60:40, 70:30, and. 90:10. The enhancement of T_g of the copolymers can be attributed to the more rigid molecular structure and possibly much higher intramolecular and intermolecular forces in the polybenzoxazine compared to the PU [14, 15]. In addition, the broadening glass transition temperature that observed from the width of $\tan \delta$ curve base is a key parameter for multiple-shape deformation process. The values of the range of the broad T_g were measured to be 80°C to 180°C in 55:45 BA-a:PU, 90°C to 180°C in 60:40 BA-a:PU, 100°C to 214°C in 70:30 BA-a:PU, and 120°C to 220°C in 80:20 BA-a:PU. In multiple-shape fixity steps, the sample was heated up to rubbery plateau state and deformed the original shape sample to the temporary shapes in this temperature range. After that, the sample was cooled down to the glassy state (room temperature)

for temporary shape fixing step. In term of shape recovery steps, the sample was reheated up to the same temperature to gradually recover to its original shape.

5.4 Mechanical Properties of Benzoxazine-Urethane Multiple-Shape Memory Polymer.

5.4.1 Flexural Properties of Benzoxazine-Urethane multiple-SMP at room temperature.

Mechanical properties of BA-a:PU multiple-SMP include flexural strength and flexural modulus were investigated by a universal testing machine (UTM) in three-point bending mode. Figures 5.6 and 5.7 show the plots of flexural strength and flexural modulus as a function of BA-a content. In Figure 5.6, the flexural strength of BA-a:PU multiple-SMP was increased with an increasing of BA-a fraction. The values were determined to be 40 MPa, 68 MPa, 74 MPa, and 98 MPa with BA-a mass content of 55%, 60%, 70%, and 80%, respectively. The addition of the softer PU fraction in the benzoxazine-urethane copolymers should result in the decrease of their strength as observed in the 20–40 wt% region, this principle was explained by Rimdusit *et al.* [33].

The flexural modulus of BA-a:PU multiple-SMP was exhibited in Figure 5.7. The trend of the modulus was also found to increase with increasing the amount of BA-a mass fraction. The values of the flexural modulus were 1.0 GPa, 1.4 GPa, 2.1 GPa, and 3.7 GPa for BA-a:PU of 55:45, 60:40, 70:30, and 80:20 mass ratios, respectively. In principle, this phenomenon was due to the fact that the addition of the softer urethane resin into the benzoxazine resin was expected to lower the stiffness of the polybenzoxazine-urethane alloys as a result of an elastomeric nature of the PU used, This phenomenon was corresponded to the report of Rimdusit *et al.* [33].

5.4.2 Flexural Properties of Benzoxazine-Urethane multiple-SMP at $T_g - 10^\circ\text{C}$ and $T_g + 10^\circ\text{C}$.

The potential applications in deforming structure of the benzoxazine-urethane multiple-SMPs were investigated by flexural testing at $T_g - 10^\circ\text{C}$ and $T_g + 10^\circ\text{C}$ which are the states used to deform the temporary shapes. In general, the enhancement 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) equipped with the thermal chamber at $T_g - 10^\circ\text{C}$ and $T_g + 10^\circ\text{C}$. Figure 5.8 illustrates the plots of the flexural strength at their $T_g - 10^\circ\text{C}$ of the benzoxazine-urethane multiple-SMPs at different BA-a mass contents. The flexural strength values at $T_g - 10^\circ\text{C}$ of BA-a:PU multiple-SMP samples were measured to be 1.1 MPa, 1.8 MPa, 4.6 MPa, and 9.0 MPa at various mass content of the BA-a resin of 55%, 60%, 70%, and 80%, respectively.

Furthermore, the relationship between the flexural modulus and BA-a mass fraction at $T_g - 10^\circ\text{C}$ was exhibited in Figure 5.9. From this figure, the values of the flexural modulus was increased with an increasing of BA-a mass fraction. This phenomenon was due to the basic principle that the addition of the rubbery urethane polymer into the adamantane polybenzoxazine was able to lower the stiffness of the resulting polybenzoxazine alloys, as previously reported by Rimdusit *et al.* [35]. The values of flexural modulus were determined to be 21.4 MPa, 31.2 MPa, 106.3 MPa, and 415.7 MPa at BA-a:PU mass content of 55:45, 60:40, 70:30, and 80:20, respectively.

In addition, the flexural properties at $T_g + 10^\circ\text{C}$ were also investigated due to this temperature is one of the state to deform the temporary shape. The flexural strength at this temperature was also found to increase with increasing BA-a mass ratio

as same as the other temperature. The values of flexural strength were measured to be 0.3 MPa, 0.5 MPa, 1.6 MPa, and 2.3 MPa, with BA-a:PU mass ratio of 55:45, 60:40, 70:30, and 80:20, respectively. In parts of flexural modulus was same trend with the modulus at room temperature and at $T_g - 10^\circ\text{C}$. The flexural modulus values were 7.9 MPa, 12.1 MPa, 25.1 MPa, and 73.2 MPa with BA-a:PU mass ratio of 55:45, 60:40, 70:30, and 80:20, respectively. . It was observed that the flexural properties including flexural strength and flexural modulus were found to decrease with temperature and were improved from room temperature to $T_g - 10^\circ\text{C}$ and to $T_g + 10^\circ\text{C}$, respectively.

5.5 Multiple-Shape Memory Properties

5.5.1 Effect of Benzoxazine Contents on Shape Fixity of Benzoxazine-Urethane Multiple-Shape Memory Polymer.

Multiple-shape memory properties were investigated by a universal testing machine in flexural mode (three-points bending). The various states of bending in multiple-SMPs were shown in Figure 5.12. The photographs show bending steps in multiple-shape memory process for BA-a/PU copolymers in five stages. The initial stage at room temperature shows the original rectangular shape of BA-a/PU multiple-SMPs as depicted in Figure 5.12(a). The sample was heated to a temperature above glass transition temperature about 10°C ($T_g + 10^\circ\text{C}$) with deforming the first temporary shape by bending for 5% as exhibited in Figure 5.12(b). Then, the sample was cooled down to $T_g - 10^\circ\text{C}$ as shown in Figure 5.12(c). In this step, the first temporary shape fixity was determined and bending again for 10% to deformed the second temporary shape. After that, the sample was left to cool down to room temperature and measured the second temporary shape fixity at this step.

Shape fixity (R_f) is one important shape memory performance indicating an ability to memorize temporary shape of multiple-shape memory polymers. Shape fixity of the first and second temporary shape were determined according to the following relationship by Equation 4.6. From Figure 5.13, the values of the first temporary shape fixity were measured to be 70.2%, 88.7%, 99.4% and 96.3% for BA-a/PU at mass ratios of 55:45, 60:40, 70:30, and 80:20. As observed that the shape fixity was increased with increasing of BA-a mass fraction from 55% to 70%. This enhancement of the shape fixity has been similarly reported by Kuang *et al.* [36]. In principle, this behavior was due to the fact that an increase of polybenzoxazine which serves as reversible net-points in the binary polymeric system resulting in an increasing of shape fixity performance. In addition, the first temporary shape fixity at BA-a:PU mass ratio of 80:20 was slightly decreased due to the excess of polybenzoxazine in the copolymers at rubbery state which could behave as switch units as same as urethane prepolymer in multiple-SMP system.

Furthermore, the second temporary shape fixity was also increased with increasing BA-a mass content from 55% to 80%. As can be seen in Figure 5.14, the second temporary shape fixity were determined to be 83.2%, 99.2%, 99.5%, and 99.6%, respectively. The improvement of the shape fixity was due to both increase of reversible net-points and decrease in switch units. This result is consistent with the research of Kuang *et al.* [36]. In addition, the number of shape memorizing cycle indicate the performance in multiple-shape deforming applications. The binary system of benzoxazine-urethane multiple-shape memory polymer illustrate number of cycle of first temporary and second temporary shape fixity in Figures 5.17 and 5.18. As seen

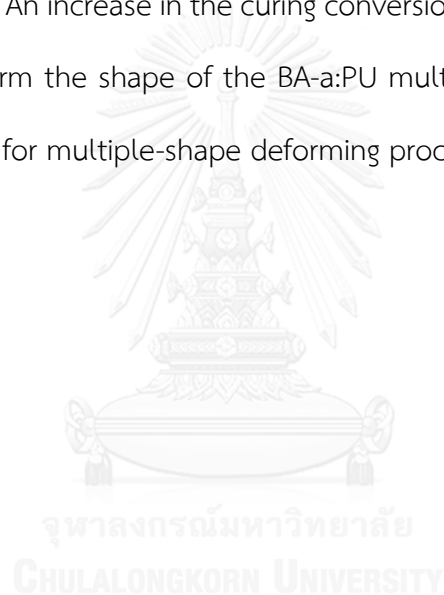
from these figure, the first and second temporary shape fixity values of each BA-a:PU mass content were similar values of each deformation cycle.

5.5.2 Effect of Benzoxazine Contents on Shape Recovery of Benzoxazine-Urethane Multiple-Shape Memory Polymer.

In shape recovery process, the bent shape of the sample was recovered to the first temporary shape by reheated up to $T_g - 10^\circ\text{C}$ as seen in Figure 5.12(d). In this step, the first temporary shape recovery was determined. Finally, the sample was reheated up again to $T_g + 10^\circ\text{C}$. It was gradually recovered to its original shape as shown in Figure 5.12(e).

Shape recovery (R_r) is one important parameter that used to reflect how well an original shape has been memorized. Shape recovery to the first temporary shape and original shape were determined according to the following relationship by Equation 4.7. The shape recovery to the first temporary shape as can be seen in Figure 5.15 were measured to be 96.2%, 92.1%, 91.8%, and 88.5% at BA-a:PU mass ratios of 55:45, 60:40, 70:30, and 80:20, respectively. The decrease of shape recovery with decreasing polyurethane content was due to the reduction of switch units, as previously reported by Kuang *et al.* [36]. Furthermore, the shape recovery to the original shape was also tended to decrease with decreasing of polyurethane fraction. Figure 5.16 illustrates the values of shape recovery to the original shape were 99.2%, 98.8%, 98.3%, and 97.6% with BA-a:PU mass fraction of 55:45, 60:40, 70:30, and 80:20. This behavior was also explained by Kuang *et al.* [36]. In addition, shape recovery performance with deforming cycle of all samples were shown in Figures 5.19 and 5.20. From these figure, the results illustrate the shape recovery to first temporary and original shape of all benzoxazine-urethane samples were decreased with increasing

recovery cycle. For one thing, the irreversible network integrity increases by post curing with thermal cycles leading to increase internal stress for the same strain. Moreover, heating cycles results in more thermodynamically stable exo-product, which would not fully open in the subsequent programming cycle, as reported by Kuang *et al.* [36]. Furthermore, Figure 5.21 shows the degree of conversion of all BA-a:PU mass content were increased with increasing the curing time at 170°C for 2 hours and 6 hours, respectively. At 12 hours of curing time, the degree of conversion of all mass fraction were closed to 100%. An increase in the curing conversion can indicate that a decrease of the ability to deform the shape of the BA-a:PU multiple-SMP due to the suitable degree of conversion for multiple-shape deforming process was 70%.



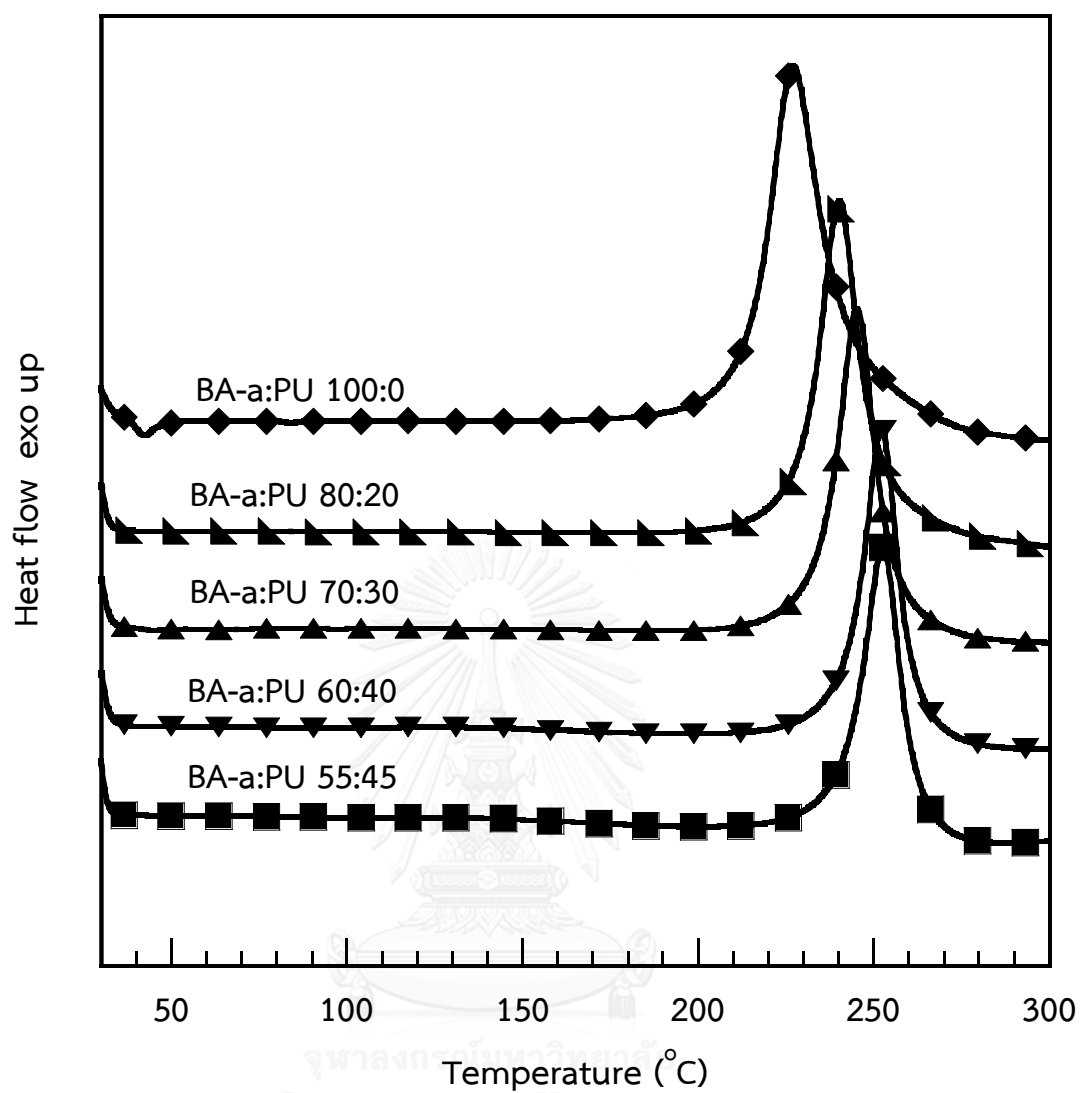


Figure 5.1 DSC thermograms of benzoxazine-urethane resin mixtures at various BA-a:PU mass ratios: (◆)100:0, (▶)80:20, (▲)70:30, (▼)60:40, and (■)55:45.

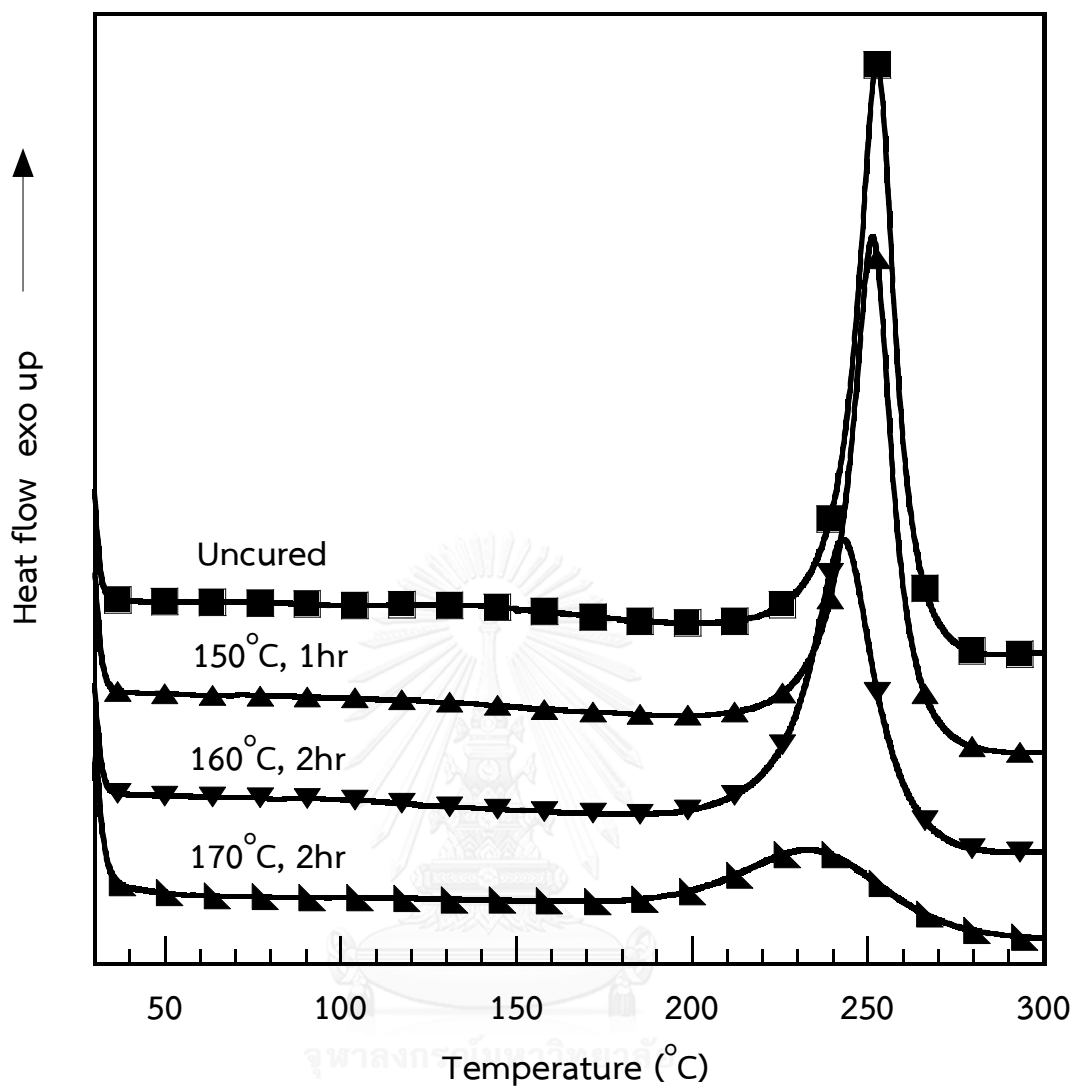


Figure 5.2 DSC thermograms of benzoxazine-urethane resin mixtures at 55:45 mass ratio at various curing conditions: (■) uncured, (▲) 150°C/1 hr, (▼) 150°C/1 hr + 160°C/2 hrs and (▴) 150°C/1 hr + 160°C/2 hrs + 170 C/2 hrs.

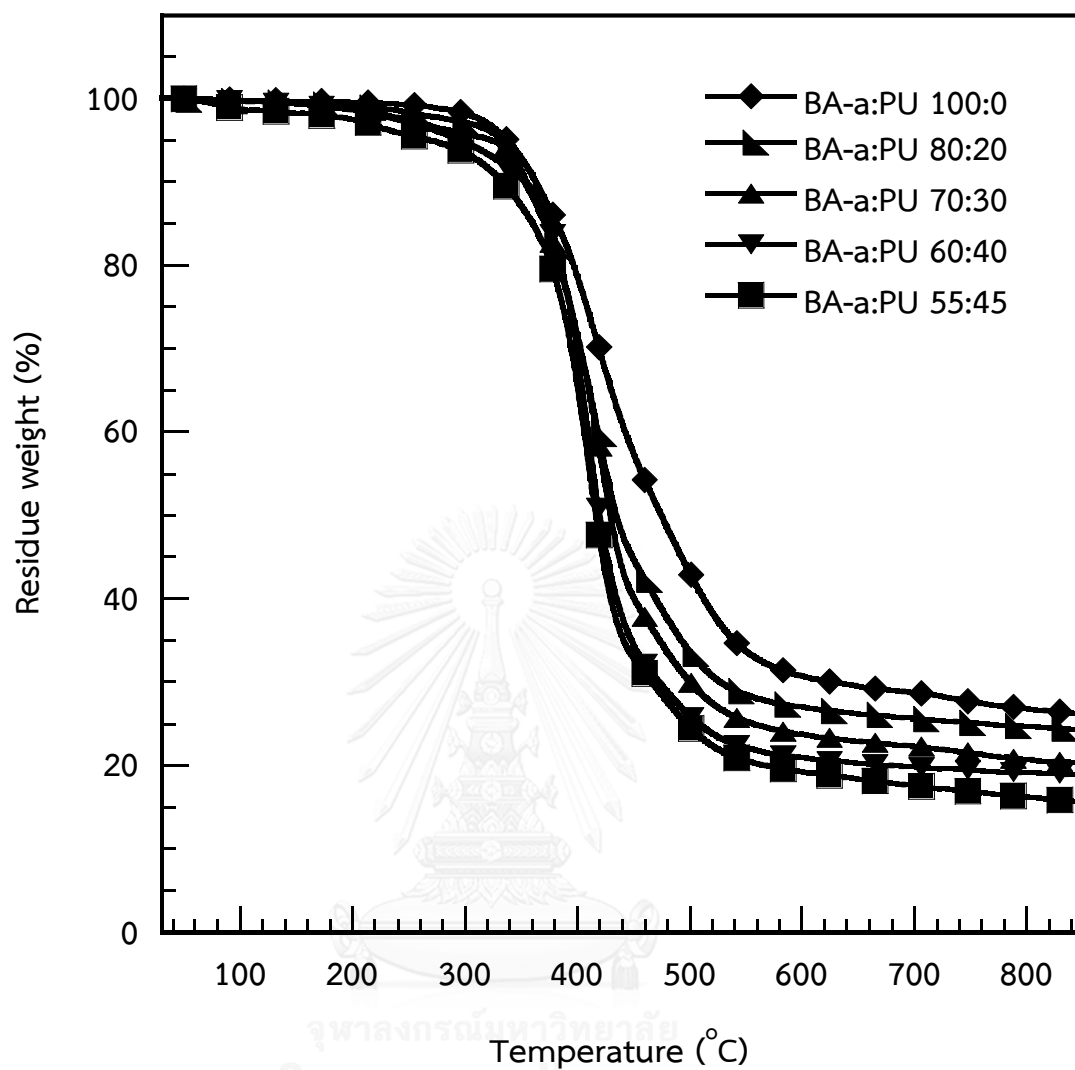


Figure 5.3 TGA thermograms of benzoxazine-urethane multiple-SMPs at various BA-a:PU mass ratios: (◆) 100:0, (◄) 80:20, (▲) 70:30, (▼) 60:40, and (■) 55:45.

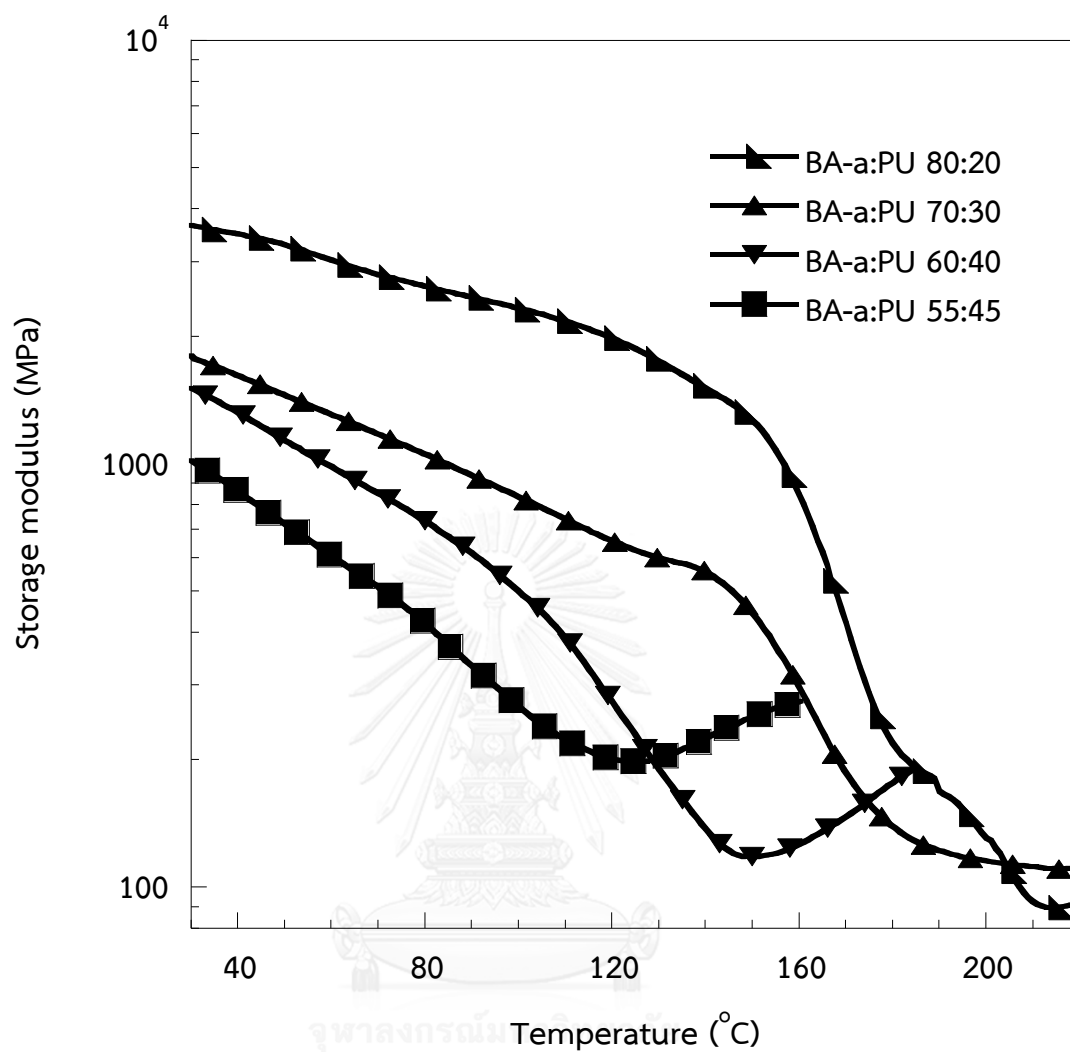


Figure 5.4 Storage modulus of benzoxazine-urethane copolymers at various BA-a:PU mass ratios: (◄) 80:20, (▲) 70:30, (▼) 60:40, and (■) 55:45.

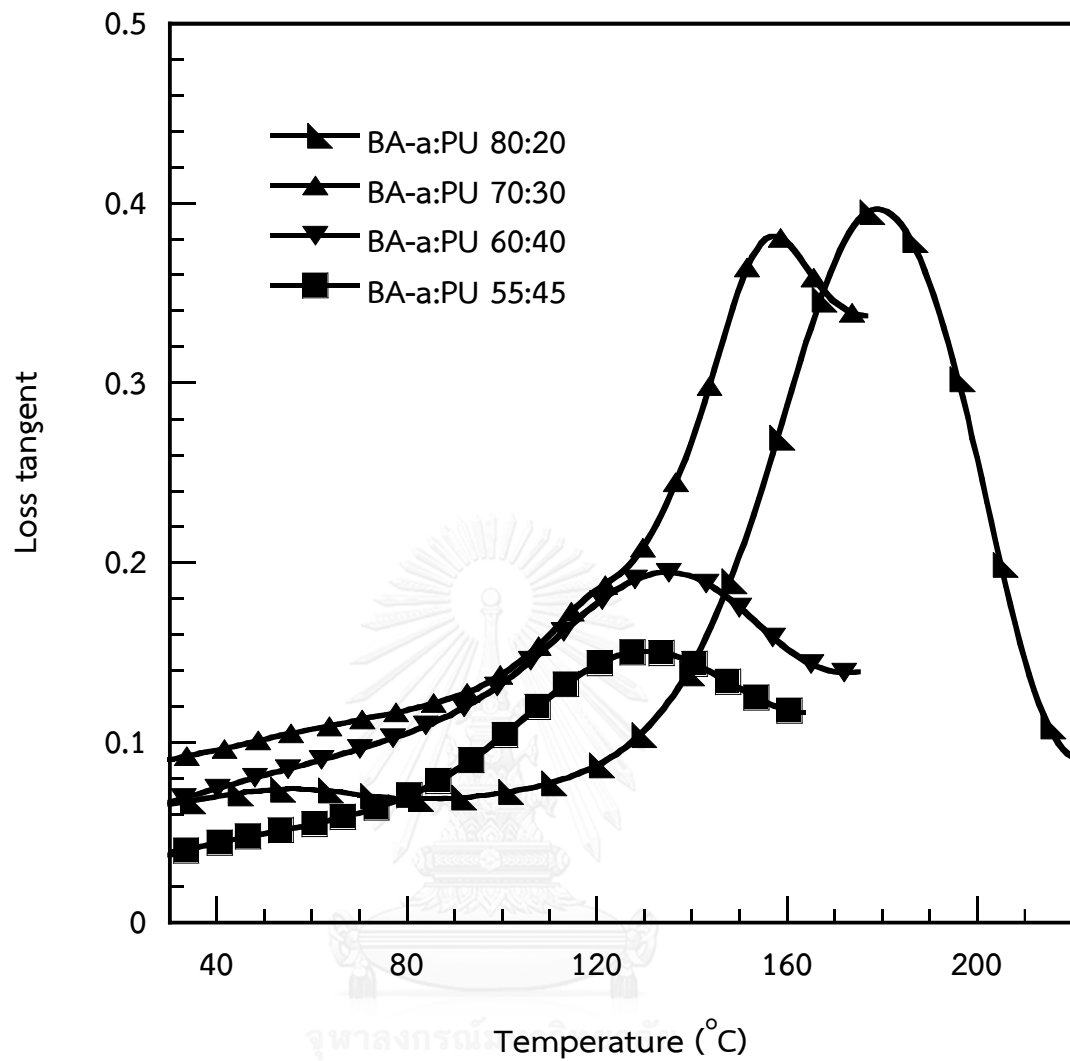


Figure 5.5 Loss tangent of benzoxazine-urethane copolymers at various BA-a:PU mass ratios: (◄) 80:20, (▲) 70:30, (▼) 60:40, and (■) 55:45.

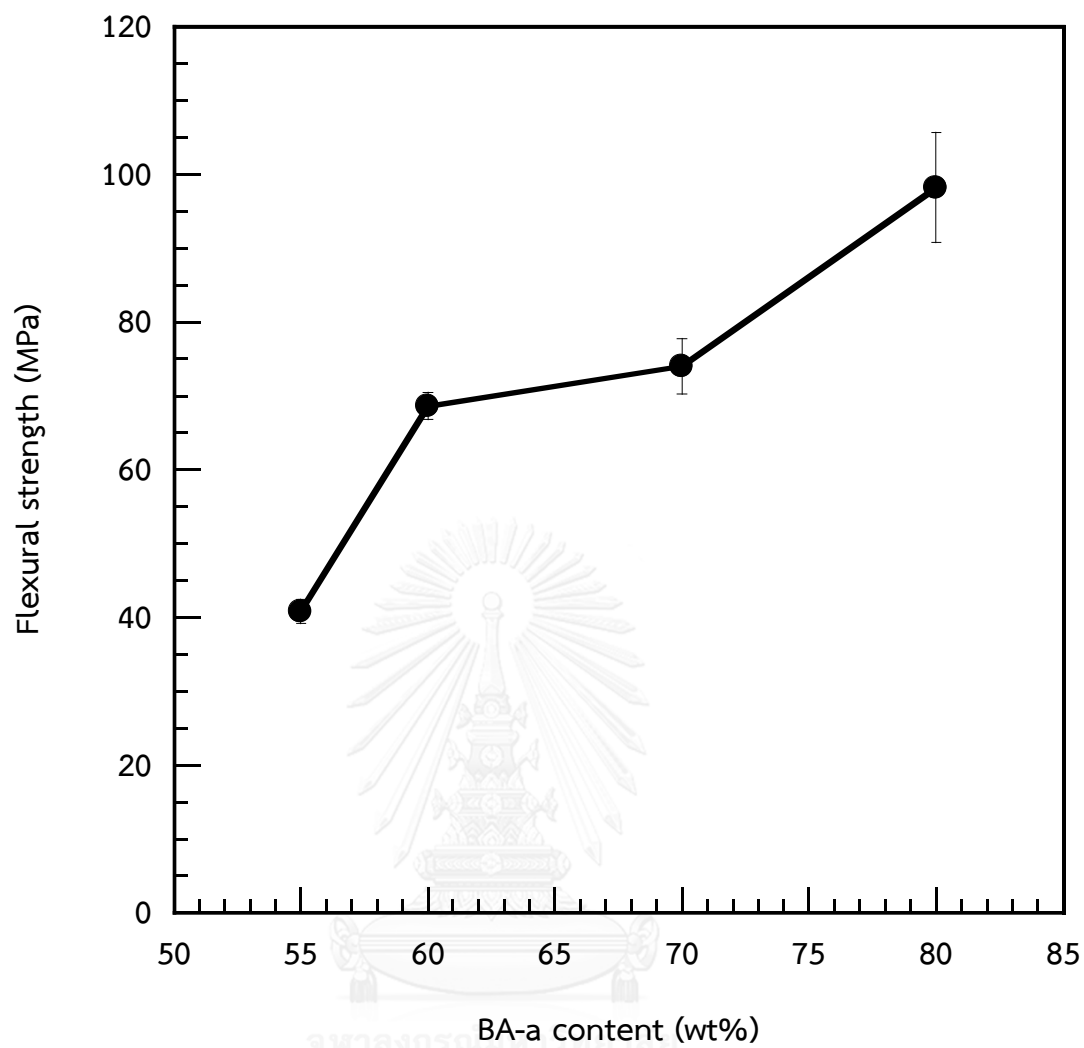


Figure 5.6 Flexural strength at room temperature of benzoxazine-urethane multiple-SMP as a function of benzoxazine mass fraction at 55%, 60%, 70%, and 80%.

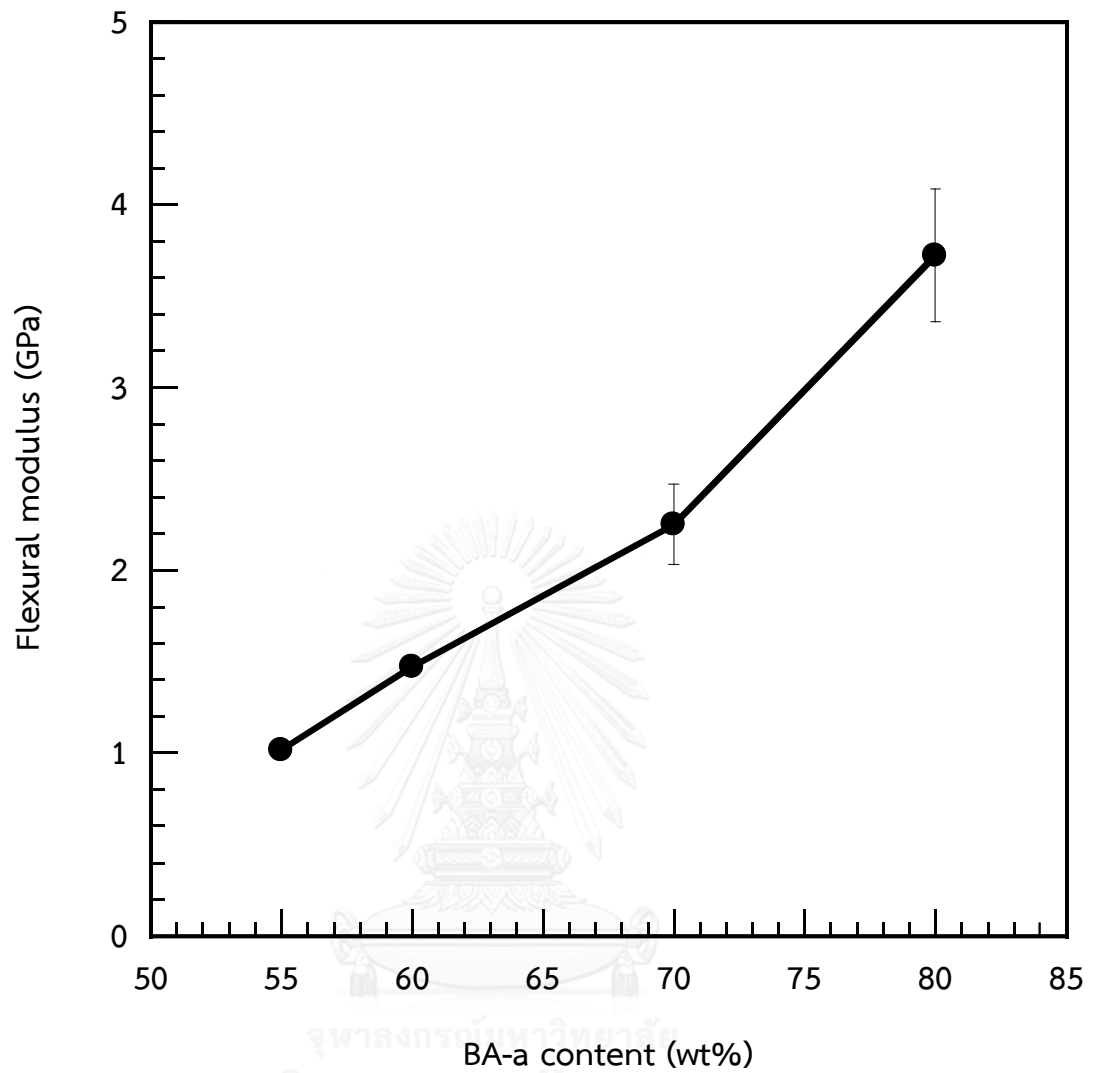


Figure 5.7 Flexural modulus at room temperature of benzoxazine-urethane multiple-SMP as a function of benzoxazine mass fraction at 55%, 60%, 70%, and 80%.

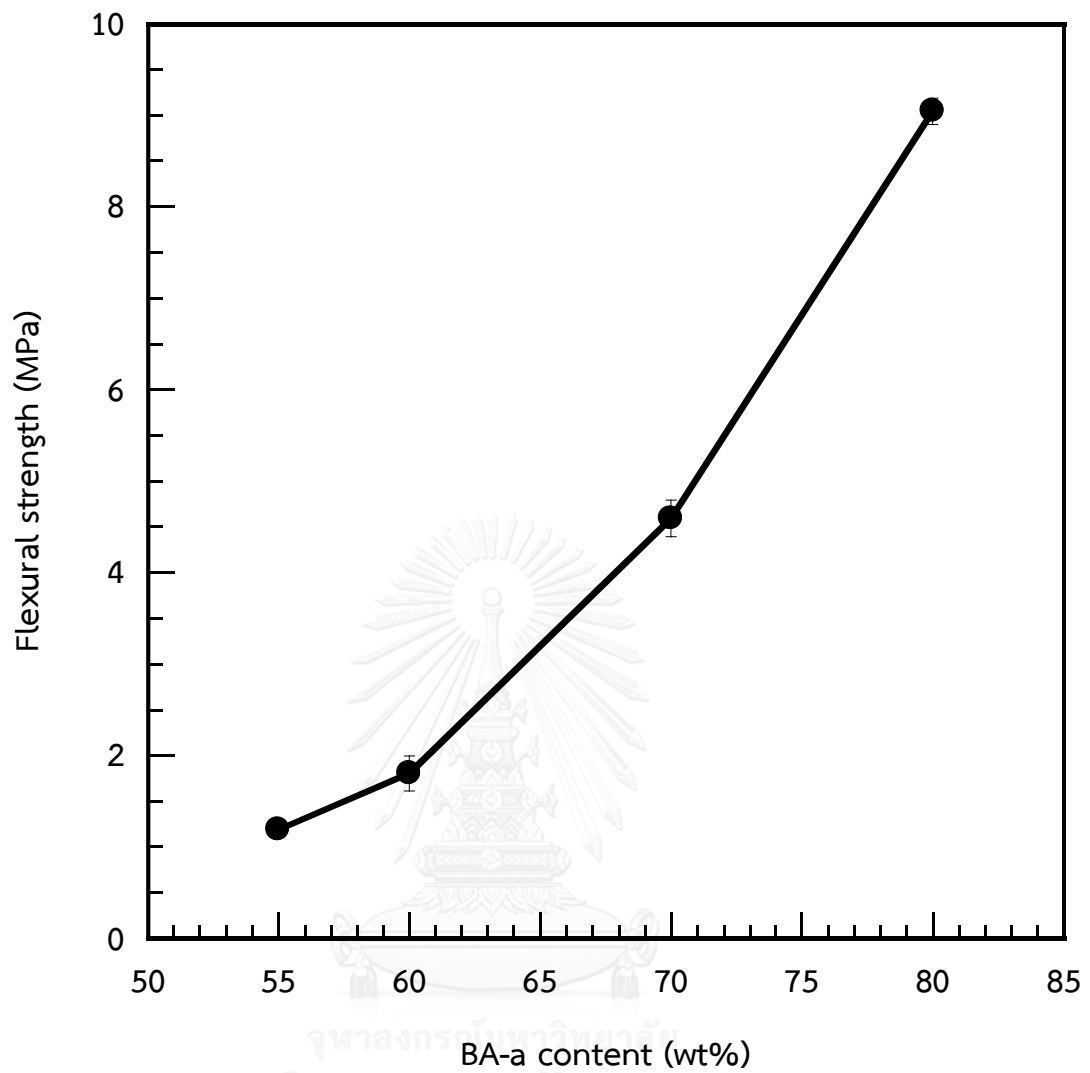


Figure 5.8 Flexural strength at $T_g - 10^\circ\text{C}$ of benzoxazine-urethane multiple-SMP as a function of benzoxazine mass fraction at 55%, 60%, 70%, and 80%.

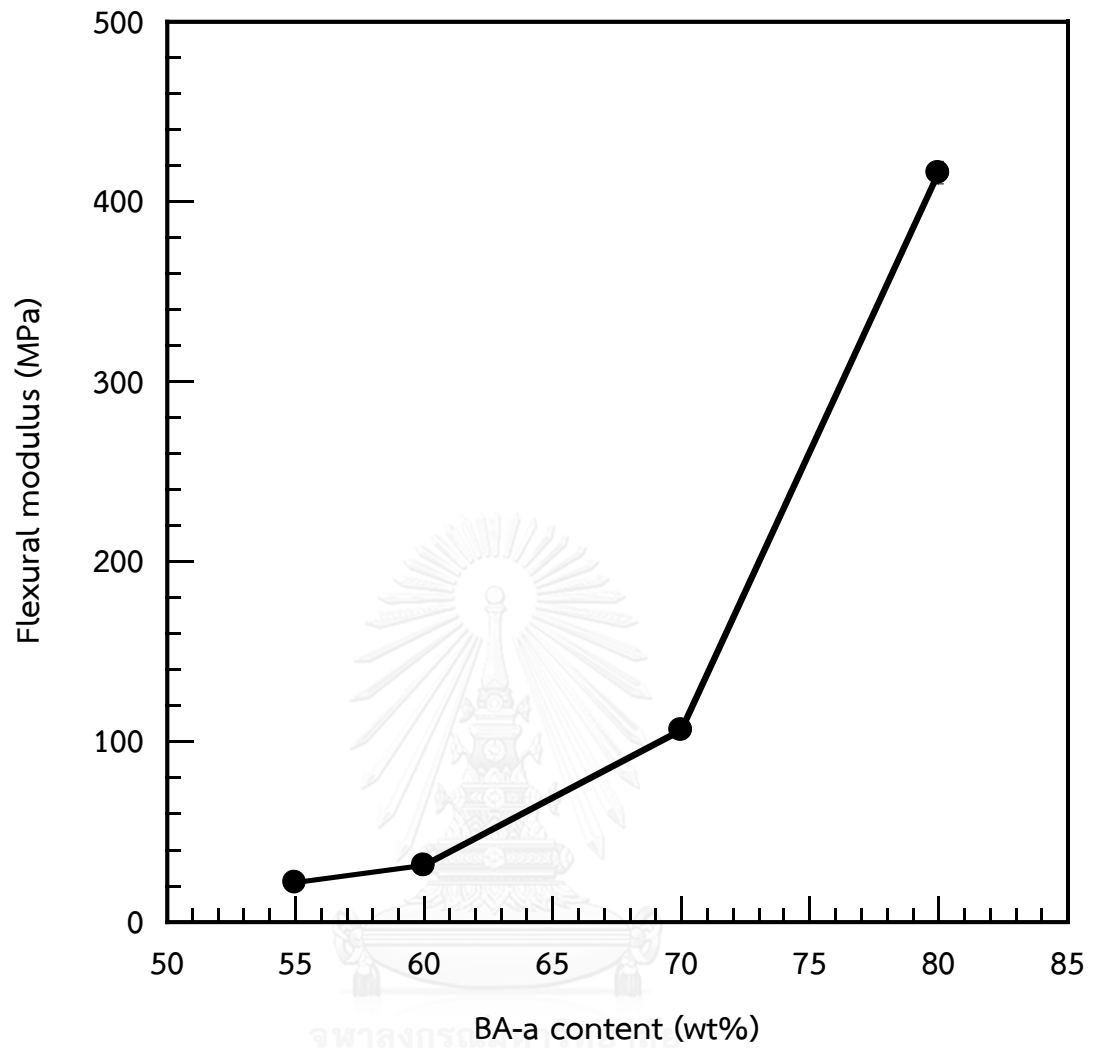


Figure 5.9 Flexural modulus at $T_g - 10^\circ\text{C}$ of benzoxazine-urethane multiple-SMP as a function of benzoxazine mass fraction at 55%, 60%, 70%, and 80%.

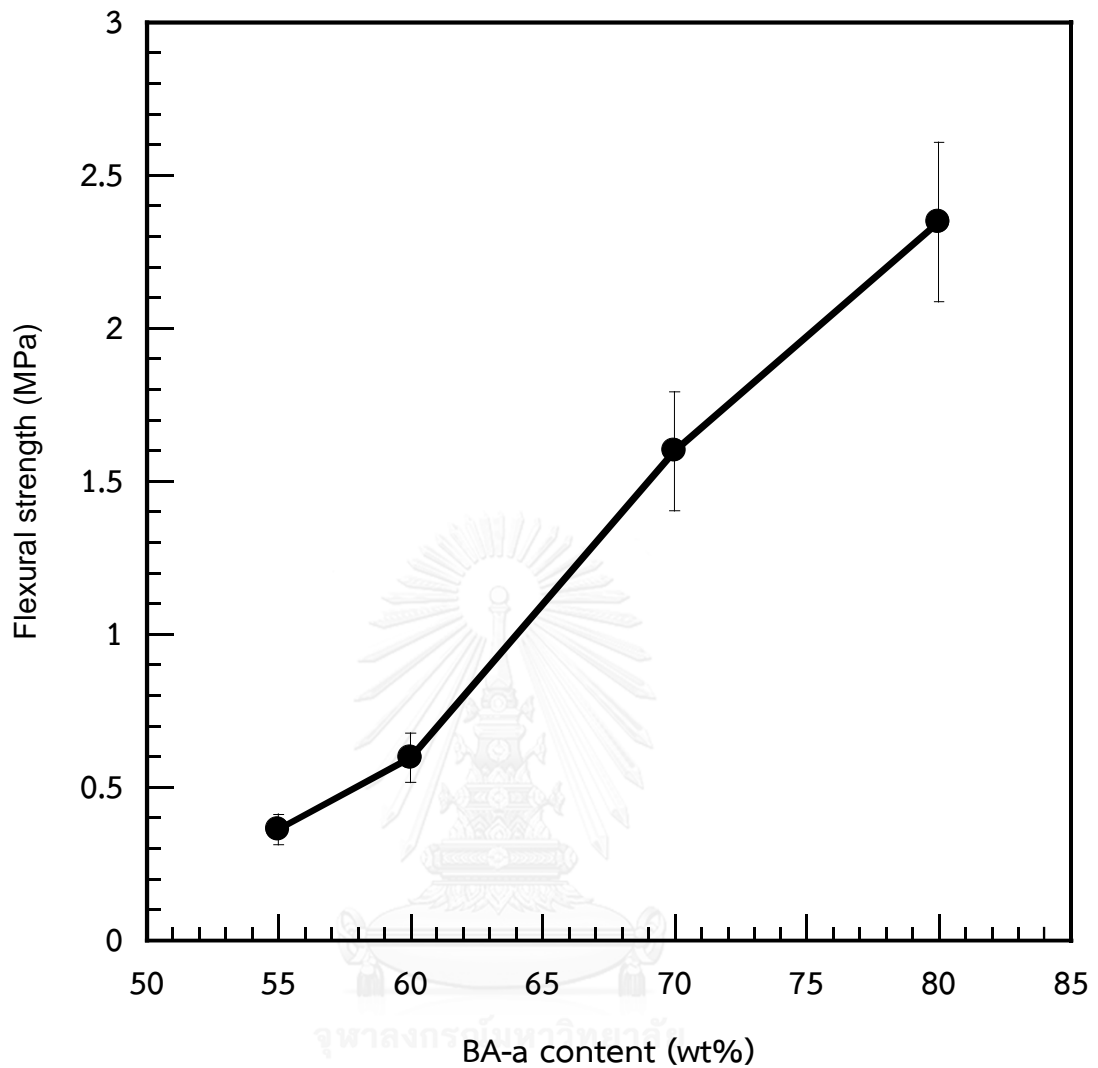


Figure 5.10 Flexural strength at $T_g + 10^\circ\text{C}$ of benzoxazine-urethane multiple-SMP as a function of benzoxazine mass fraction at 55%, 60%, 70%, and 80%.

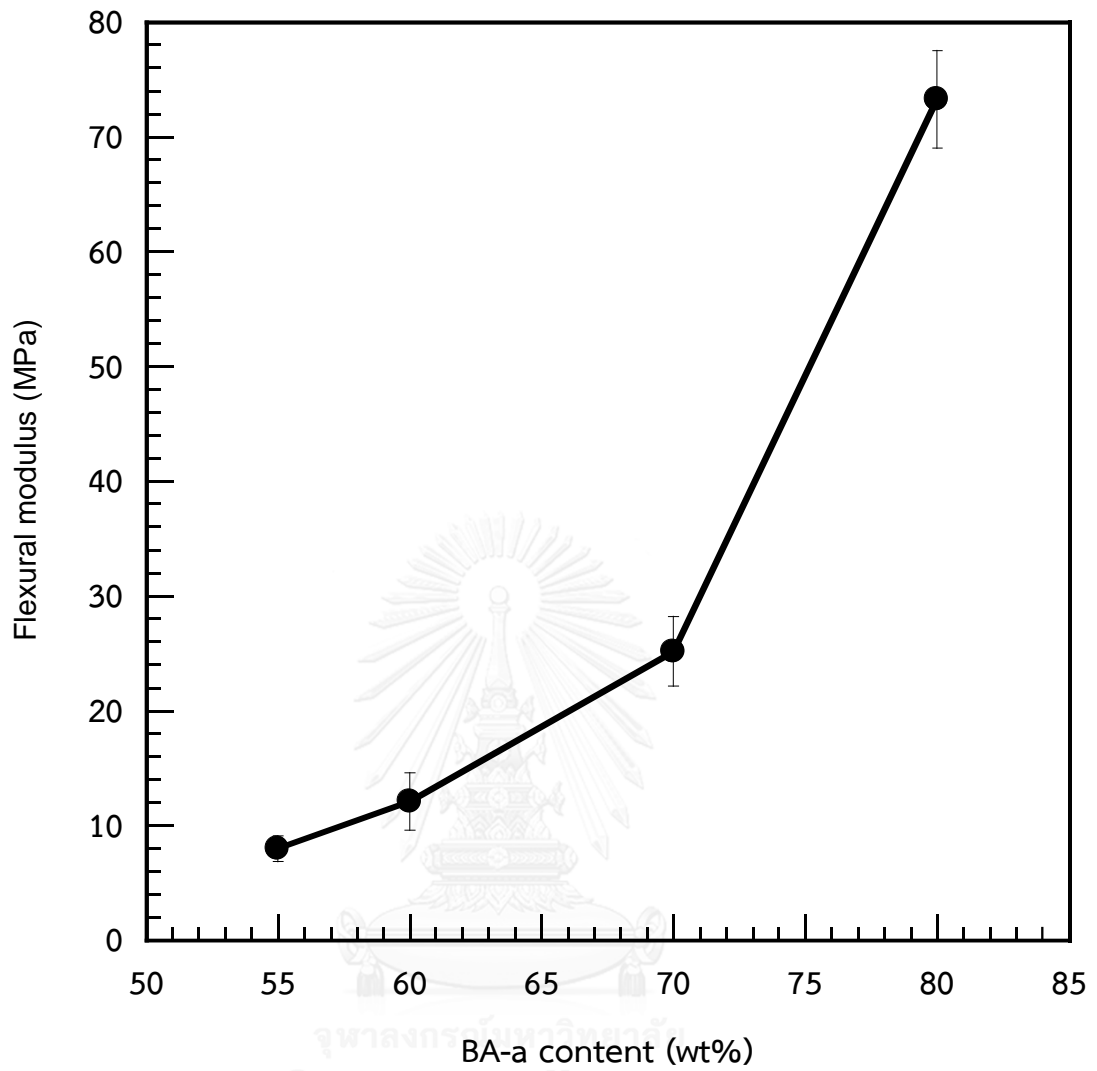


Figure 5.11 Flexural modulus at $T_g + 10^\circ\text{C}$ of benzoxazine-urethane multiple-SMP as a function of benzoxazine mass fraction at 55%, 60%, 70%, and 80%.

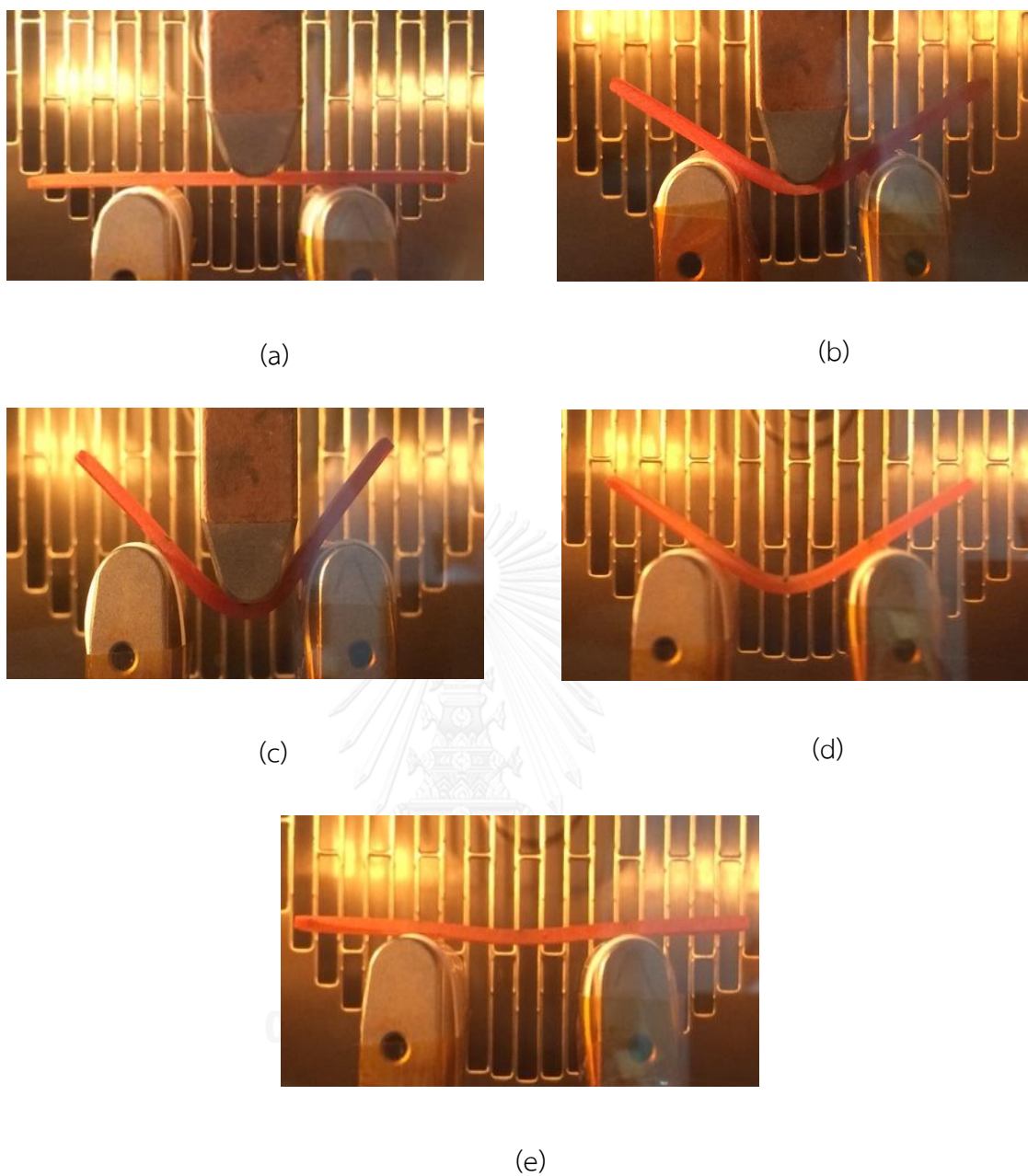


Figure 5.12 Photographs showing various states of bending in multiple-shape memory process for BA-a/PU samples: (a) original state of sample, (b), deformed state of first temporary shape at $T_g + 10^\circ\text{C}$, (c) deformed state of second temporary shape at $T_g - 10^\circ\text{C}$, (d) shape-recovered state to first temporary shape with reheating to $T_g - 10^\circ\text{C}$ and (e) shape-recovered state to original shape with reheating again to $T_g + 10^\circ\text{C}$.

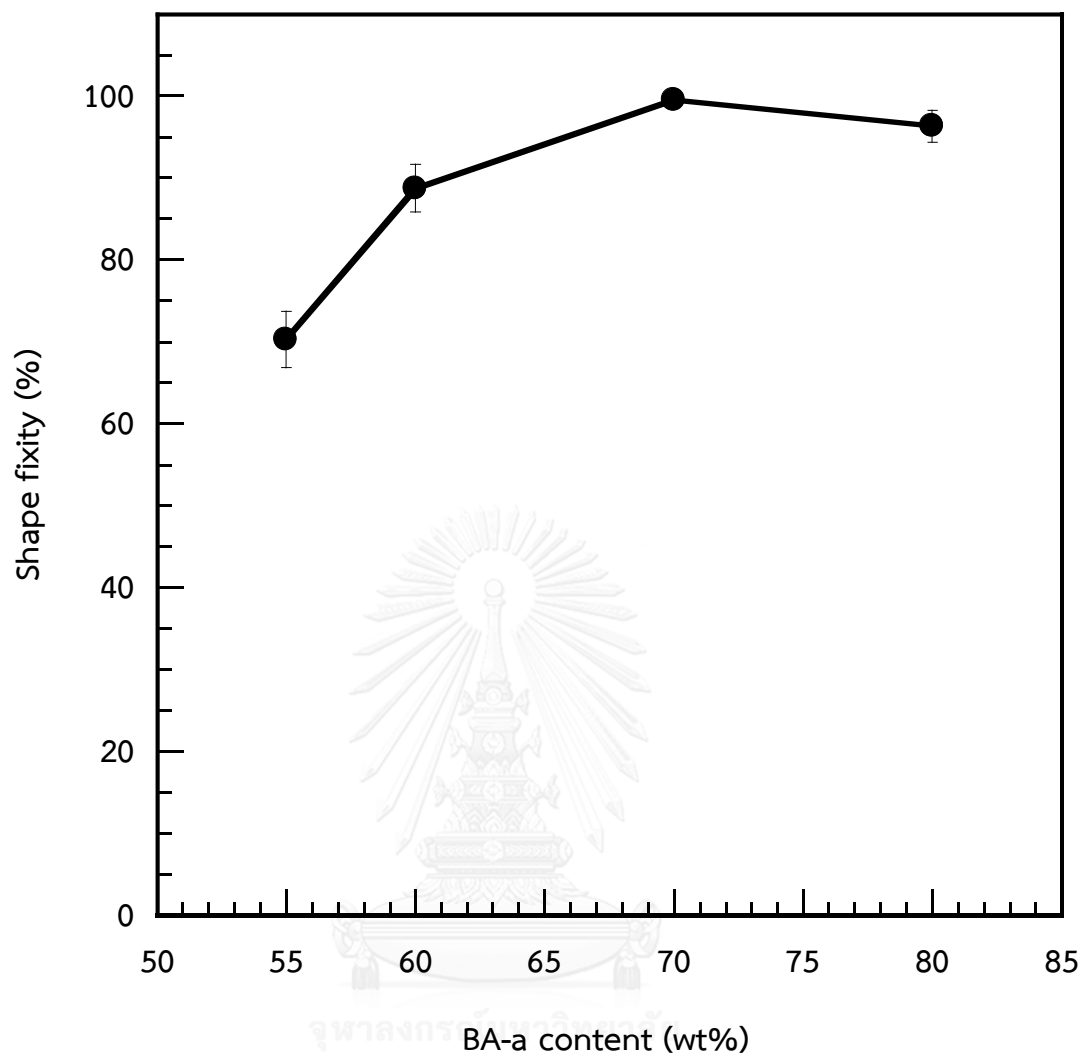


Figure 5.13 Shape fixity of the first temporary shape of benzaoxazine-urethane multiple-SMP at $T_g + 10^\circ\text{C}$ as a function of benzoxazine mass fraction at 55%, 60%, 70%, and 80%.

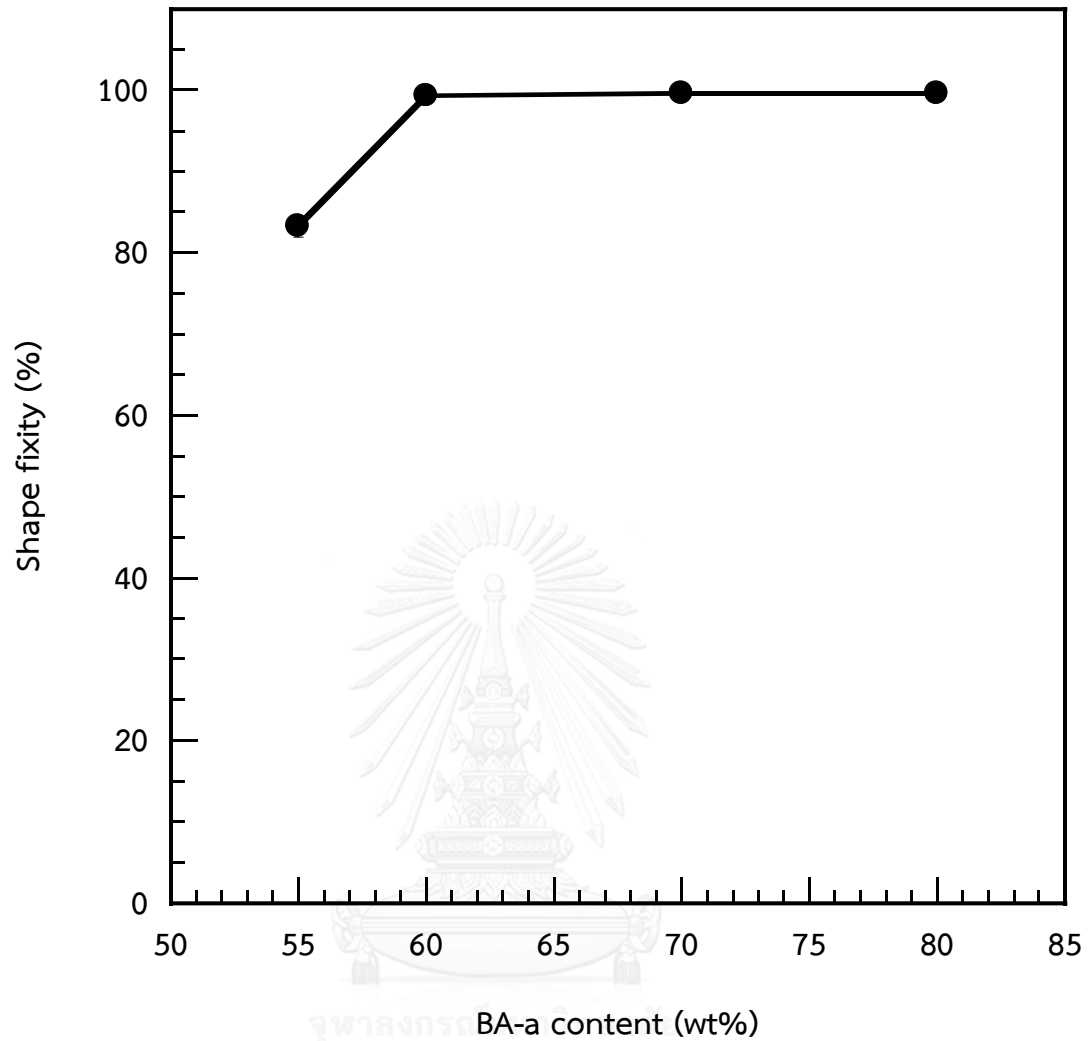


Figure 5.14 Shape fixity of the second temporary shape of benzaoxazine-urethane multiple-SMP at $T_g = 10^\circ\text{C}$ as a function of benzoxazine mass fraction at 55%, 60%, 70%, and 80%.

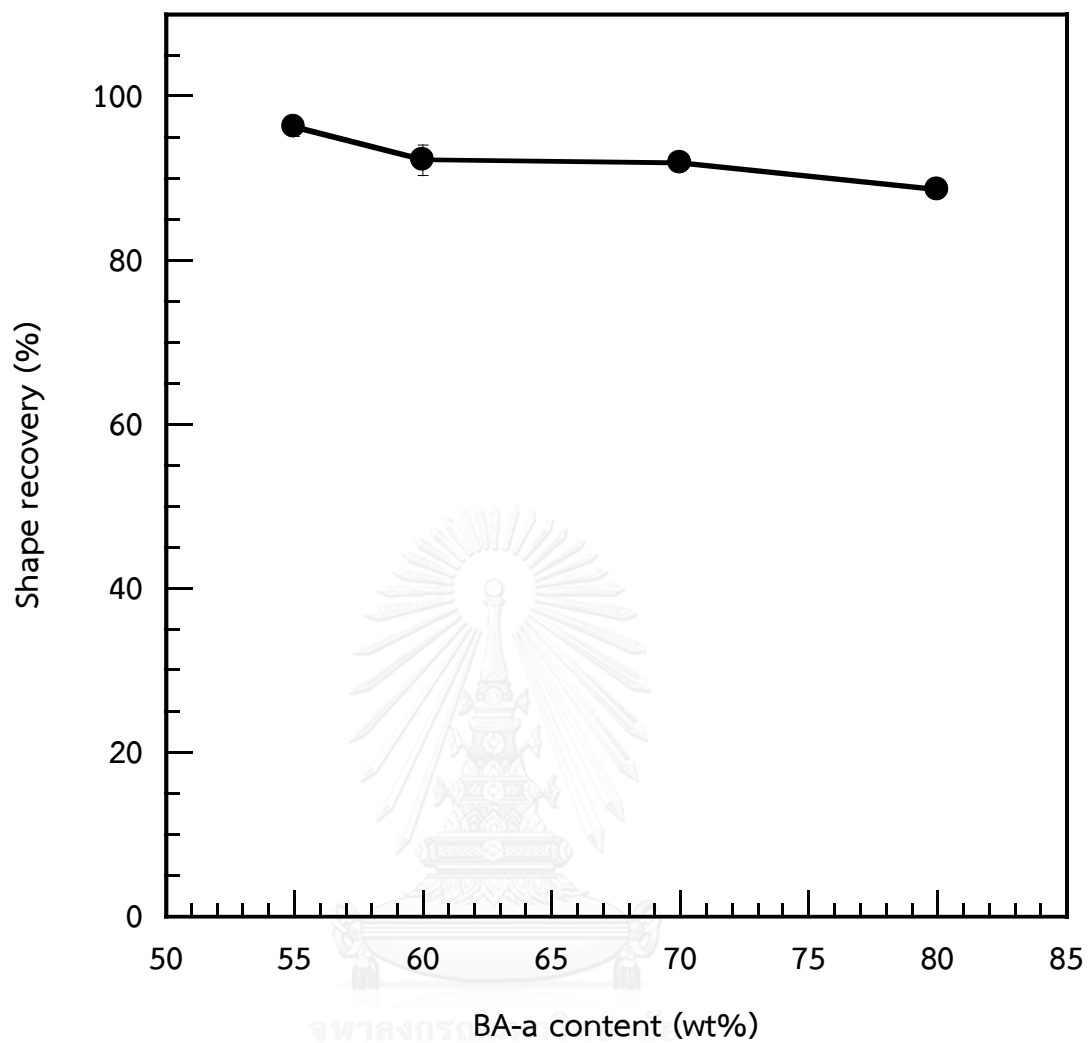


Figure 5.15 Shape recovery to the first temporary shape of benzaoxazine-urethane multiple-SMP at $T_g = 10^\circ\text{C}$ as a function of benzoxazine mass fraction at 55%, 60%, 70%, and 80%.

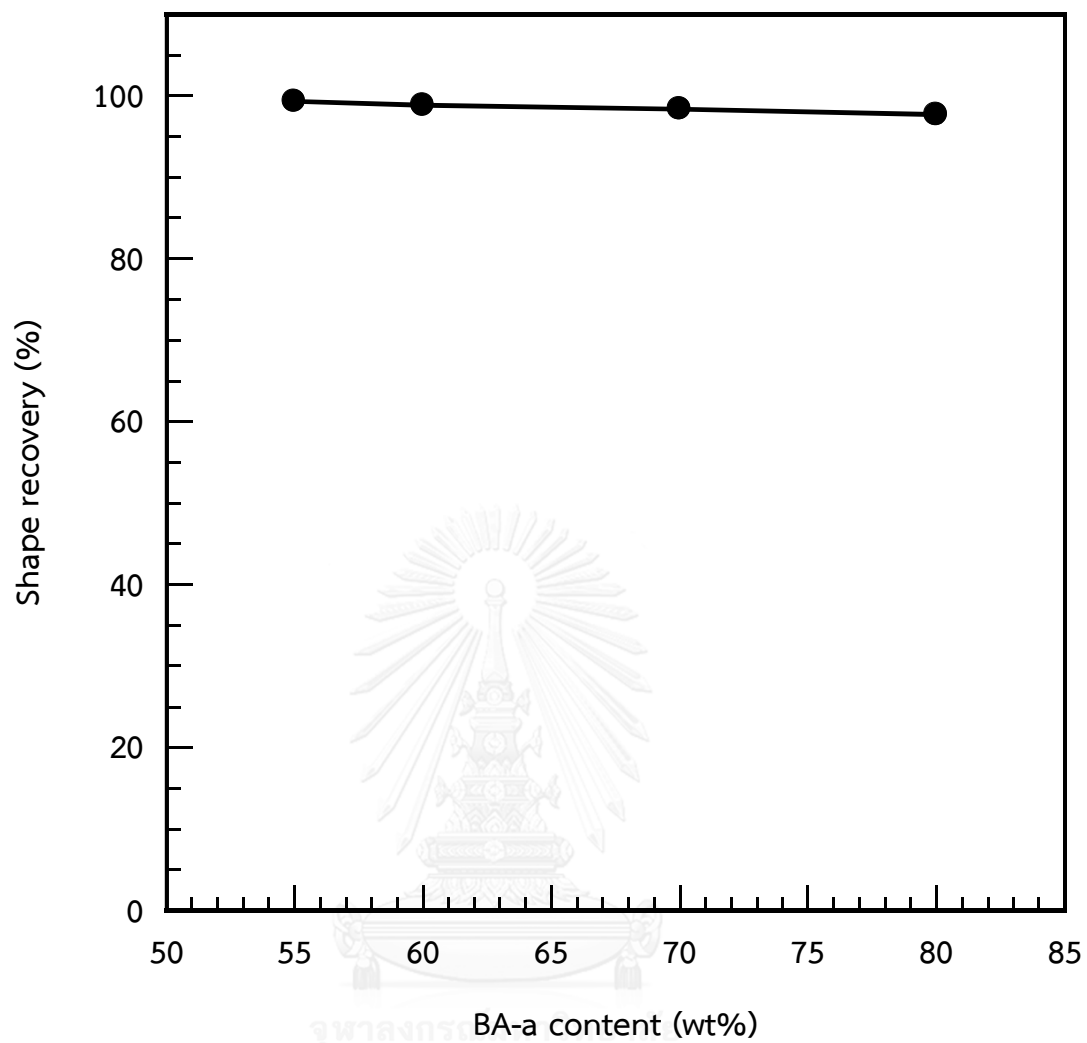


Figure 5.16 Shape recovery to the original shape of benzoxazine-urethane multiple-SMP at $T_g + 10^\circ\text{C}$ as a function of benzoxazine mass fraction at 55%, 60%, 70%, and 80%.

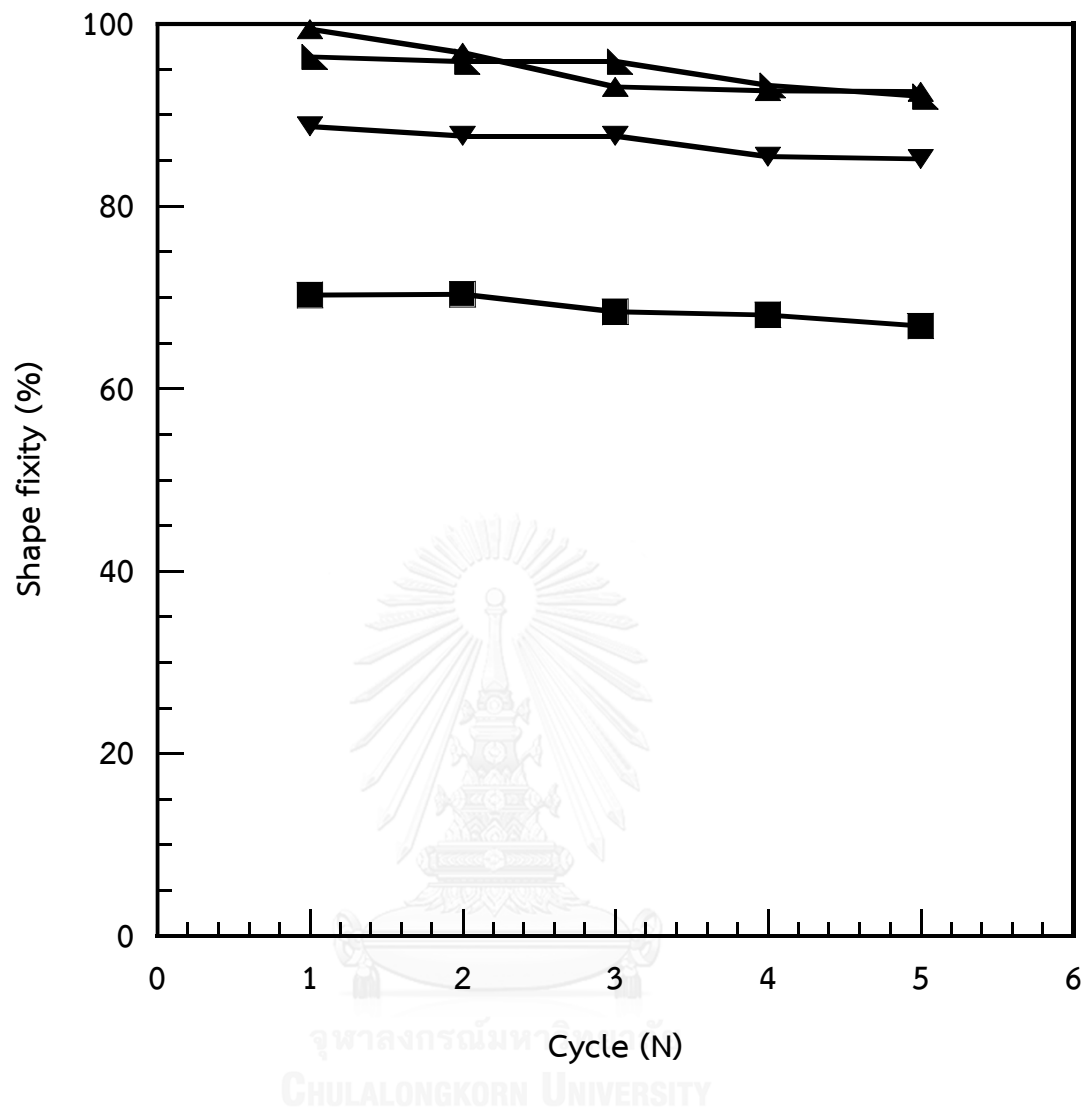


Figure 5.17 Shape fixity of first temporary shape versus deformation cycle at $T_g + 10^\circ\text{C}$ at various BA-a:PU mass ratios: (▲) 80:20, (▲) 70:30, (▼) 60:40, and (■) 55:45.

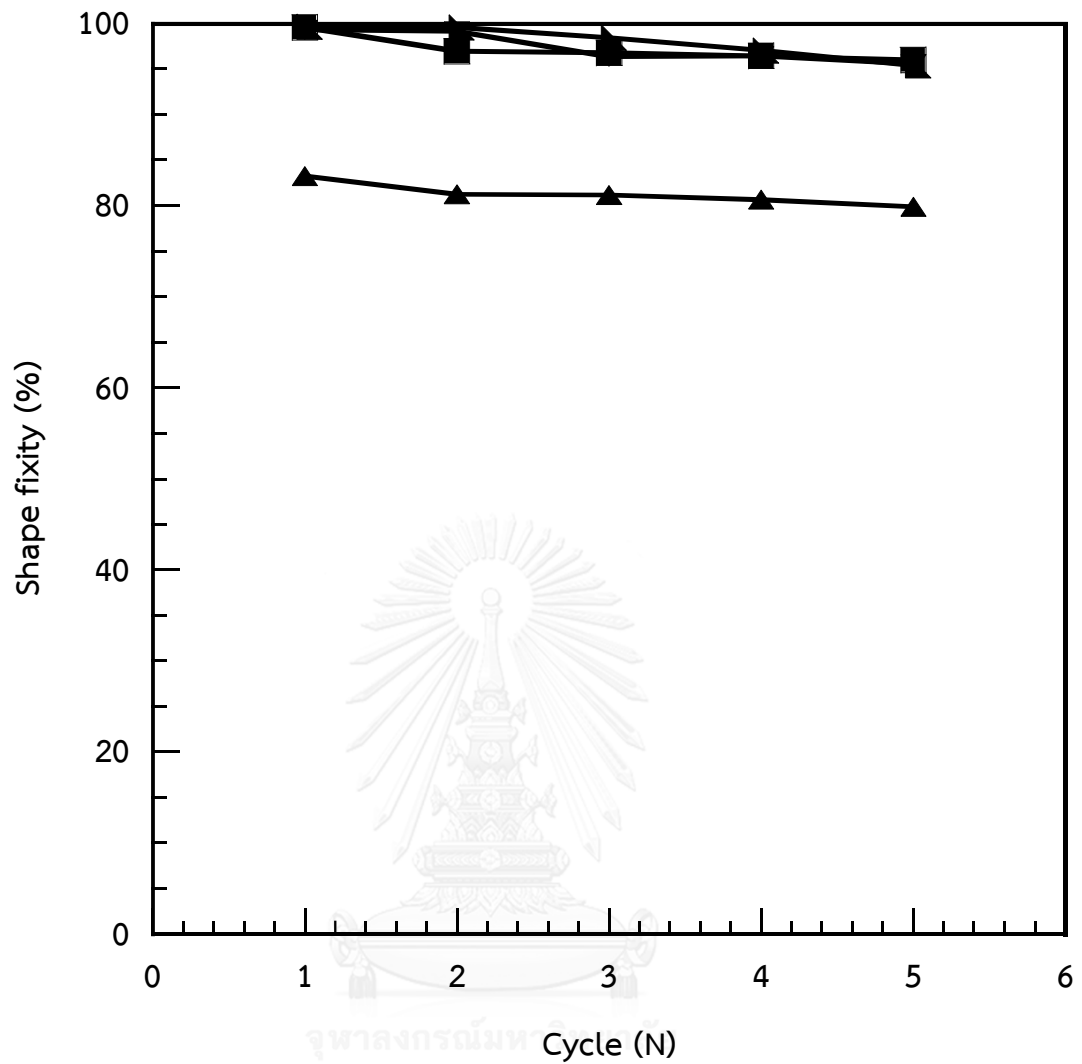


Figure 5.18 Shape fixity of second temporary shape versus deformation cycle at $T_g - 10^\circ\text{C}$ at various BA-a:PU mass ratios: (▲) 80:20, (▲) 70:30, (▼) 60:40, and (■) 55:45.

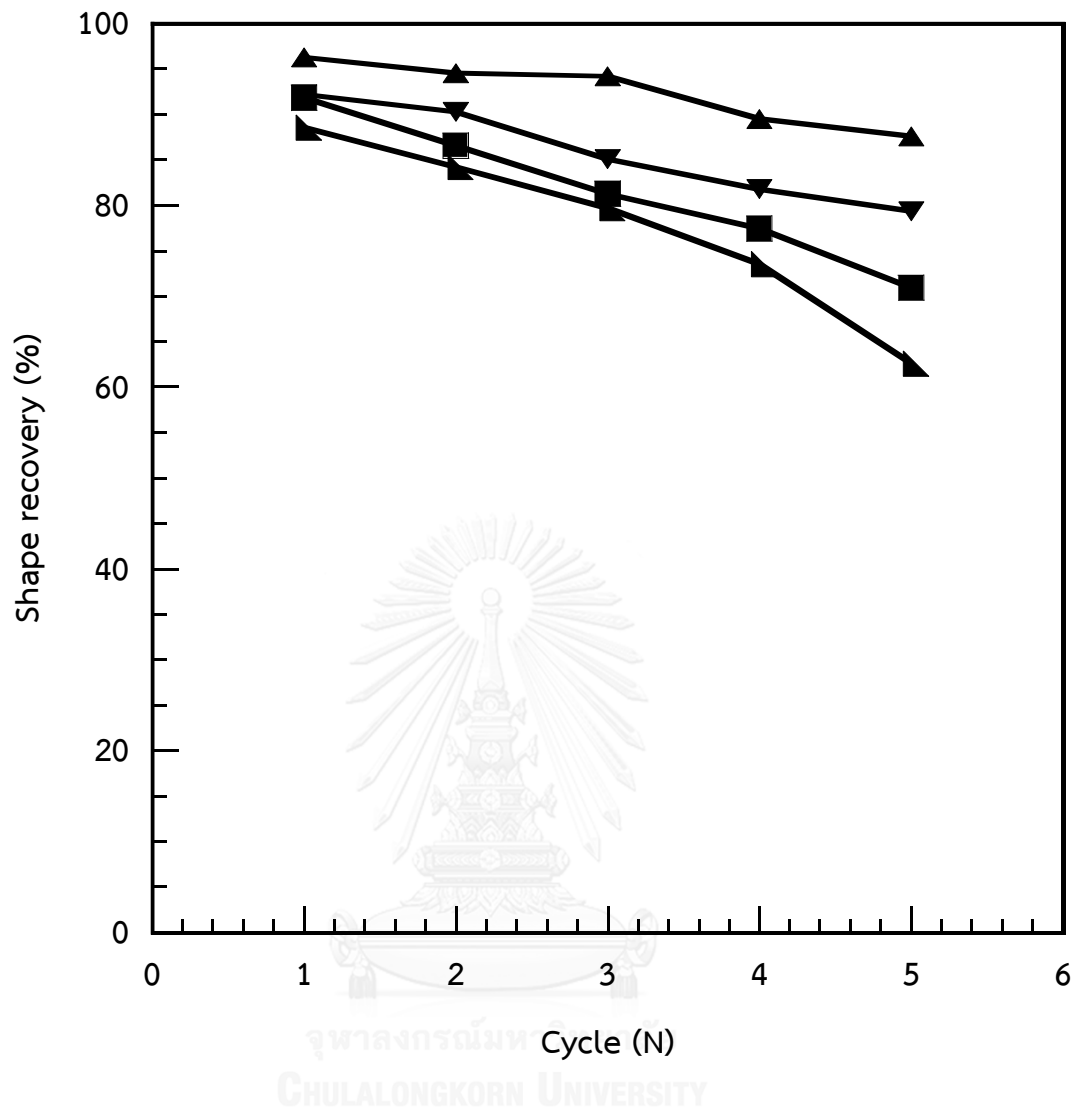


Figure 5.19 Shape recovery to first temporary shape versus deformation cycle at $T_g - 10^\circ\text{C}$ at various BA-a:PU mass ratios: (\blacktriangle) 80:20, (\blacktriangledown) 70:30, (\blacksquare) 60:40, and (\blacksquare) 55:45.

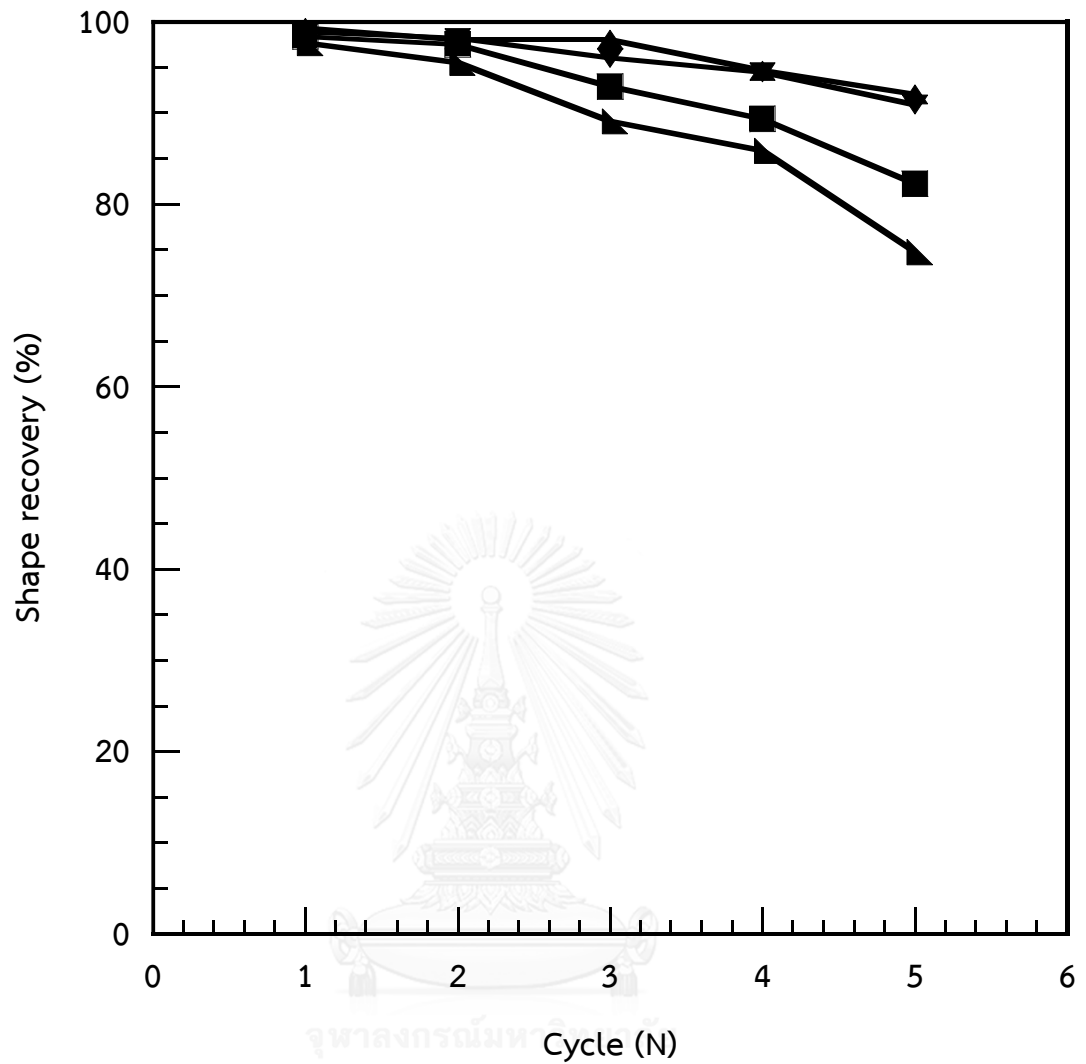


Figure 5.20 Shape recovery to original shape versus deformation cycle at $T_g + 10^\circ\text{C}$ at various BA-a:PU mass ratios: (\blacktriangleleft) 80:20, (\blacktriangleright) 70:30, (\blacktriangledown) 60:40, and (\blacksquare) 55:45.

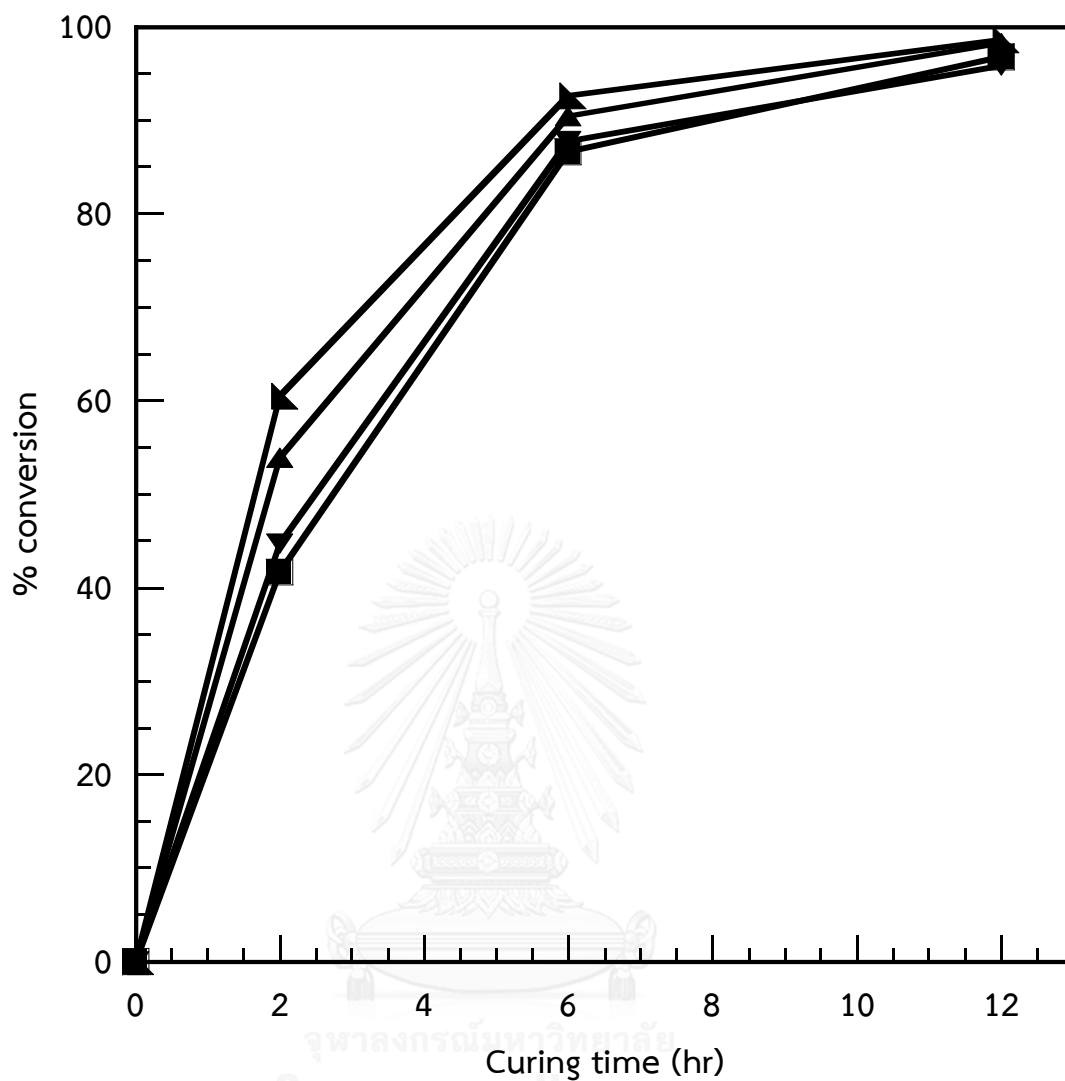


Figure 5.21 Relationship of degree of conversion versus curing time at 170°C of benzoxazine-urethane multiple-SMP at various BA-a:PU mass ratios: (▲) 80:20, (▲) 70:30, (▼) 60:40, and (■) 55:45.

CHAPTER VI

CONCLUSIONS

The binary system of benzoxazine-urethane copolymers based multiple-shape memory polymer (multiple-SMP) was developed to be used in a wider range of multiple-shape memory applications. In this research, effect of urethane prepolymer filled in benzoxazine resin on curing behavior, thermal stability, mechanical properties, and multiple-shape memory properties were investigated.

In the study of multiple-shape memory properties, benzoxazine-urethane copolymers at BA-a:PU mass ratio of 55:45, 60:40, 70:30, and 80:20 were successfully demonstrated to possess multiple-shape memory behaviors. The BA-a/PU multiple-SMPs showed excellent shape fixity values of 70-96% for first temporary shape and 83-99% for second temporary shape. In parts of shape recovery, the multiple-SMPs also provided outstanding values of 88-96% for first temporary shape and 97-99% for original shape by increasing of amount of BA-a resin. However, the original shape was deformed to other temporary shapes with the width range of broad glass transition temperature that observed from the width range of loss tangent. Interestingly, the BA-a:PU multiple-shape memory samples can be deformed for 5 cycles. From these results, the obtained benzoxazine-urethane multiple-SMPs are attractive as a good candidate for multiple-shape memory materials to be used in a wide range of applications.

Furthermore, the appropriate curing conversion about 70% was sufficient for benzoxazine-urethane binary system behaves as multiple-SMPs. In addition, glass transition temperature and thermal stability were found to systematically increase with increasing BA-a content. Furthermore, the flexural strength and flexural modulus at room temperature, $T_g - 10^\circ\text{C}$ and $T_g + 10^\circ\text{C}$ were also found to increase with increasing BA-a content.





APPENDIX

Characterization of Benzoxazine-Urethane Multiple-SMP Samples

Appendix A Glass transition temperature and broad glass transition temperature of benzoxazine-urethane multiple-SMP samples at various mass content from loss tangent of DMA analysis.

BA-a:PU mass content	Glass transition temperature (°C)	Broad glass transition temperature (°C)
55:45	130	80 to 180
60:40	135	90 to 180
70:30	157	100 to 214
80:20	180	120 to 220

Appendix B Flexural strength and flexural modulus of benzoxazine-urethane multiple-SMP samples at various mass content at room temperature, $T_g - 10^\circ\text{C}$ and $T_g + 10^\circ\text{C}$.

BA-a:PU mass content	At room temperature		At $T_g - 10^\circ\text{C}$		At $T_g + 10^\circ\text{C}$	
	Flexural strength (MPa)	Flexural modulus (GPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)
55:45	40.7±1.6	1.0±0.04	1.1 ± 0.02	21.4 ± 0.5	0.3 ± 0.04	7.9 ± 1.1
60:40	68.5±1.8	1.4±0.03	1.8 ± 0.2	31.2 ± 4.7	0.5 ± 0.1	12.1 ± 2.5
70:30	73.9±3.7	2.1±0.1	4.6 ± 0.1	106.3 ± 4.6	1.6 ± 0.2	25.1 ± 3.0
80:20	98.1±7.4	3.7±0.4	9.0 ± 0.1	415.7 ± 6.2	2.3 ± 0.2	73.2 ± 4.2

Appendix C Multiple-shape fixity of benzoxazine-urethane multiple-SMP samples at various mass content at $T_g + 10^\circ\text{C}$ for first temporary shape and $T_g - 10^\circ\text{C}$ for second temporary shape.

BA-a:PU mass content	First temporary shape fixity at $T_g + 10^\circ\text{C}$	Second temporary shape fixity at $T_g - 10^\circ\text{C}$
55:45	70.2 ± 3.4	83.2 ± 1.2
60:40	88.7 ± 2.8	99.2 ± 0.2
70:30	99.4 ± 0.5	99.5 ± 0.2
80:20	96.3 ± 1.9	99.6 ± 0.3

Appendix D Multiple-shape recovery of benzoxazine-urethane multiple-SMP samples at various mass content at $T_g - 10^\circ\text{C}$ for first temporary shape and $T_g + 10^\circ\text{C}$ for original shape

BA-a:PU mass content	First temporary shape recovery at $T_g - 10^\circ\text{C}$	Original shape recovery at $T_g + 10^\circ\text{C}$
55:45	96.2 ± 1.1	99.2 ± 0.1
60:40	92.1 ± 1.8	98.8 ± 0.9
70:30	91.8 ± 0.9	98.3 ± 0.4
80:20	88.5 ± 0.2	97.6 ± 1.0

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