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EFFECTS OF CARBON FIBER AND GLASS FIBER ON SHAPE MEMORY POLYMERS BASED
ON BENZOXAZINE-EPOXY BINARY SYSTEMS



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

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ความเค้นในการคืนรูปเป็นหนึ่งในตัวแปรที่สำคัญมากของพอลิเมอร์จำรูปร่างโดยทั่วไปวิธีที่ง่ายในการเพิ่มความเค้นในการคืนรูปในพอลิเมอร์จำรูปร่าง คือ การเสริมแรงเพื่อทำเป็นวัสดุคอมพอสิต เช่น การเสริมแรงด้วยเส้นใยคาร์บอนและเส้นใยแก้ว งานวิจัยนี้ได้ศึกษาผลของเส้นใยคาร์บอนและเส้นใยแก้วต่อพอลิเมอร์จำรูปร่างของเบนซอกซาซีน-อีพอกซีต่อสมบัติทางความร้อน สมบัติทางกล และสมบัติการจำรูปร่างได้จากพอลิเมอร์ โดยองค์ประกอบของเส้นใยคาร์บอนและเส้นใยแก้วที่เสริมเข้าไปอยู่ในช่วงตั้งแต่ 30 ถึง 50 เปอร์เซ็นต์โดยปริมาตร การขึ้นรูปวัสดุคอมพอสิตเพื่อทดสอบสมบัติต่าง ๆ ทำได้โดยผสมเบนซอกซาซีน-อีพอกซีเป็นพอลิเมอร์เมทริกซ์ และเสริมแรงด้วยเส้นใยคาร์บอนและเส้นใยแก้ว ใช้ความดันและอุณหภูมิจากเครื่องขึ้นรูปแบบอัด คือ 10 เมกะปาสคาล และ 170 องศาเซลเซียส ตามลำดับ เวลาในการขึ้นรูปแบบอัด คือ 3 ชั่วโมง จากผลการทดลองพบว่า อุณหภูมิการเปลี่ยนสถานะคล้ายแก้วสูงขึ้นเมื่อลดอัตราส่วนการเสริมแรงด้วยเส้นใย โดยมีอุณหภูมิการเปลี่ยนสถานะคล้ายแก้วสูงสุดที่ 162 องศาเซลเซียส ที่ปริมาณเส้นใยคาร์บอน 30 เปอร์เซ็นต์โดยปริมาตร เมื่อเพิ่มอัตราส่วนการเสริมแรงด้วยเส้นใยจะทำให้มีค่ามอดูลัสสะสม รวมถึงมอดูลัสภายใต้แรงดัดโค้ง และค่าความแข็งแรงภายใต้แรงดัดโค้งสูงขึ้น เมื่อนำวัสดุคอมพอสิตมาทดสอบสมบัติการจำรูปร่าง พบว่ามีค่าการคงรูปร่างมากกว่า 85 เปอร์เซ็นต์ ค่าการคืนรูปร่างเดิม มากกว่า 96 เปอร์เซ็นต์ และเวลาในการคืนรูปอยู่ในช่วง 1.71 ถึง 121.2 วินาที ทำให้มีช่วงเวลาที่กว้างเพื่อการใช้งานที่หลากหลาย นอกจากนี้การเสริมแรงด้วยเส้นใยคาร์บอนให้ค่าความเค้นในการคืนรูปสูงถึง 138.8 เมกะปาสคาลที่ปริมาณเส้นใยคาร์บอน 30 เปอร์เซ็นต์โดยปริมาตร จึงมีความน่าสนใจที่จะนำวัสดุคอมพอสิตที่พัฒนาขึ้นไปประยุกต์ใช้ในงานประยุกต์ขั้นสูง เช่น บานพับ และ โครงสร้างที่พับได้ เป็นต้น

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Recovery stress is an important parameter of shape memory polymers.

Generally, recovery stress in SMPs can be enhanced by using fiber reinforced composites with suitable reinforcing agents such as carbon fiber or glass fiber. We aim to study effects of carbon fiber and glass fiber on thermal, mechanical, and shape memory properties of benzoxazine-epoxy SMPs, particularly on recovery stress enhancement. The compositions of carbon fiber and glass fiber reinforced benzoxazine-epoxy SMPs were in a range of 30 to 50vol%. The carbon fiber and glass fiber reinforced benzoxazine-epoxy shape memory polymer was compression-molded at 170°C under a pressure of 10 MPa for 3 hours. The experimental results revealed that glass transition temperature of the composite samples increased with decreasing fiber contents. The maximum glass transition temperature of benzoxazine-epoxy SMPs was 162°C at 30vol% of the carbon fiber. In addition, storage modulus, flexural strength, and flexural modulus values of the SMP specimens increased with increasing carbon and glass fiber contents. Benzoxazine-epoxy SMPs exhibited shape fixity and shape recovery values more than 85% and 96%, respectively. The recovery time of benzoxazine-epoxy SMPs was in a range of 1.71 to 121.2 seconds. Furthermore, the carbon fiber reinforced benzoxazine-epoxy SMPs provides outstandingly high recovery stress up to 138.8 MPa at 30vol% of the carbon fiber. These results suggested potential usages of these materials in advanced applications, such as hinge or deployable structure.

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CHAPTER I

INTRODUCTION

1.1 Overview

Shape memory polymers (SMPs) are smart materials that can be applied for varieties of applications. SMPs have an ability to recover their original shape upon receiving an external stimulation such as mechanical force, electric current, magnetic field, light induction, pH, and temperature change [1, 2]. There are many advantages of SMPs when compared to shape memory metal alloy (SMA), such as high percentage of strain with over 200%, low cost, low density, ease of processing, simple design, good manufacturability, and high shape deformability [3]. SMPs can be deformed at the temperature above the transition temperature (T_{trans}). They can maintain this temporary shape when temperatures are below T_{trans} . SMPs are able to change to its original shape when they are heated up above T_{trans} again [4].

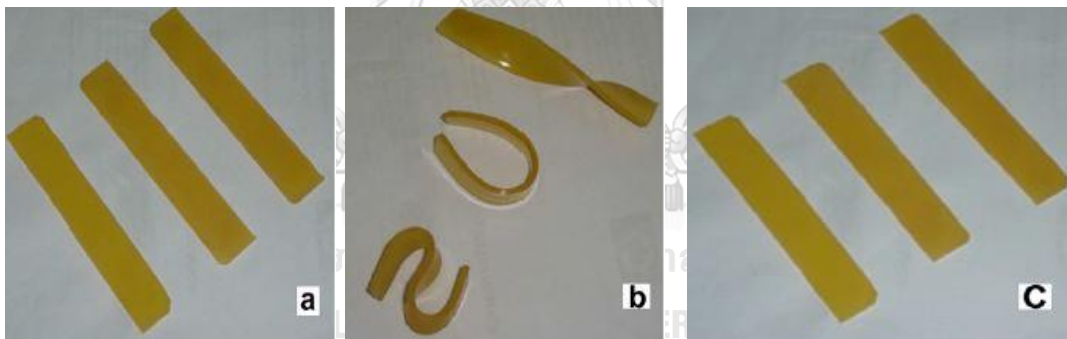


Figure 1.1 Shape memory properties of cyanate ester-epoxy-poly(tetramethylene-oxide) co-reacted (CEP)-38 (a) original/permanent shapes, (b) fixed temporary shapes and (c) recovered shapes [5].

Nowadays, the thermoset-type SMPs (TS-SMPs) have attracted academic and research attention because they exhibit superior properties when compared to thermoplastics-type SMPs (TP-SMPs), such as higher chemical resistance, a greater storage modulus, a higher glass transition temperature, and chemical cross-linking capabilities [6]. Epoxy resin is one of the most popular thermosets that has been used in structures and can be applied for extreme applications. Shape memory epoxies

possess excellent shape memory performance. Shape memory epoxies were earned a special mention among various SMPs such as polyurethane, polynorbornene, cross-linked polyethylene, styrene rubbers, and acrylate systems as they are unique thermoset shape memory polymer systems [7]. SMPs fabricated from aromatic epoxy, aliphatic epoxy, and curing agent (Jeffamine D230) showed high percentage of shape fixity and nearly 100% shape recovery [8].

Polybenzoxazine (PBA-a) is a new type of thermosetting polymers. The PBA-a has excellent properties, such as high thermal stability, simple processability, low water absorption, almost near zero shrinkage and no by-product upon curing, and high glass transition temperature. Benzoxazine resin (BA-a) can be synthesized by a solventless method from bisphenol A, paraformaldehyde, and aniline [9]. BA-a can also be used as a curing agent of epoxy. In addition, copolymers from benzoxazine and epoxy showed enhanced mechanical properties [10].

In principle, recovery stress is defined as the stress required to maintain the sample from shape recovery during heating [9]. The recovery stress for shape memory polymers are lower than those of shape memory alloys because SMPs have rather low modulus and strength, especially in the rubbery state [7]. This characteristic limits their use for many advanced applications, for example self-deployable structure and morphing of aircraft wings. Thus, to obtain higher recovery stress, SMP's stiffness or their elastic modulus have to be increased. This could be accomplished by incorporating more rigid molecular moieties into the SMP structure [11, 12], providing mesomorphic characteristics to SMPs [13], enhancing cross-linking density of the SMPs, and including reinforcing fillers, e.g. carbon nanotubes, carbon fibers, and glass fibers to improve recovery stress [4, 14-17].

S. Rimdusit *et al.* (2013) developed shape memory copolymers based on benzoxazine resin (BA-a), aliphatic-aromatic epoxy mixtures, and Jeffamine D230 as the epoxy curing agent. Enhanced thermo-mechanical performances of the epoxy SMPs was achieved by an addition of the BA-a resin. The incorporation of the BA-a into epoxy

shape memory copolymers promoted higher cross-linking density, higher storage modulus in the glassy state. Flexural strength and flexural modulus at room temperature were also enhanced. Their recovery stress were increased with increasing BA-a content up to 33% by mole with the reported recovery stress of 38 kPa, comparing with 20.4 kPa of the unmodified shape memory epoxy [18]. Tanpitaksit *et al.* (2014) investigated SMPs from binary mixtures based on benzoxazine-modified aliphatic epoxy. They showed good thermo-mechanical and outstanding shape memory properties. The highest value of the recovery stress of these binary benzoxazine-epoxy mixtures up to 1.59 MPa was reported [11].

In general, The most common method for increasing elastic modulus and recovery stress in SMPs is to reinforce in the polymer matrix but shape memory composite (SMPC) is reinforced with particles or short fibers cannot be used as structural materials, as the improvement in their mechanical properties is quite limited and their strength and stiffness remain low [19, 20]. In contrast, continuous fiber-reinforced SMPs offered significant improvements in both strength and stiffness, providing excellent mechanical properties. As both functional and structural materials, these SMPs were promising for many advanced applications [20]. When used as actuator materials, they required no moving parts. Fiber-reinforced SMPs were also demonstrated in deployable structures including antennas, trusses, and solar arrays [20]. Fejos *et al.* (2012) studied shape memory characteristics of a woven glass fabric reinforced epoxy composite. Recovery stress (RS) of the composites reinforced with woven glass fibers increased to 42.33 MPa, which was higher than that of the composites without glass fibers (i.e. 0.44 MPa) [16]. Furthermore, Bin Hong *et al.* (2015) studied woven carbon fiber reinforced shape memory polymer composites. The recovery stress of the composites increased with reinforcing woven carbon fibers [21].

Consequently, the purposes of this research is to study effects of woven carbon fibers and woven glass fibers on recovery stress of SMPs based on benzoxazine (BA-a)/epoxy alloys in order to broaden their applications. It was expected that the outstanding mechanical properties of reinforcing fibers might contribute to the substantial enhancement of the recovery stress of the obtained SMPs. Some essential

properties of the SMPs, such as glass transition temperature, flexural modulus, flexural strength, shape recovery performances, and recovery stress were also investigated.

1.2 Objectives

1. To develop woven carbon fiber and glass fiber reinforced benzoxazine-epoxy SMPs for recovery stress enhancement.
2. To evaluate effects of woven carbon fibers and glass fibers on shape memory properties, thermal properties, and mechanical properties of shape memory polymers based on binary system of aliphatic epoxy and benzoxazine resin.

1.3 Scope of the study

1. Synthesis of BA-a typed benzoxazine resin by solventless synthesis technology.
2. Preparation of shape memory polymers based on benzoxazine resin (B)-cured aliphatic epoxy (E) at molar ratios (B:E) of 50:50.
3. Determination of the appropriate matrix contents of woven carbon fibers (CF) and glass fibers (GF) in benzoxazine-epoxy shape memory polymers (SMPs).
4. Determination the optimum number of layers of woven carbon fiber and glass fiber to behave shape memory properties.
5. Study effects of substitution of woven carbon fiber (CF) and glass fiber (GF) for shape memory polymers behavior.
6. Property evaluation of woven carbon fiber and glass fiber reinforced benzoxazine-epoxy SMPs as follows.

6.1 Physical properties

- Density of composites by Density kit

6.2 Thermal properties

- Curing behaviors by Differential scanning calorimeter (DSC)

6.3 Mechanical properties

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

6.4 Shape memory properties

- Shape fixity ratio
- Shape recovery ratio
- Recovery time
- Recovery stress

1.4 Procedure of the study

1. Reviewing related literatures.
2. Preparation of chemicals and equipment to be used in this research.
3. Synthesis of benzoxazine resins (BA-a) by solventless technique.
4. Preparation of benzoxazine-epoxy shape memory polymers.
5. Preparation of woven carbon fiber (CF) and glass fiber (GF) reinforced benzoxazine (BA-a)-epoxy binary systems.
6. Determine properties of the composites as follow:
 - 6.1 Physical properties: Interfacial bonding of composites.
 - 6.2 Thermal properties: glass transition temperature and curing temperature of composites
 - 6.3 Mechanical properties: flexural strength and flexural modulus
 - 6.4 Shape memory properties: shape fixity ratio, shape recovery ratio, recovery time and recovery stress.
7. Analysis of the experimental results.
8. Preparation of the final report.

CHAPTER II

THEORY

2.1 Shape memory polymers

Shape memory materials (SMMs) represent a technologically important class of stimuli-responsive materials for which the response lies in the shape change 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 [21].

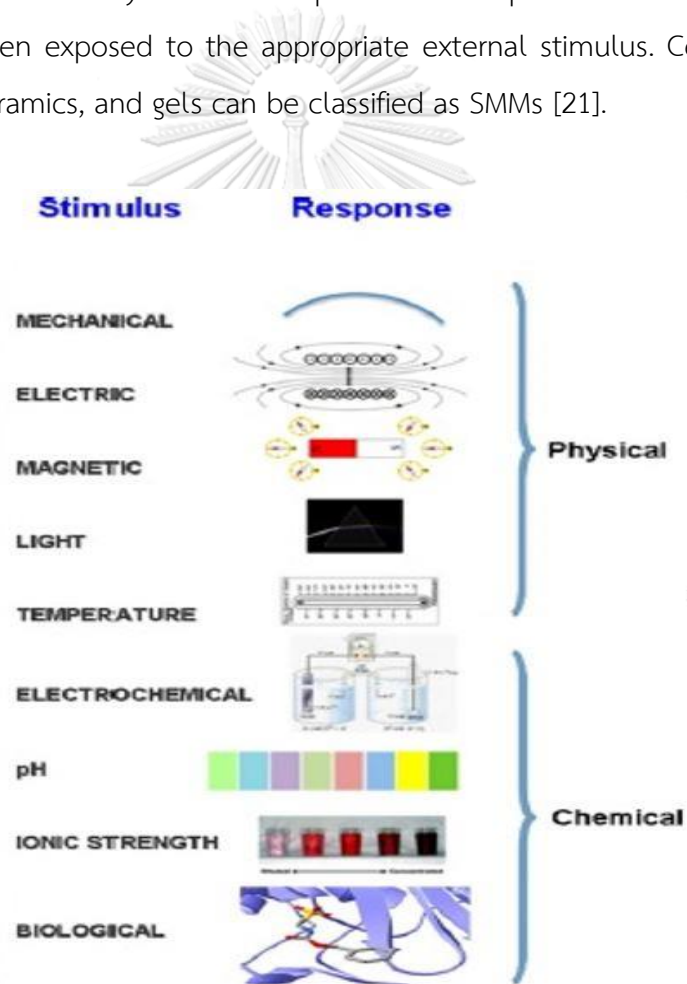


Figure 2.1 Physical and chemical stimulations [14].

All SMMs, shape memory alloys (SMAs) and shape memory polymers (SMPs) are the most widely studied shape memory materials. More specifically, the conventional definition of shape memory polymers (SMPs) are polymeric materials

that have an ability to recover their original shape when receiving an external physical or chemical stimulus, such as temperature change, electricity, light induction, mechanical force, magnetic field, or even pH variation [1, 2]. Accordingly, the associated behavior of SMP is called shape memory effect (SME) [2]. The external physical or chemical response as shown in Figure 2.1.

The SMPs draw attention from many researchers due to their excellent properties, ease in fabrication, and low density. When compared with shape memory alloys, the SMPs possess greater benefits, such as higher process ability, higher elastic deformation with over 200% of the strain, lower cost, and it is easier to adjust the transition temperature to suit applications [7]. Figure 2.2 illustrate some comparison of mechanical properties among some typical materials, where SMPs perform a large strain but a relatively low stress.

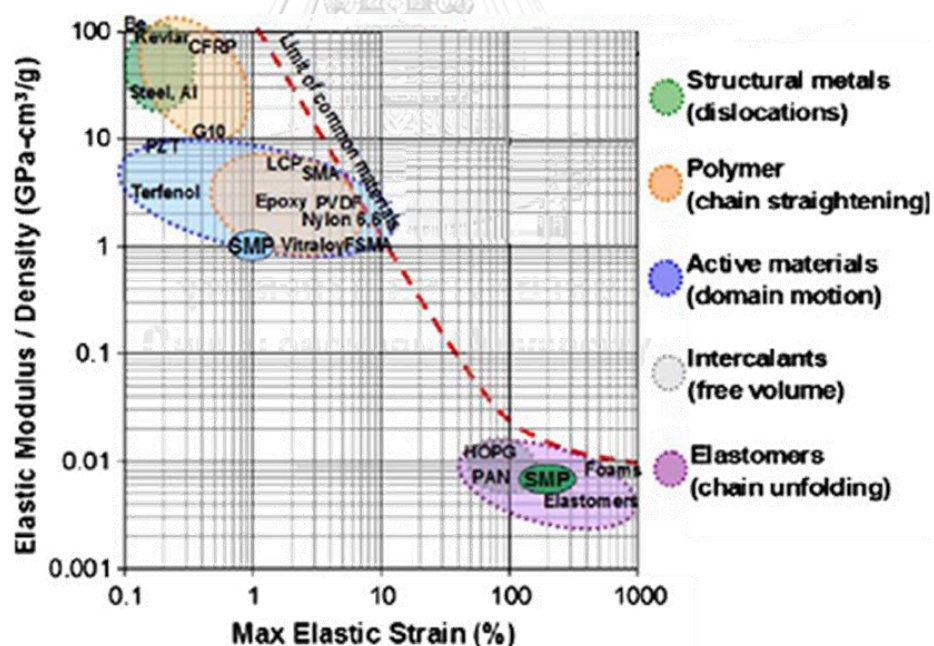


Figure 2.2 Comparison of mechanical properties among some typical materials [3].

2.1.1 Class of shape memory polymers

There are four classes of SMPs based on the criteria of their transition networks and their types of polymeric components [19].

2.1.1.1 Class I: Chemically cross-linked glassy thermosets.

In this 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 thermoset epoxy systems are commercially available with proprietary formulation [19].

2.1.1.2 Class II: Chemically cross-linked semi-crystalline rubbers.

Here, the permanent shape is again set by the chemical cross-links 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 temperatures. 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 ($\approx 100\%$) shape fixity and recovery were reported [19].

Therefore, class II SMPs can be tailored to optimize performance and reach shape fixity and recovery values up to 95%. However, 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, because the temporary shape is fixed through crystallization. Moreover, because the 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 [19].

2.1.1.3 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 temperature. In contrast, the permanent shape of the network is provided by physical cross-linking of the hard segments through molecular interactions such as van der Waals force, 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 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.* 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, albeit only five

consecutive thermo-mechanical cycles were tested. In addition, Lin and Chen tested their polyether-based PU SMP through 200 consecutive SM cycles. They observed an improvement in shape fixity and shape recovery for subsequent cycles with increasing cycle number although with a slight decrease in these properties relative to the initial, starting strain of the first cycle. In conclusion, class III SMPs generally exhibit slightly lower SM performances compared to class I and II SMPs, specifically shape recovery and fixity. This is mainly explained by a loss in physical cross-link 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 [19]

2.1.1.4 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 cross-linking 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 polycaprolactonediol (PCL) as a soft segment, methylene diisocyanate (MDI) as a hard segment, and butandiol (BD) as the cross-linker. Commercially available PU formulations have also been used. For this class of SMPs, shape fixity and recovery have been stated to range anywhere from 65 to 96% and 56 to 100%, depending on the composition (soft segments length and/or molecular weight distribution and hard segment content). For instance, hard segment contents varying from 10 to 33% have been reported as optimum values for increased SM behavior in the PU systems described by Li *et al.* and Park *et al.*, respectively. In addition, Li *et al.* also stated that their PCL/MDI/BD-based PU exhibited a lower limit of soft segment molecular weight of 2000 to 3000 g/mol [19]

2.1.2 Shape memory effects (SME)

Characteristics of the shape memory effects (SMEs) of the SMPs in a thermo-mechanical cycle could be presented as Fig. 2.3 [8]. It could be seen that the shape of the heat triggered SMPs can be deformed at the temperature above the transition temperature (T_{trans}), which is either at the glass transition temperature (T_g) or the melting temperature (T_m) of the polymeric component [9]. The shape could be held during cooling for a temporary shape. Subsequently, the shape of the materials is able to autonomously change to its original shape when the SMP is heated.

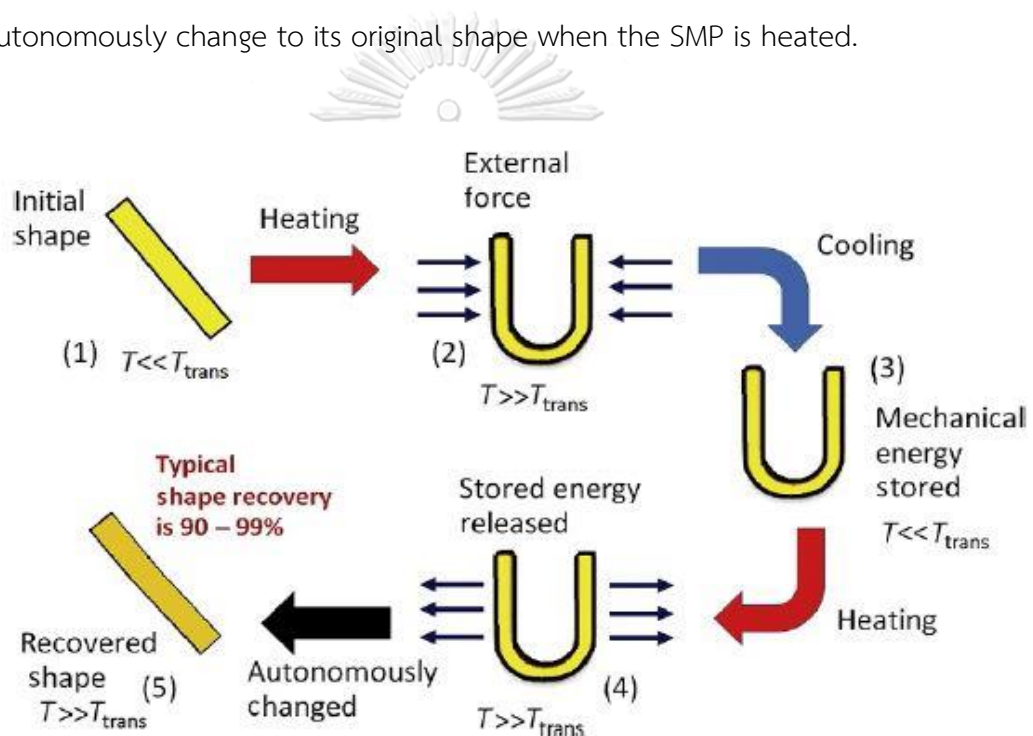


Figure 2.3 Schematic diagram of shape memory effects [8].

The two prerequisites for the shape memory effect (SME) are a stable polymer network and a reversible switching transition of the polymer (see Fig. 2.4). The stable network of SMPs determines the original shape, which can be formed by molecule entanglement, crystalline phase, chemical cross-linking, or interpenetrated network. The reversible switching transition of SMPs determines the reversible molecule crosslinking, crystallization/melting transition and glass transition [22].

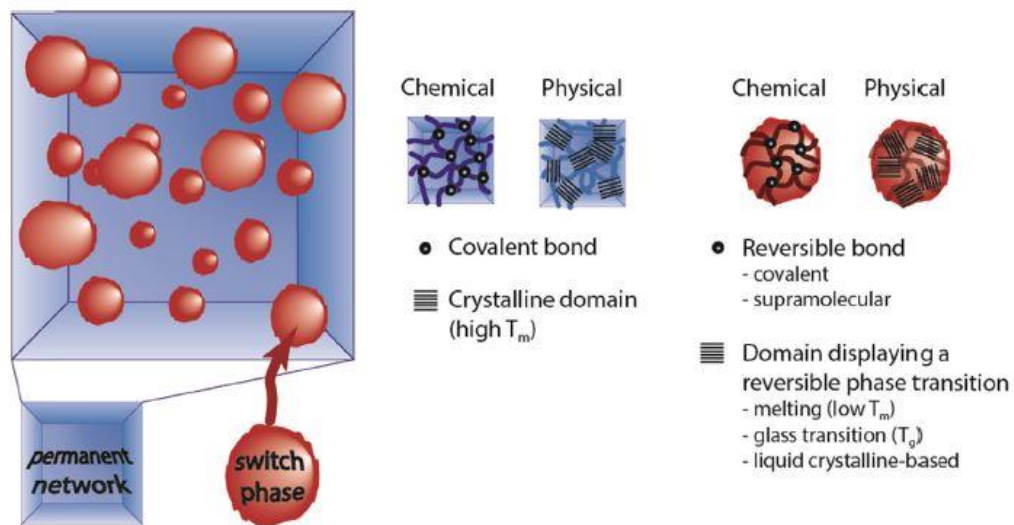


Figure 2.4 A stable network and a reversible switching transition [22].

2.1.3 Parameters for characterization of SMPs [23].

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 as follow [23].

2.1.3.1 Shape fixity (R_f)

When a shape memory polymer is heated to a temperature above the transition temperature for triggering shape memory behaviors (T_g), it can develop large deformations which can be mostly fixed by cooling to a temperature below T_g . This parameter was proposed to describe the extent of a temporary shape being fixed in one cycle of shape memorization. Shape fixity is equal to the amplitude ratio of the fixed deformation to the total deformation. Shape fixity is 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 [23].

$$\text{Shape fixity} = \frac{\text{Fixed deformation}}{\text{Total deformation}} \times 100$$

$$\text{Shape fixity} = 1 - \frac{E_r}{E_g}$$

E_r = the glassy modulus

E_g = the rubbery modulus

2.1.3.2 Shape recovery (R_r)

A given SMP holding a deformation by low temperature can return 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 various 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 [23].

2.1.3.3 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 will be 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 [23].

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.

2.1.3.4 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 was called as speed of recovery process, deformation recovery speed, or shape recovery speed. The parameter can be measured qualitatively and quantitatively [23].

$$\text{Recovery rate} = \frac{\text{Deformation recovered by sample in reheating process}}{\text{Fixed deformation}} \times 100$$

2.2 Shape memory polymer composites [2].

2.2.1 Fiber-reinforced shape memory polymers

In general, SMP composite's reinforced with particles or short fibers cannot be used as structural materials since the improvement in their mechanical properties is quite limited and their strength and stiffness remain low [23]. In contrast, continuous fiber-reinforced SMPs offer a significant improvement in strength, stiffness, and resistance against relaxation and creep, thus providing better mechanical properties. As both a functional and structural material, these SMPs exhibit good potential for several advanced applications. When used as actuator materials, they require no moving parts. Considerable interest has therefore been generated for the use of fiber-reinforced SMPs in deployable structures including antennas, trusses, and solar arrays. In addition, the most studies regarding SMP composites are focused on thermoplastic SMP resins such as polyurethane SMP. However, the relatively poor thermal and mechanical properties (e.g., temperature, moisture, and chemical resistance) of thermoplastic SMPs cannot fully meet practical requirements [3].

In comparison between the properties of the thermoset-type SMPs (TS-SMPs) and the thermoplastics-type SMPs (TP-SMPs), the TS-SMPs possess a higher chemical resistance, a greater storage modulus, and a higher glass transition temperature. Thus, they are more desirable for certain severe environments, such as high temperatures, or for advance applications [6]. A carbon fabric reinforced polyurethane SMP was developed for industrial applications. The bending recovery ratio of this SMP based laminates was larger than that of pure SMP sheet for any given recovery time. Epoxy SMP composites (elastic memory composite, EMC) show a great potential for light weight deployable spacecraft structures applications. Composite Technology Development (CTD), Inc. firstly started to comprehensively be researched the EMC and the relevant applications in deployable structures since the 1990s. A study of the micro-mechanisms of deformation in EMC materials has been conducted

by CTD and Gall *et al.* Their studies have investigated several interaction phenomena between the reinforcement fibers and the SMP resin in an epoxy EMC laminate. Due to the effects of micro buckling and the shift in the neutral-strain surface, the fiber-reinforced SMP composites laminate can achieve much larger compressive strains than traditional hard-resin composite [2].

2.2.2 Applications of shape-memory polymers and their composites

As a popular kind of smart materials, SMPs presently cover a broad range of application areas ranging from outer space to automobiles. Recently, they are being developed and qualified especially for deployable components and structures in aerospace. The applications include hinges, trusses, booms, antennas, optical reflectors, and morphing skins. In addition, SMPs also present additional potential in the areas of biomedicine, smart textiles, self-healing composite systems, and automobile actuators. Additionally, there are many patents in relation to SMPs applications, such as gripper, intravascular delivery system, hood/seat assembly and tunable automotive brackets in vehicles [2].

2.2.2.1 Deployable structures

For the traditional aerospace deployable devices, the change of structural configuration in-orbit is accomplished through the use of a mechanical hinge, stored energy devices, or motor driven tools. There are some intrinsic drawbacks for the traditional deployment devices, such as complex assembling process, massive mechanisms, large volumes and undesired effects during deployment. In contrast, the deployment devices fabricated using SMPs and their composites may overcome certain inherent disadvantages [2].



Figure 2.5 Shape-memory polymer composite-reflector: (a) pre-deformed shape and (b) recovered shape [24].

2.2.2.2 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 2.5 Lockheed Martin is addressing technologies to achieve a z-shaped morphing change under the DARPA's program fund [2].

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]

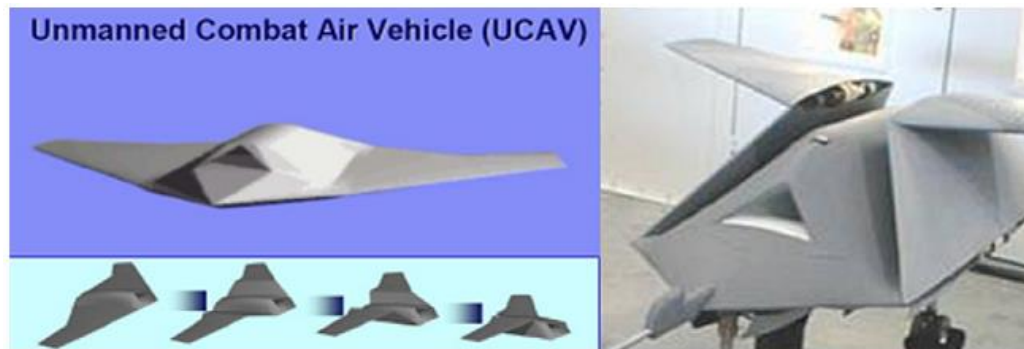


Figure 2.6 Shaped morphing wings produced by Lockheed Martin [2].

2.2.2.3 Biomedicine and bioinspiration

SMPs show a great potential for employing in biomaterials and bioinspiration. For instance, polyurethane SMP performs excellent biocompatibility, and it can be used for the deployment of different clinical devices when contacted or implanted in the human body [25, 26]. Recently, Wache *et al.* [27] have conducted a feasibility study and preliminary development on a polymer vascular stent with an SMP as the drug delivery system (see Fig. 2.7). The field of applications of this polymer stent was demonstrated in pre-trials. The use of the SMP stent as a drug delivery system leads to significant reduction of restenosis and thrombosis. An improved biological tolerance in general is expected when using biocompatible SMP materials.

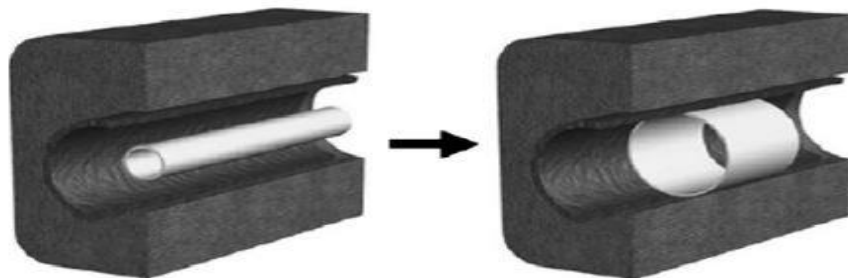


Figure 2.7 Schematic illustration of the shape-memory effect prior to application (left) and right after reset (right) [27].

2.2.2.4 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 [3].

2.3 Polybenzoxazine

Polybenzoxazine is a new type of thermosetting resin developed from phenolic resin to overcome its barrier. Benzoxazine resins are synthesized by mixing phenol, aldehyde, and amine functional group together, using solvent or solventless technique [28]. Polybenzoxazine is able to be polymerized by oxazine ring opening of benzoxazine monomer. This new thermosetting resin has many essential advantages, such as no catalyst or curing agent required, no by-product upon curing, excellent mechanical properties, high thermal stability, low water absorption, low viscosity, ability to alloy with various types of resins, and good interfacial adhesion with fillers [28-32].

The most popular type of benzoxazine resin is bisphenol-A because of its very low viscosity and good thermal properties [30]. Its properties are shown in Table 2.1

Table 2.1 Properties of Polybenzoxazine [29-31].

Properties	Values
<u>Mechanical Properties</u>	
Storage Modulus at 25 °C (GPa)	2.2
Tensile Modulus (GPa)	5.2
Tensile Strength (MPa)	64
Flexural Modulus (GPa)	4.5
Flexural Strength (MPa)	126
<u>Physical Properties</u>	
Monomer Density (g/cm ³)	1.2
Polymer Density (g/cm ³)	1.195
Water Absorption (% at 25 °C 24 h)	0.11
<u>Thermal Properties</u>	
Curing temperature (°C)	160 - 220
Glass transition temperature (°C)	150-180
Degradation temperature at 5% weight loss (°C)	310
Char yield (%)	32

Bisphenol-A based benzoxazine resin can be synthesized using solventless process disclosed by Ishida [32]. This process is carried out by mixing bisphenol-A, paraformaldehyde, and aniline at a molar ratio of 1:4:2 at 110 °C. The synthesis reaction is shown in Figure 2.8

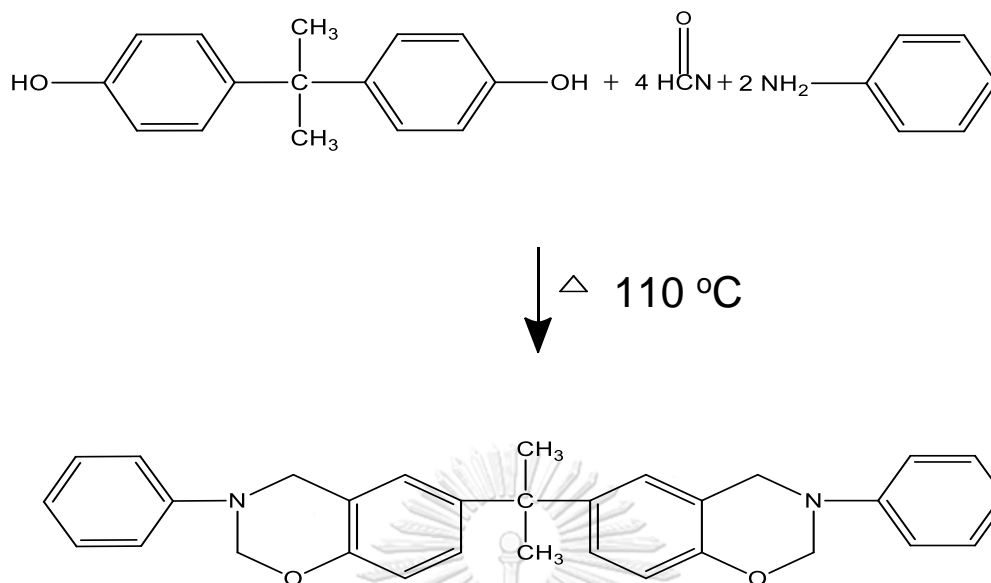


Figure 2.8 Synthesis reaction of BA-a [29].

2.4 Epoxy resin

The term epoxy, epoxy resin, or epoxide (Europe) refers to a broad group of reactive compounds that are characterized by the presence of an oxirane or epoxy ring, as shown in Fig. 2.9. This is represented by a three-membered ring containing an oxygen atom that is bonded with two carbon atoms already united in some other way [33].

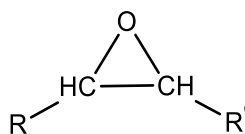


Figure 2.9 General structure of an epoxy resin [33].

An epoxy resin can be any molecule containing more than one of these epoxy groups. The number of epoxy groups per molecule is the functionality of the resin. The groups can be situated internally, terminally, or on cyclic structures. Epoxy groups are capable of reacting with suitable curing agents or catalytically

homopolymerized to form higher molecular weight polymers. Once cured, the epoxy polymers have a densely cross-linked, thermosetting structure with high cohesive strength and adhesion properties. However, the term epoxy can also be used to indicate an epoxy resin in the thermoplastic or uncured state [33].

For some types of processing, the viscosity of the uncured resin system has to be reduced. In the event of hand lay-up, reactive diluents must be used. In this research, neopentyl glycol diglycidyl ether (NGDE) was employed as diluents. They are low viscosity liquids containing epoxide groups (Figure 2.10).



Figure 2.10 Structure of Neopentyl glycol diglycidyl ether (NGDE) [18].

Neopentyl glycol diglycidyl ether (NGDE) is an ether-alcohol derivative. The ether being relatively unreactive. Flammable and/or toxic gases are generated by the combination of alcohols with alkali metals, nitrides, and strong reducing agents. They react with oxoacids and carboxylic acids to form esters and water. Oxidizing agents convert alcohols to aldehydes or ketones. Alcohols exhibit both weak acid and weak base behavior. They may initiate the polymerization of isocyanates and epoxides [34].

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Applications

- Electrical potting, encapsulation, impregnation
- Flooring
- Adhesives and Tooling

2.5 Carbon fiber (CF)

Carbon Fiber is a polymer and is sometimes known as graphite fiber. It is a very strong material that is also very lightweight. Carbon fiber is five-times stronger than steel and twice as stiff. Though carbon fiber is stronger and stiffer than steel, it is lighter than steel, making it the ideal manufacturing material for many parts. These are just a few reasons why carbon fiber is favored by engineers and designers for manufacturing [35].

Carbon fiber is made of thin, strong crystalline filaments of carbon that is used to strengthen material. Carbon fiber can be thinner than a strand of human hair and gets its strength when twisted together like yarn. It can be woven together to form cloth and if needed to take a permanent shape, carbon fiber can be laid over a mold and coated in resin or plastic. In addition, there are several advantages of carbon fiber such as high stiffness, high tensile strength, low weight to strength ratio, high chemical resistance, and low thermal expansion [35]. Carbon fiber is very popular in many industries such as aerospace, automotive, military, and recreational applications.

Carbon fiber (CF) has been widely used to fabricate high performance composites. The high interfacial bond between CF and matrix leads to the excellent mechanical properties of carbon fiber such as high strength, high modulus, corrosion resistance, fatigue resistance, and creep resistance [36]. Accordingly, the interface between polymer matrix and CF plays an important part in stress transfer, the extent of which effects important design criteria including strength, stiffness, and weight. However, the interface bonding between untreated CF and resin matrix limits the excellent performance of carbon fiber composite, due to the large surface inertia of carbon fiber [36]. The woven carbon fibers is shown in Figure 2.11.

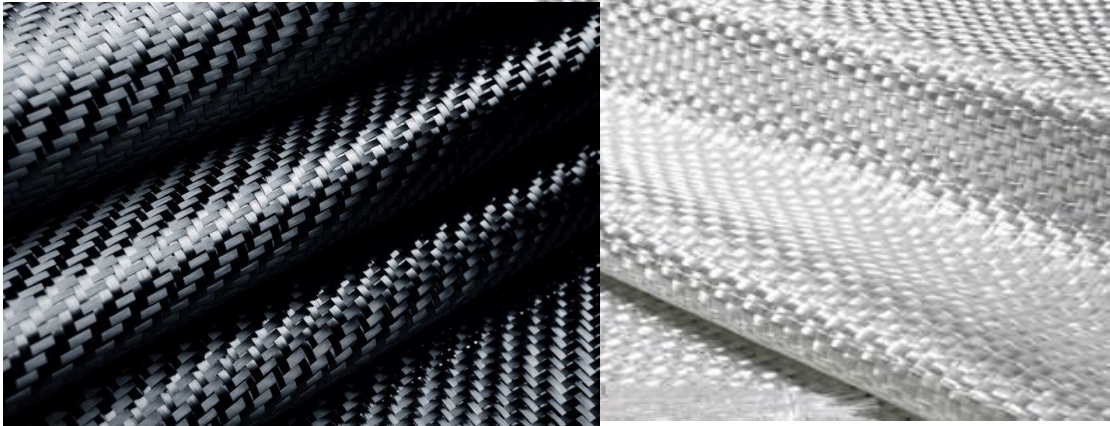


Figure 2.11 Woven carbon fibers and glass fibers [35].

2.6 Glass fiber (GF)

Fiberglass refers to a group of products made from individual glass fibers combined into a variety of forms. Glass fibers can be divided into two major groups according to their geometry: continuous fibers used in yarns and textiles, and the discontinuous (short) fibers used as batts, blankets, or boards for insulation and filtration. Fiberglass can be formed into yarn much like wool or cotton, and woven into fabric which is sometimes used for draperies. Fiberglass textiles are commonly used as a reinforcement material for molded and laminated plastics. Fiberglass wool, a thick, fluffy material made from discontinuous fibers, is used for thermal insulation and sound absorption. It is commonly found in ship and submarine bulkheads and hulls, automobile engine compartments and body panel liners, furnaces and air conditioning units, acoustical wall and ceiling panels, and architectural partitions. Fiberglass can be tailored for specific applications, such as Type E (electrical), used as electrical insulation tape, textiles and reinforcement; Type C (chemical), which has superior acid resistance, and Type T, for thermal insulation [37].

In recent years significant growth is observed in the manufacture of composite materials. Intensively developed reinforced plastics are used in different sectors of industry and technology. They successfully replace traditional construction

materials and also can be applied to conditions that substitute the use of metals. Glass fibers (GF) are necessary components of different composite materials and reinforced plastics are the most important of them [37]. The woven glass fibers are shown in Figure 2.11.



CHAPTER III

LITERATURE REVIEW

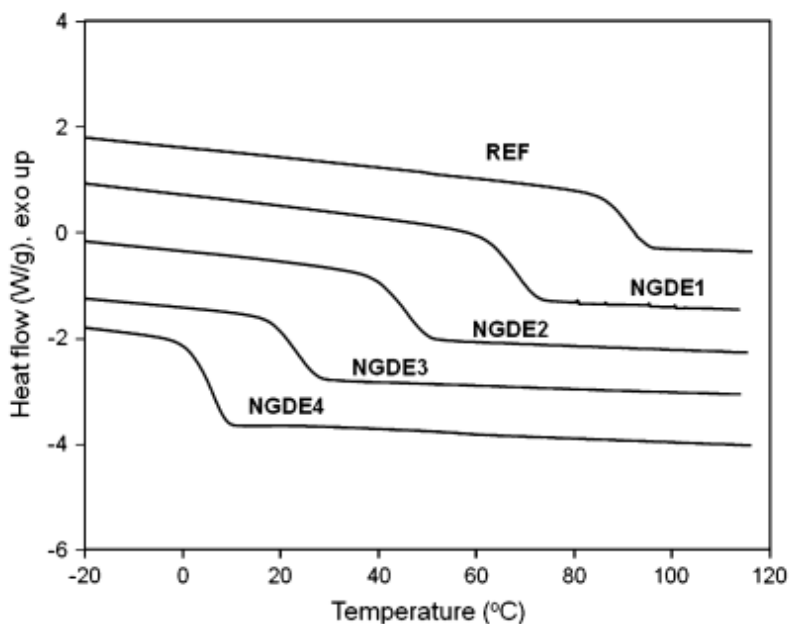
Xie and Rousseau (2009) developed methods to tailored T_g of shape memory epoxy polymer. Starting with an amine (Jeffamine D230) cured aromatic epoxy (EPON 826) system, epoxy polymers were synthesized by either reducing the cross-link density by substituting the diamine curing agent with a monoamine such as decylamine (DA) or introducing flexible segments by replacing the EPON 826 with a flexible aliphatic epoxy (NGDE). The molar compositions for all epoxy synthesized are summarized in Table 3.1 [19].

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 appeared that the shape fixity for the DA and NGDE series including the REF seems to increase as more DA and NGDE were presented 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 cross-linker led to decrease in the average molecular weight between cross-link points (M_c) (Table 3.1).

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 3.1 and 3.2 suggest that the impact of increasing the cross-link density by introducing NGDE is overcompensated by the increase in the overall chain flexibility, resulting in a net reduction in T_g and rubbery modulus. The result corresponded to the decreasing of M_c , as present in Table 3.1 [19].

Table 3.1 Compositions, shape fixity, and shape recovery of the epoxy samples [19].

Sample	EPON826 (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

**Figure 3.1** DSC curves for the NGDE epoxy series [19].

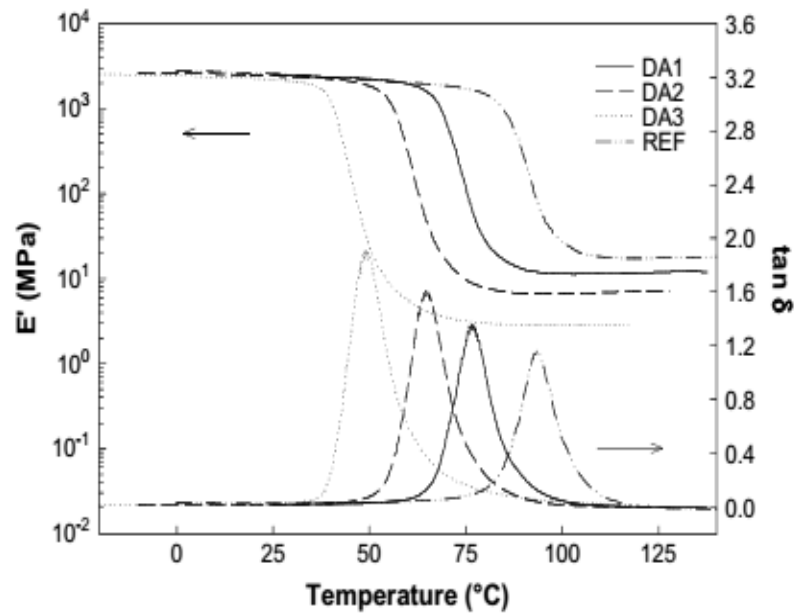


Figure 3.2 DMA curves for the NGDE epoxy series [19].

However, several kinds of SMPs have intrinsic low mechanical strength and shape recovery stress, which have largely restricted the applications of SMPs. There are several workers who are interested in enhancing recovery stress of their shape memory polymers. Some of the research works are reviewed and discussed as follows.

CHULALONGKORN UNIVERSITY

Erden and Jana (2013) studied 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 resin (BA-a). Molar ratio of ingredients and weight percentages of hard segment (HS) are shown in Table 3.2 [12].

Table 3.2 Corresponding molar ratio of raw materials [12].

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 3.3 and 3.4. It was evident that all three materials exhibited a single peak of $\tan \delta$, indicating a single value of T_g of 51, 65, and 91°C for sample I, II, and III, respectively. The increasing of T_g was 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 sample I, II, and III, respectively. The larger ratio of storage modulus below 20°C and above 20°C indicated that samples II and III would exhibit much better shape memory properties than sample I [12].

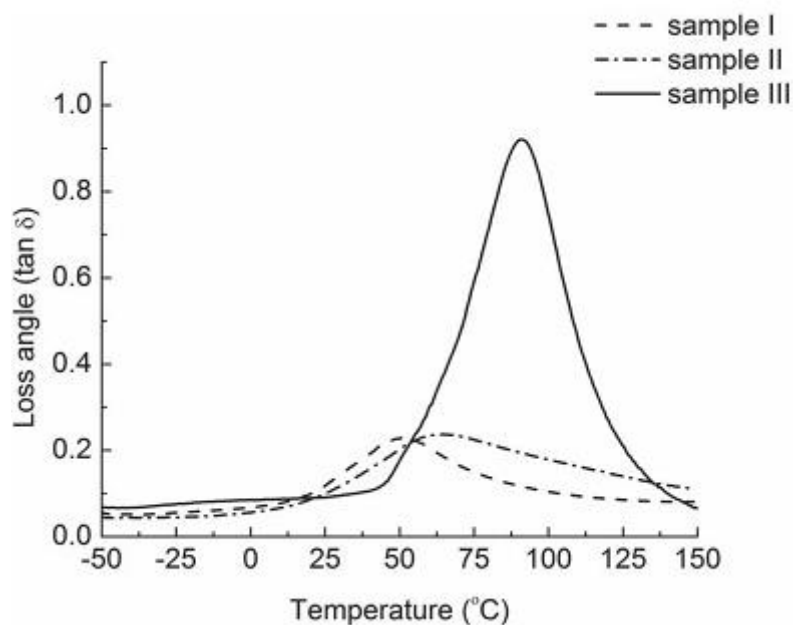


Figure 3.3 Loss tangent as a function of Temperature heating rate 4 °C min⁻¹, frequency 1 Hz [12].

The recovery stress is shown in Figure 3.5 the recovery stress under tension mode increased with an addition of benzoxazine resin. 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) for sample II and III, respectively [12].

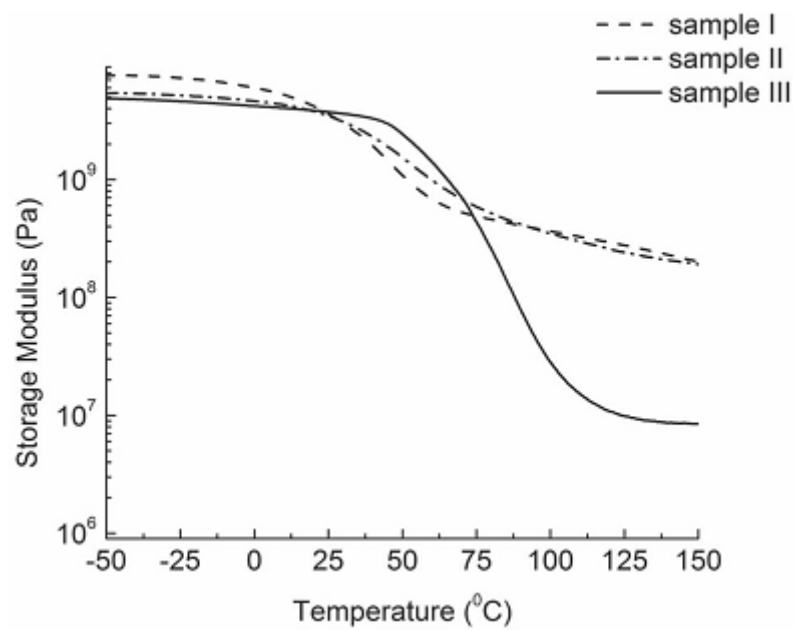


Figure 3.4 storage modulus as a function of temperature. The heating rate was $4^{\circ}\text{C min}^{-1}$ and frequency was 1 Hz. [12]

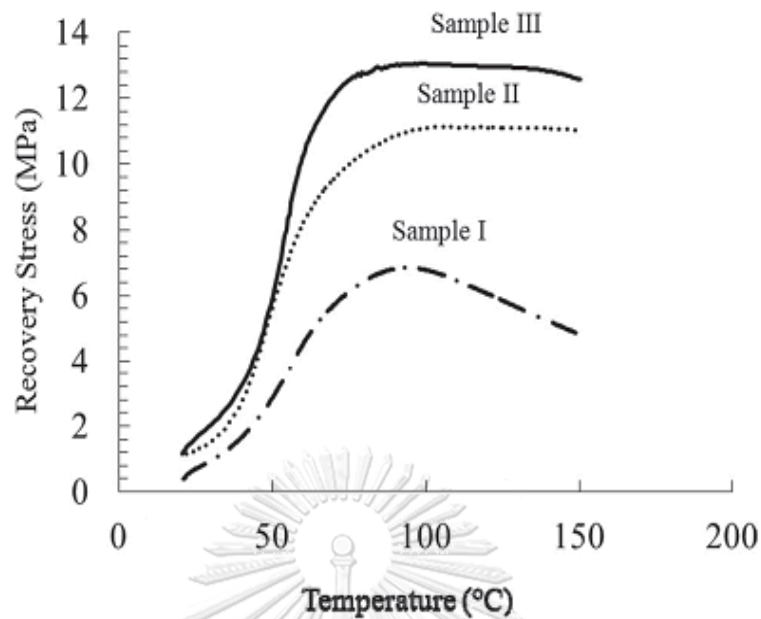


Figure 3.5 Recovery stress behaviors of 100% strained samples. Heating rate was 4°C/min and stretching rate was 50 mm/min [12].

Rimduisit *et al.* (2013) studied the effects of benzoxazine resin and Jeffamine D230 molar ratios on glass transition temperature, mechanical and shape memory properties. As shown in Table 3.3, the notation E, N, D, and B stand for EPON 826, NGDE, Jeffamine D230 and BA-a, respectively. The digits after the notation give the molar ratio of the monomer in the corresponding order. It was found that the storage modulus and cross-link 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. Moreover, the glass transition temperature also increased when BA-a content increased [18].

Table 3.3 Properties of benzoxazine-modified epoxy SMP samples from DMA analysis [18].

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 3.6. All of the samples 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. This caused an increase in the recovery force on the samples [18].

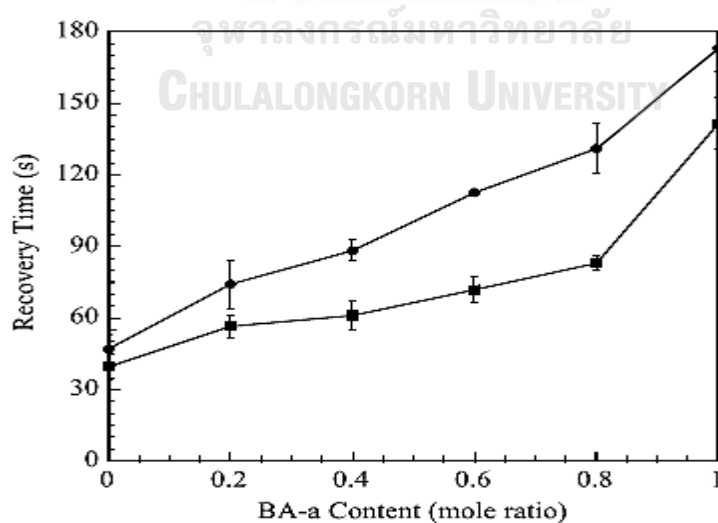


Figure 3.6 Recovery time as a function of BA-a content of the benzoxazine-modified epoxy SMP samples at various composition: (●) T_g , (■) $T_g+20^\circ\text{C}$ [18].

The recovery stress under flexural mode of the SMPs was measured from the transition stage of the shape-fixed stage to the shape-recovery stage. The benzoxazine-modified epoxy SMPs samples with 0, 0.2, 0.4, 0.6, 0.8, and 1.0 mol ratio of BA-a showed recovery stresses about 20.42 ± 0.39 , 23.36 ± 2.39 , 29.77 ± 0.87 , 30.97 ± 0.97 , 33.70 ± 3.01 , and 38.18 ± 2.82 kPa, respectively, as seen in Figure 3.7. Based on their results, the benzoxazine resin can substantially improve the recovery stress of epoxy-based SMPs. This was due to the fact that the BA-a might be able to store elastic strain energy [18].

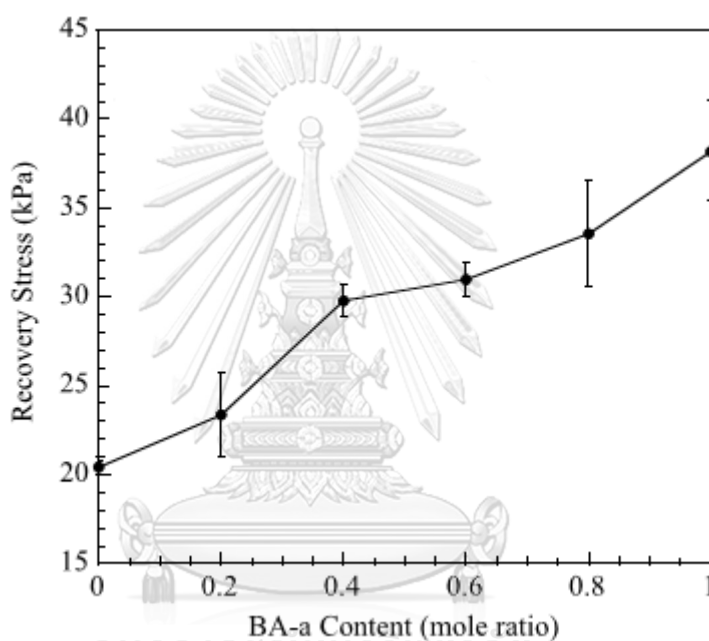


Figure 3.7 Recovery stress as a function of BA-a content of the benzoxazine-modified epoxy SMP samples at various compositions [18].

Tanpitaksit *et al.* (2014) reported SMPs from binary mixtures based on benzoxazine-modified aliphatic epoxy. The benzoxazine (BA-a) was used to cure aliphatic epoxy instead of Jeffamine D230. Moreover, this system did not employ aromatic epoxy. In other words, the BA-a resin was used both as the epoxy curing agent and rigid segments in the resulting SMPs. Still, the SMP system retained good thermo-mechanical and excellent shape memory properties with additional ease of sample preparation and processing. In Figure 3.8, it was observed that recovery stress under flexural mode could be increased with increasing BA-a contents from 0.25 MPa

at 30 mol% to 1.59 MPa at 50mol%. The phenomenon was attributed to an increase in cross-link density with the addition of the BA-a in the alloys, which improved storage modulus at rubbery state of the alloys and thus their recovery stress. Moreover, the recovery time also increased with increasing BA-a contents as show in Figure 3.9 while the shape fixity slightly decreased with increasing BA-a content [11].

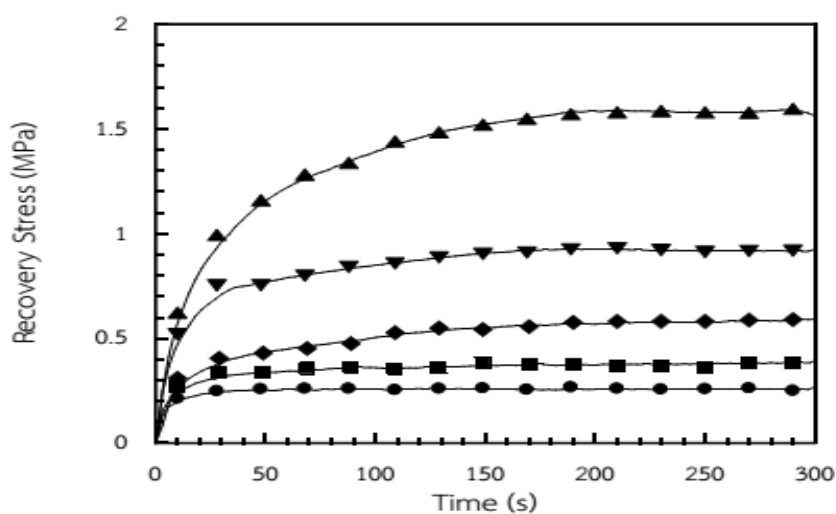


Figure 3.8 Recovery stress versus time of aliphatic epoxy/benzoxazine SMPs at various mole percents of the BA-a: (●) 30 mol%, (■) 35 mol%, (◆) 40 mol%, (▼) 45 mol% and (▲) 50 mol% [11].

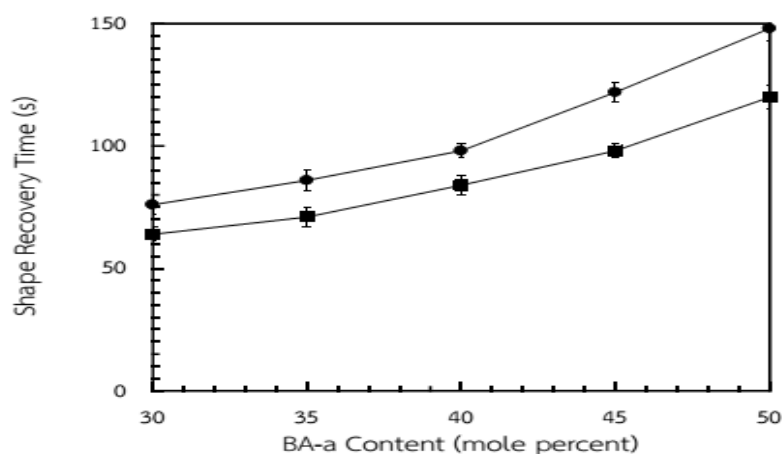


Figure 3.9 Recovery time as a function of BA-a contents of the aliphatic epoxy/benzoxazine SMP samples at various temperatures: (●) T_g and (■) $T_g + 20^\circ\text{C}$ [11].

M. Fejos *et al.* (2012) compared the shape memory characteristics of an EP resin and its composite containing four layers of woven GF fabric reinforcement (EPGF4; GF content = 38 vol%). The dynamic mechanical analysis (DMA) curves (Figure 3.10) clearly show the effect of the woven GF reinforcement. The storage modulus of EPGF4 was supremely increased with increasing glass fiber content. Note that both samples show very good shape recovery ratio (99% each). On the other hand, EPGF4 exhibited a lower maximal recovery rate compared to the neat EP (Figure 3.11). The recovery rate decreased from 0.51 to 0.37%/min due to the GF reinforcement [16]. In addition, the composite SMP with woven GF reinforcement exhibited increased recovery stress (Figure 3.12). In this case, the recovery stress was defined as the maximum stress values observed during bending deformation (step II) and during recovery (step IV/B), respectively.

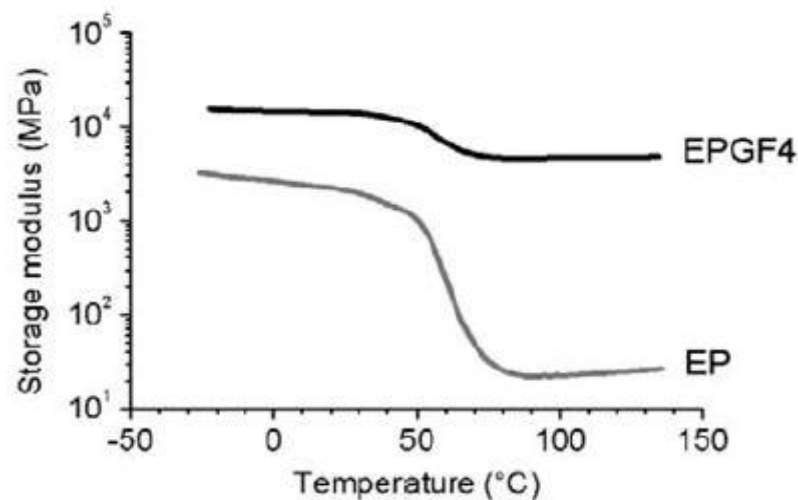


Figure 3.10 Dynamic mechanical analysis (DMA) curves of EP and EPGF4 [16].

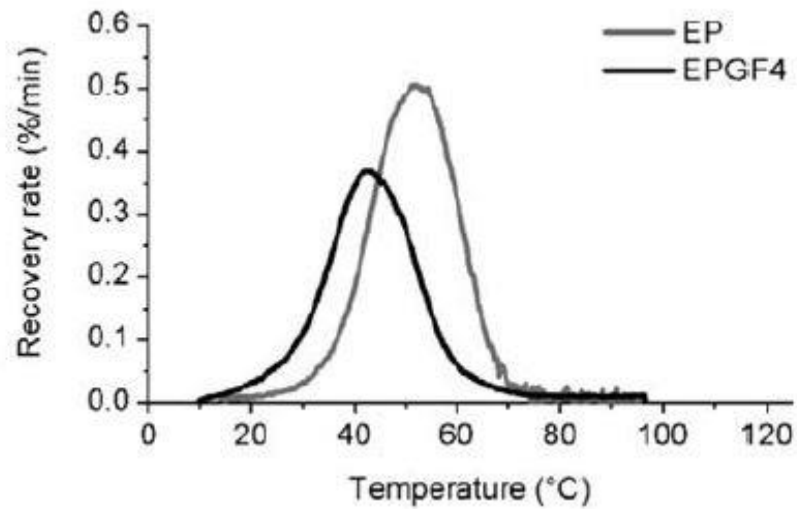


Figure 3.11 Recovery rate of EP and EPGF4 as a function of temperature [16].

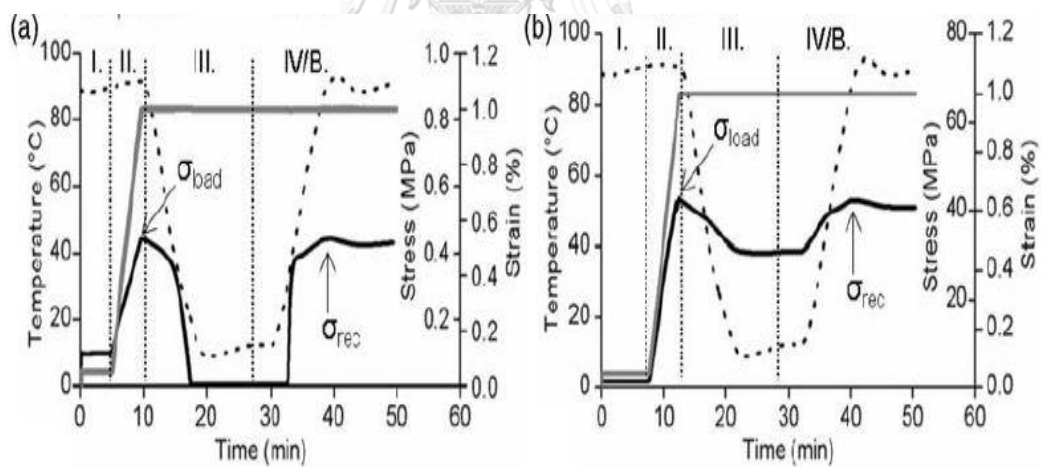


Figure 3.12 Constrained recovery tests on (a) EP and (b) EPGF4 [15].

Seok Bin Hong *et al.* (2015) studied carbon fiber reinforced shape memory polymer composites (CF-SMPCs) to design self-deployable structures in harsh space conditions. A thermoset shape memory polymer was used as a matrix. The weight ratio of resin and curing agent was set to be 6:4. The glass transition temperature of such

SMP after curing was about 60°C. The time-strain and time-stress behavior of the SMP during the test are shown in Fig 3.13

In addition, it is observed that the recovery and fixity rate were 90 and 96%, respectively. The maximum recovery stress in one-way shape memory test was about 4 MPa [22].

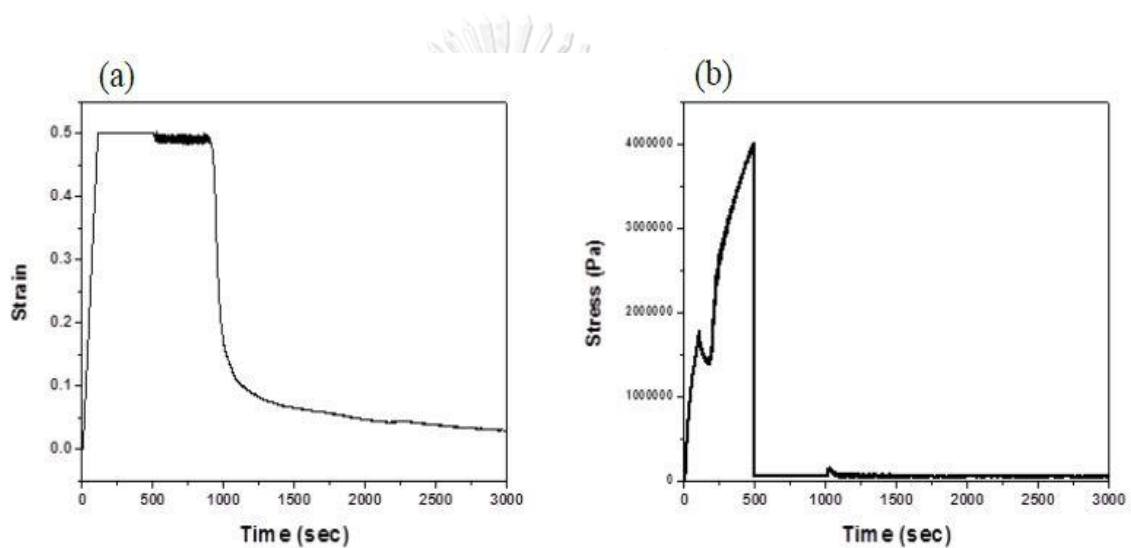


Figure 3.13 Strain and stress curve of SMP. (a) time-strain and (b) time-stress curve for 3000 s [22].

Ivens *et al.* (2011) studied the thermoset-type SMPs of styrene-based resin cured with benzoyl peroxide in a 24:1 ratio. The matrix was reinforced with a quasi-unidirectional non-crimp E-glass fabric (UDG1200; areal weight 1200 g/m²), an E-glass plain woven fabric (WGF540; areal weight 540 g/m²), and a T300 carbon fibre twill-weave (TWC300; areal weight 300 g/m²). Composite plates were produced using resin transfer moulding in a heated aluminium mould, containing a single layer of reinforcement. The resulting plate thickness was 3.2 mm. The fibre volume fractions were 16.5% (UDG1200), 7.7% (WGF540), and 5% (TWC300) [37].

Table 3.4 Numerical data, obtained from the TMA experiments [37].

Sample	Strain [%]	Temperature [°C]	Peak stress [MPa]	Recovery stress [MPa]
SMP	10	75	0.085±0.005	0.05±0.01
TWC300	10	75	0.5	0.3
WGF540	10	75	1.0±0.1	0.55±0.03
UDG1200	10	65	3.65±0.45	1.65±0.3
		75	2.4±0.2	1.60±0.06
		85	2.2±0.2	1.65±0.12
	20	75	5.9±1.3	3±1
	20(2)	75	4.5±0.7	2.5 ±0.7

Table 3.4 shows numerical data of the neat SMP and for the different SMPC from TMA experiments. The results of the experiments on UDG1200 show the highest of recovery stress compared with the resin without glass fiber. In addition, at 65°C below the transformation temperature, the switching segments still had some stiffness. The peak stress drops significantly when the T_g was exceeded. For 10% deformation, recovery stresses were built up to 1.65MPa, i. e. 94% of the plateau stress level during the deformation stage. The effect of the deformation temperature on the recovery stress was insignificant [37].

X. Lan *et al.* (2011) studied the shape recovery behavior of styrene-based shape-memory polymer composite (SMPC) reinforced by carbon fiber fabrics, and demonstrated the feasibility of using an SMPC hinge as a deployable structure. Results revealed that the SMPC exhibits a higher storage modulus than that of a pure SMP (Fig 3.14). At the temperature above T_g , the shape recovery ratio of the SMPC upon bending was more than 90% (Figure 3.15). The shape recovery properties of the SMPC became

relatively stable after some packaging/deployment cycles. Additionally, fiber microbuckling is the primary mechanism for obtaining a large strain in the bending of the SMPC. Moreover, an SMPC hinge was fabricated, and a prototype of a solar array actuated by the SMPC hinge was successfully deployed [38].

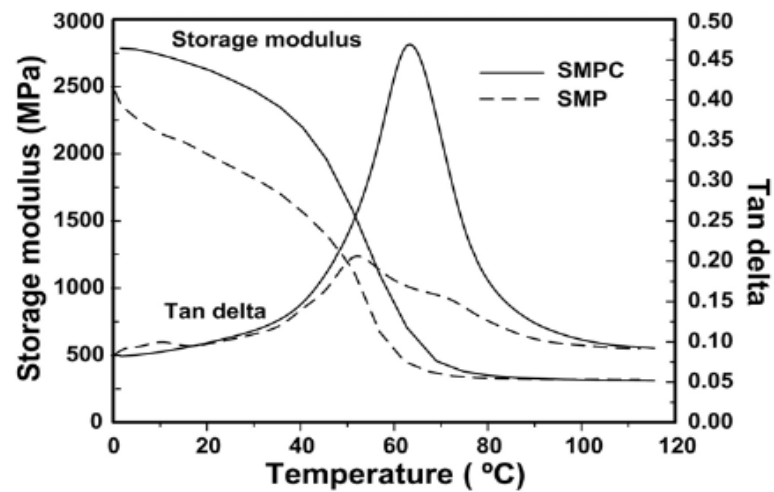


Figure 3.14 Storage modulus and loss tangent versus temperature of the pure SMP and SMPC. [38].

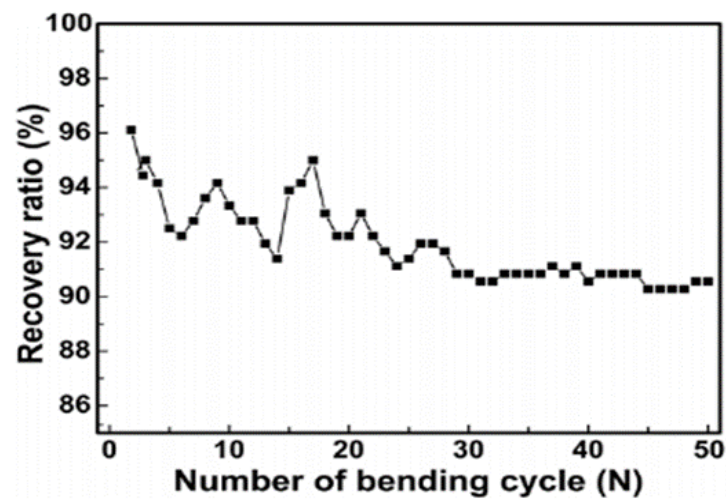


Figure 3.15 Shape recovery ratio versus the number of bending cycles at $T_g + 20^\circ\text{C}$. [38]

CHAPTER IV

EXPERIMENTAL

4.1 Raw Materials

The materials used in this research were benzoxazine resin and an aliphatic epoxy. Benzoxazine resin (BA-a) is based on bisphenol-A, paraformaldehyde and aniline. Bisphenol-A (AR grade) was supported by PTT Phenol Company Limited. Paraformaldehyde (AR grade) and aniline (AR grade) were purchased from Merck Company and Panreac Quimica SA Company, respectively. The aliphatic epoxy was neopentyl glycol diglycidyl ether (NGDE) and was supported by Adiya Birla Chemical (Thailand).

4.2 Specimen Preparation

4.2.1 Benzoxazine Resin Preparation

Benzoxazine monomer (BA-a) was synthesized from bisphenol A, aniline, and paraformaldehyde at a 1:2:4 molar ratio based on a solventless technique. The mixture was stirred continuously at 110°C until it became transparent yellow liquid. After that, the resulting benzoxazine monomer was solidified to transparent yellow solid at room temperature. The solid monomer was then ground into powder for further characterizations or processing.

4.2.2 Composite Preparation

Firstly, the BA-a monomer was mixed with the aliphatic epoxy at a fixed molar ratio of 1:1 at a temperature of 80°C and stirred for 45 minutes. Secondly, the mixture was heated in an oven at a temperature of 130°C for 12 hours and 150°C for 1 hour. Then, the BA-a/NGDE mixture was pre-impregnated with woven carbon fibers and woven glass fibers having various volume percentages including 30, 35, 40, 45 and 50vol% by a hand lay-up technique. The 2-ply and 4-ply prepregs obtained were heated in an oven at a temperature of 160°C for 1 hour. The 2-ply and 4-ply prepregs

were finally compressed with a compression molder at a temperature of 170°C and a pressure of 15 MPa for 3 hours.

4.3 Characterization Methods

4.3.1 Differential Scanning Calorimetry (DSC)

Curing conditions of benzoxazine-epoxy matrixes were investigated by a differential scanning calorimeter (DSC) model DSC 1 Star^e System from Mettler Toledo. We sealed each sample having a mass in a range of 3–5 mg in an aluminum pan with lid. The sample temperature was systematically scanned from 50°C to 320°C under nitrogen purging with 10 °C /min of heating rate. The purge nitrogen gas flow rate was maintained at 50 mL/min.

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

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

Where: H_{rxn} = the heat of reaction of the partially cured samples
 H_0 = the heat of reaction of the uncured resin mixture

4.3.2 Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical properties of BA-a/NGDE composites reinforced with woven carbon fibers and woven glass fibers were obtained by dynamic mechanical analysis (DMA, model DMA24, NETZSCH, Germany). The specimens were tested using a three-point bending mode. All the tests were performed under a nitrogen atmosphere with a heating rate of 2°C/min from 35°C to 200°C at a test frequency of 1 Hz and a strain amplitude of 5 µm. Glass transition temperatures (T_g) of the specimens were obtained from the peak maximum of the loss modulus curves

4.3.3 Flexural Properties

Universal testing machine (model 5567) from Instron Co., Ltd was used for determining mechanical properties of the polymers or polymer composites. The

flexural mode was used as the test method on three-point loading with the supporting span of 32 mm and a crosshead speed at 1.0 mm/min. Dimensions of the specimens were 10×50×13, 10×50×15, and 10×50×17 mm³. Flexural properties were determined based on ASTM D 790M. The flexural strength and modulus were calculated by the following equations:

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

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

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)

4.3.4 Shape Memory Performance

Shape memory properties including shape fixity, shape recovery, and recovery stress of the BA-a/NGDE composites reinforced with woven carbon fibers and woven glass fibers were obtained using a universal testing machine equipped with an environmental chamber. The experimental setup for determining the recovery stress of the sample is shown in Figure 4.1. Primarily, a fixed shape was prepared by applying a flexural force on a specimen with a dimension of 10×50×13, 10×50×15, or 10×50×17 mm³ at its $T_g+20^\circ\text{C}$. Then, the sample was cooled down to room temperature. The force was then removed completely and the temporary shape was obtained. The deflection after unloading was varied at 1%, 3% 5% and 7% strain. Afterwards, the specimen was heated up to its $T_g+20^\circ\text{C}$ and the recovery stress during heating was measured.

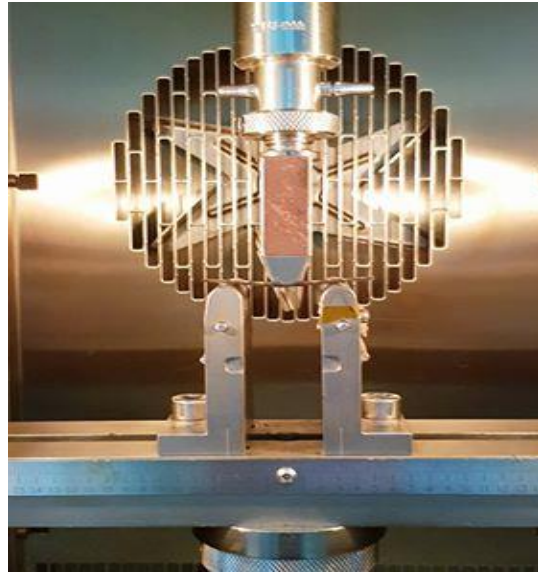


Figure 4.1 A photograph of experimental setup for shape recovery stress determination.

4.3.5 Optical Microscope

To investigate interfacial bonding between the fiber and the matrix used a Carl Zeiss Axio Scop.A1 couple with AxioCam HRc 3. The micrographs of the sample fracture surface were used to qualitatively evaluate the interfacial interaction between the fiber and the matrix.

CHAPTER V

RESULTS AND DISCUSSION

5.1 Curing Condition Investigation of Benzoxazine-Epoxy Shape Memory Polymers

Figure 5.1 exhibits DSC thermograms of benzoxazine-epoxy (BA-a/NGDE) at 1:1 molar ratio under various curing conditions. The thermograms showed that the resin mixtures had three exothermic peaks. The overlapping peaks at lower temperature is attributed to the polymerization reaction of the BA-a monomers. The third exothermic peak at a higher temperature is the cross-linking reaction between phenolic hydroxyl groups of the polybenzoxazine (PBA-a) and epoxide groups of the NGDE [11]. This result is in good agreement with the curing behaviors of bisphenol-A based epoxy [31]. The optimal curing condition of BA-a/NGDE was determined from the area under the exothermic peak. The heat of curing reaction of uncured BA-a/NGDE was 482 J/g. After step curing at 130°C/12 hours, 140°C/1 hour, 160°C/1 hour, and 170°C/3 hours, the values decreased to 399, 364, 309, and 177 J/g and the degree of conversions estimated by equation 4.1 were 17.0, 24.5, 35.9, and 63.3%, respectively. The optimal degree of conversion at 63.3% was selected. Liu *et al.* [39] suggested that the degree of conversion about 60% of shape memory epoxy provided samples with good balanced properties between shape memory performance and thermo-mechanical properties. In addition, Tanpitaksit *et al.* [11] also utilized the curing conversion at 60% for investigating shape memory performances of BA-a/NGDE mixtures.

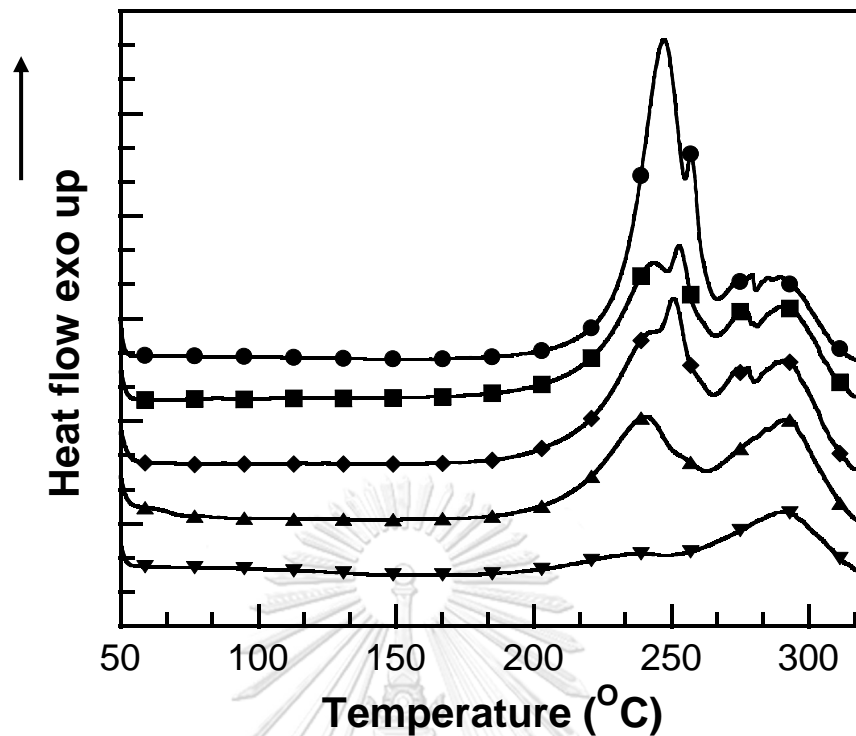
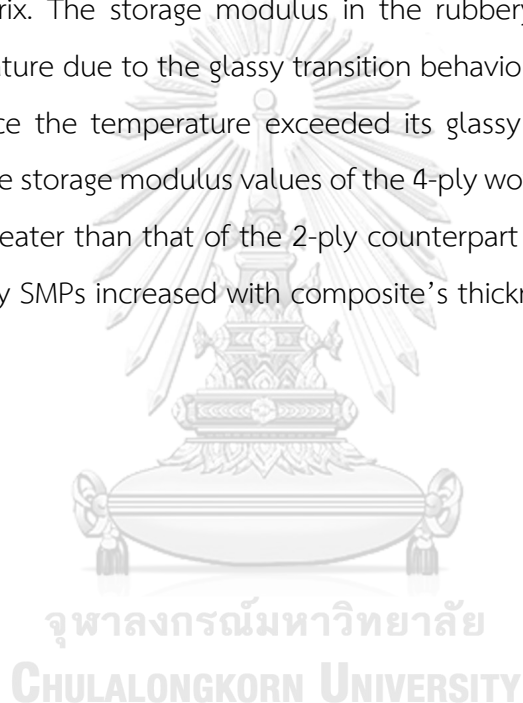


Figure 5.1 DSC thermograms of benzoxazine-epoxy SMP samples at various curing conditions: (●) uncured, (■) 130°C/12 hours, (◆) 140°C/1 hour, (▲) 160°C/1 hour and (▼) 170°C/3 hours.

5.2 Dynamic Mechanical Analysis (DMA)

Polymeric materials are viscoelastic. Dynamic mechanical analysis evaluates mechanical properties as a function of temperature, complex transition and relaxation phenomena when polymeric materials are presented. Figures 5.2–5.9 display dynamic mechanical properties of 2-ply and 4-ply woven carbon fiber reinforced benzoxazine/epoxy SMPs. All samples were investigated in a flexural mode. Dynamic mechanical properties such as storage modulus and loss tangent were obtained as a function of temperature from 35–185°C with a heating rate of 2°C/min. The storage moduli at glassy state of 2-ply and 4-ply woven carbon fiber reinforced benzoxazine/epoxy SMPs were presented in Figure 5.2 and 5.3, respectively. The storage modulus of samples tended to increase with increasing the woven carbon fiber contents as a result of more rigid characteristics of the composites. The storage

modulus at room temperature (30°C) of 2-ply woven carbon fiber reinforced benzoxazine-epoxy SMPs increased from 1.9 GPa (the neat matrix) to 16.2, 18.4, 23.9, 24.4, and 25.9 GPa when the volume percentages of the woven carbon fibers were 30%, 35%, 40%, 45%, and 50% respectively. For the 4-ply SMPs, the storage modulus values at room temperature were 22.4, 26.5, 27.8, 28.1, and 30.2 GPa at the woven carbon fiber volume percentages of 30%, 35%, 40%, 45%, and 50%, respectively. Woven carbon fiber reinforcement increased rigidity of the benzoxazine-epoxy SMPs. The results also suggested a good interfacial adhesion between the woven carbon fiber and the SMP matrix. The storage modulus in the rubbery state was constant with increasing temperature due to the glassy transition behavior of the resin. The polymer lost its rigidity once the temperature exceeded its glassy transition temperature (T_g) [40]. In addition, the storage modulus values of the 4-ply woven carbon fiber reinforced SMP have value greater than that of the 2-ply counterpart because the rigidity of the benzoxazine/epoxy SMPs increased with composite's thickness.



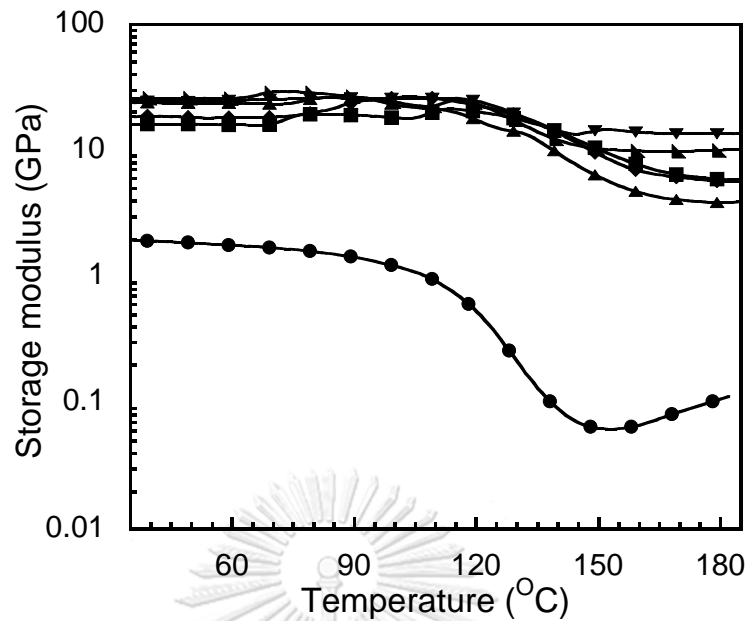


Figure 5.2 Storage moduli of 2-ply woven carbon fiber reinforced benzoxazine/epoxy SMPs at various woven carbon fiber contents: (●) BA-a/NGDE, (■) 30vol%, (◆) 35vol%, (▲) 40vol%, (▼) 40vol% and (▴) 50vol%.

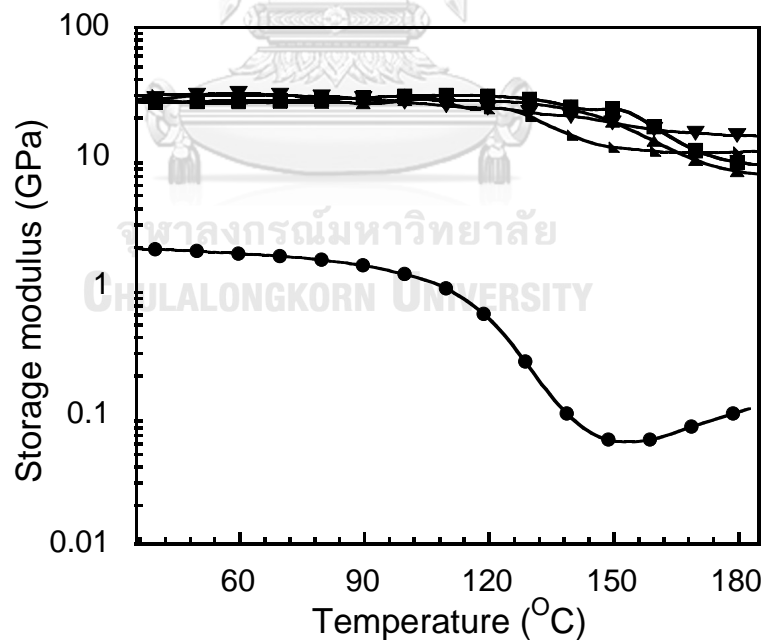


Figure 5.3 Storage moduli of 4-ply woven carbon fiber reinforced benzoxazine/epoxy SMPs at various woven carbon fiber contents: (●) BA-a/NGDE, (■) 30vol%, (◆) 35vol%, (▲) 40vol%, (▼) 40vol% and (▴) 50vol%.

Figure 5.4 and 5.5 illustrates loss modulus curves of 2-ply and 4-ply woven carbon fiber reinforced benzoxazine/epoxy SMPs. The glass transition temperature of the composite specimen was obtained from the peak maximum of the loss modulus curve. The glass transition temperatures (T_g) of the benzoxazine-epoxy SMPs was enhanced by an addition of the woven carbon fiber. T_g of the 2-ply woven carbon fiber reinforced benzoxazine-epoxy SMPs at the volume percentages of the woven carbon fibers of 30%, 35%, 40%, 45%, and 50% were 143°C, 138°C, 132°C, 127°C, and 127°C respectively. The T_g of 4-ply SMPs at the volume percentages of the woven carbon fibers of 30%, 35%, 40%, 45%, and 50% were 162°C, 161°C, 154°C, 142°C and 135°C respectively, where the T_g of the neat BA-a/NGDE was only 125°C. The results showed that T_g of the samples decreased with increasing woven carbon fiber contents. However, T_g of the 2-ply SMPs at 50vol% of the woven carbon fibers decreased because of the formation of an interphase with higher chain flexibility [15]. 4-ply woven carbon fiber reinforced SMPs possessed higher T_g than 2-ply SMPs at the same volume percentage of woven carbon fibers because of the restricted polymer chain movement imposed by increasing fiber reinforcement layer.

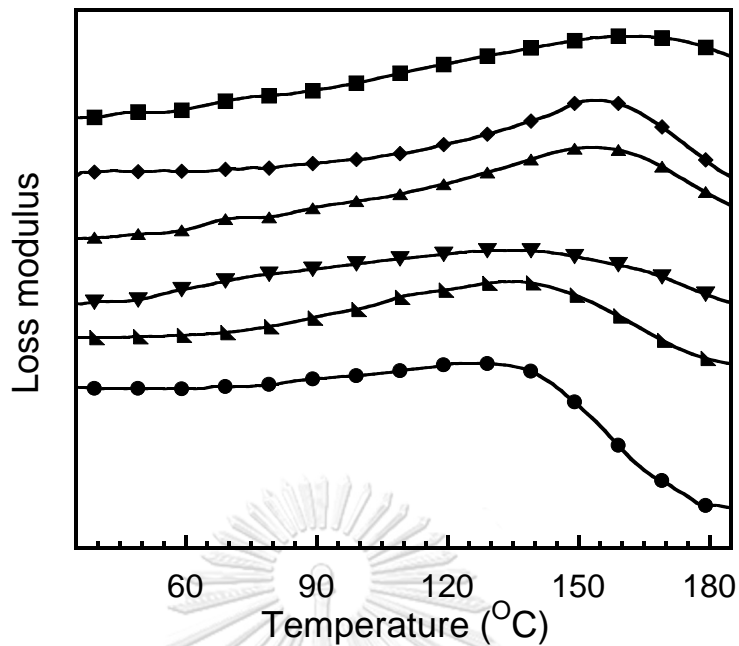


Figure 5.4 Loss modulus curves of 2-ply woven carbon fiber reinforced benzoxazine/epoxy SMPs at various woven carbon fiber contents: (●) BA-a/NGDE, (■) 30vol%, (◆) 35vol%, (▲) 40vol%, (▼) 40vol% and (▲) 50vol%.

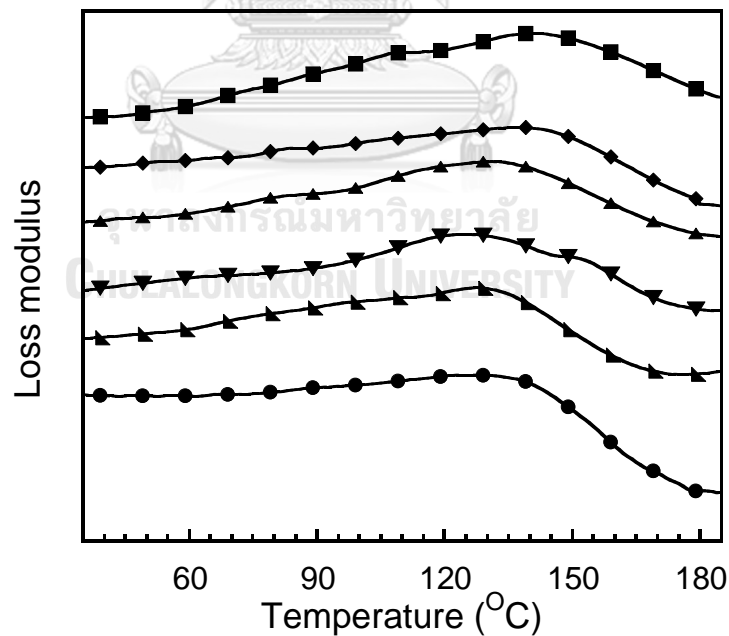


Figure 5.5 Loss modulus curves of 4-ply woven carbon fiber reinforced benzoxazine/epoxy SMPs at various woven carbon fiber contents: (●) BA-a/NGDE, (■) 30vol%, (◆) 35vol%, (▲) 40vol%, (▼) 40vol% and (▲) 50vol%.

Figure 5.6 and 5.7 illustrate storage modulus curves of 2-ply and 4-ply woven glass fiber reinforced benzoxazine-epoxy SMPs, respectively. The storage modulus curves and T_g of the samples exhibited a similar trend as woven carbon fiber reinforced benzoxazine-epoxy SMPs. The storage modulus values at room temperature (30°C) of 2-ply woven glass fiber reinforced benzoxazine-epoxy SMPs increased from 1.9 GPa (the neat matrix) to 14.2, 14.4, 16.9, 18.2, and 17.5 GPa when the volume percentages of the woven glass fibers were 30, 35, 40, 45, and 50vol%, respectively. The 4-ply woven glass fiber reinforced SMPs exhibited the storage modulus values at room temperature of 16.4, 16.8, 17.0, 20.8, and 22.7 GPa when the volume percentages of the woven glass fibers were 30, 35, 40, 45, and 50vol%, respectively.

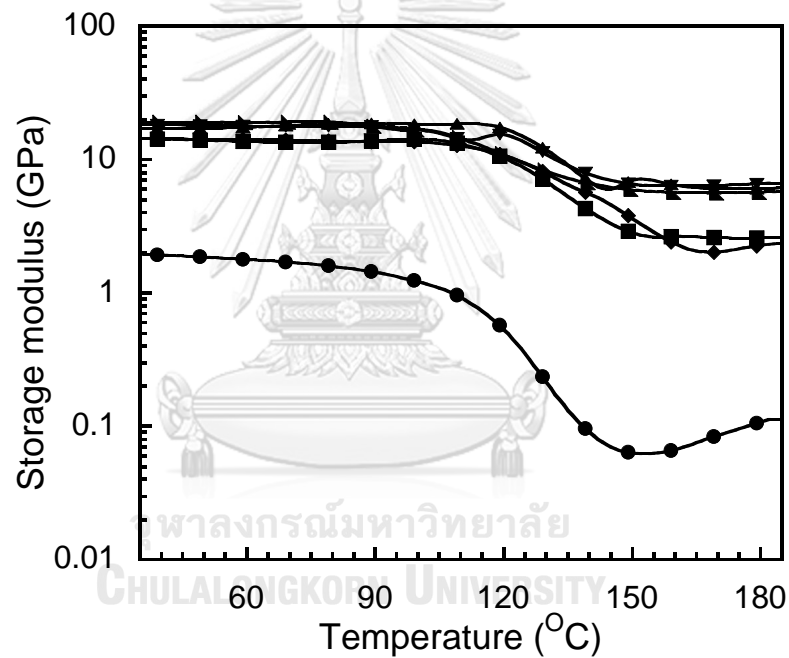


Figure 5.6 Storage modulus of benzoxazine-epoxy shape memory polymer reinforced woven carbon fiber with 2-ply at various woven glass fiber contents: (●) Ba-a/NGDE, (■) 30vol%, (◆) 35vol%, (▲) 40vol%, (▼) 40vol% and (▲) 50vol%.

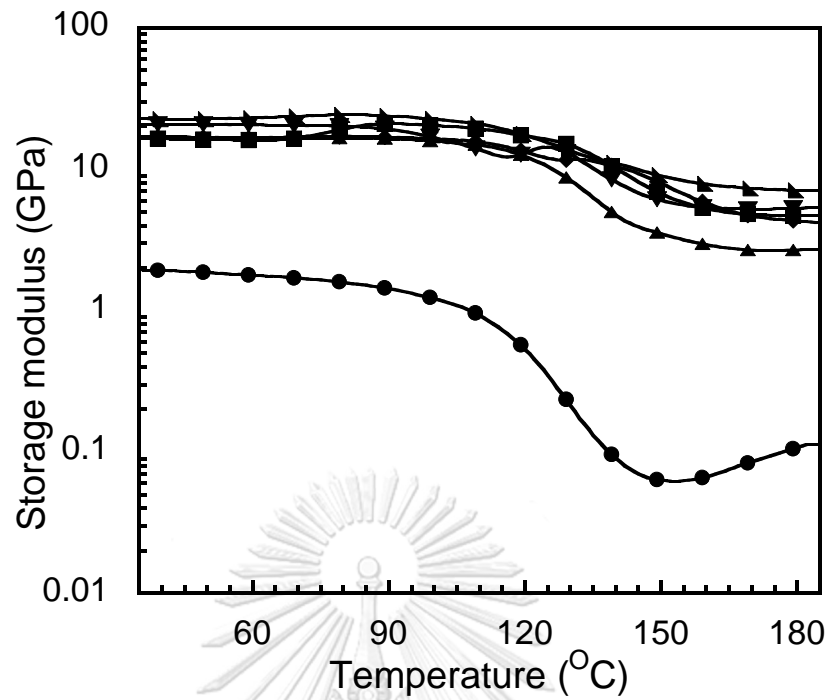


Figure 5.7 Storage modulus of benzoxazine-epoxy shape memory polymer reinforced woven carbon fiber with 4-ply at various woven glass fiber contents: (●) Ba-a/NGDE, (■) 30vol%, (◆) 35vol%, (▲) 40vol%, (▼) 40vol% and (▴) 50vol%.

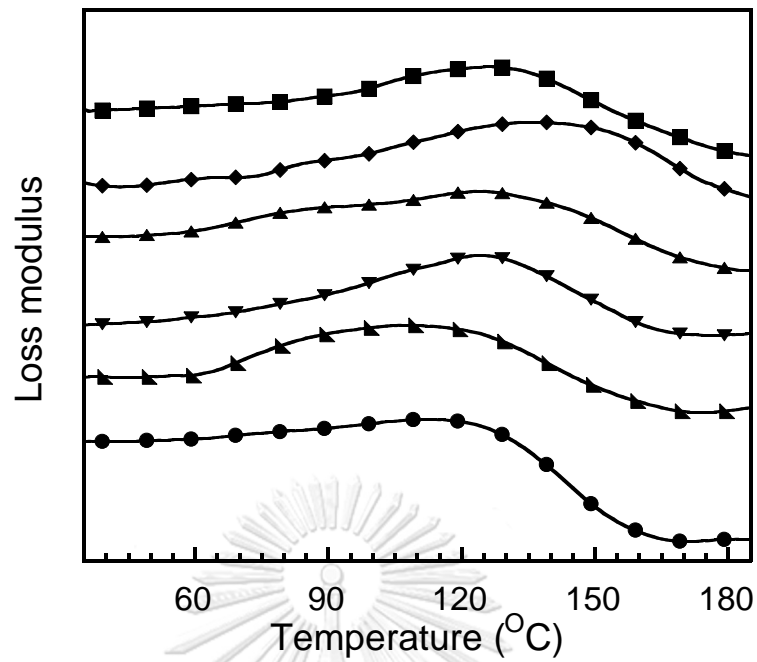


Figure 5.8 Loss modulus curves of 2-ply woven glass fiber reinforced benzoxazine-epoxy SMPs at various woven glass fiber contents: (●) Ba-a/NGDE, (■) 30vol%, (◆) 35vol%, (▲) 40vol%, (▼) 40vol% and (▲) 50vol%.

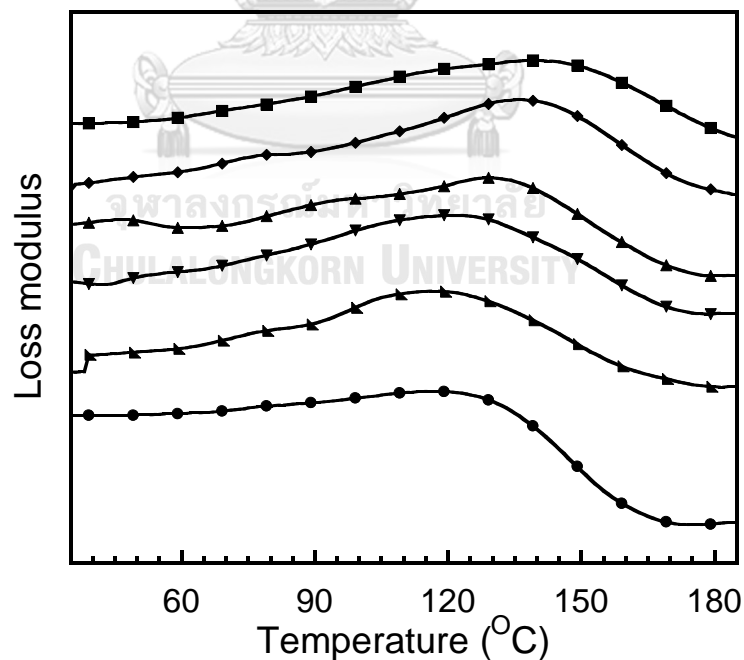


Figure 5.9 Loss modulus curves of 4-ply woven glass fiber reinforced benzoxazine-epoxy SMPs at various woven glass fiber contents: (●) Ba-a/NGDE, (■) 30vol%, (◆) 35vol%, (▲) 40vol%, (▼) 40vol% and (▲) 50vol%.

T_g of the woven glass fiber reinforced SMPs were obtained from the peak maxima of the loss modulus curves (Figure 5.8 and 5.9). At 30vol% of the woven glass fibers, T_g of the 2-ply and 4-ply woven glass fiber reinforced benzoxazine-epoxy SMPs were 135°C and 151°C, respectively, whereas the T_g of the neat BA-a/NGDE was 125°C.

The comparison of the storage modulus values 4-ply woven carbon fiber reinforced SMPs and 2-ply woven glass fiber reinforced SMPs were made because the specimens possessed nearly the same thickness (1.7, 1.6, 1.5, 1.4, and 1.3 mm at the woven carbon fiber volume percentages of 30, 35, 40, 45, and 50vol%, respectively). The storage modulus of the woven carbon fiber reinforced SMPs was greater than that of woven glass fiber reinforced SMPs because woven carbon fibers have young's modulus more than that of woven glass fibers. O'Masta *et al.* [41] reported young's modulus of carbon fibers and glass fibers to be 85 and 345-520 GPa, respectively. Furthermore, the T_g values 4-ply woven carbon fiber reinforced SMPs was greater than that of 2-ply woven glass fiber because the oxide groups presented on the surface of carbon fibers facilitated the better interaction between carbon fibers and the polymer matrix.[42].

5.3 Effect of woven carbon fiber and woven glass fiber reinforced benzoxazine-epoxy SMPs on Mechanical Properties

5.3.1 Flexural Properties at Room Temperature (Glassy State)

The mechanical properties of the benzoxazine-epoxy SMPs reinforced woven carbon fiber and glass fiber were investigated at glassy state (room temperature) and rubbery state ($T_g+20^\circ\text{C}$). Mostly, SMPs were commonly utilized at these temperatures.

Figures 5.10 and 5.11 show the plots of the flexural modulus and flexural strength of woven carbon and glass fibers reinforced benzoxazine-epoxy SMPs at room temperature as a function of the fibers content, respectively. Figures 5.10 showed the flexural modulus are the ratio of stress to strain values. At 30, 35, 40, 45 and 50vol% of the fiber contents, 2-ply and 4-ply woven carbon fiber reinforced SMPs had flexural

modulus values of 1.7, 6.3, 12.2, 19.5, 23.9 GPa and 87.0, 97.4, 112.8, 138.7, 327.5 GPa, respectively. In addition, the flexural modulus values of 2-ply and 4-ply woven glass fiber reinforced SMPs were 17.3, 20.6, 24.9, 29.5, 31.2 GPa, and 27.0, 33.7, 76.2, 86.4, 109.0 GPa when the volume percentages of the woven glass fibers were 30, 35, 40, 45, and 50vol%, respectively. The woven carbon and woven glass fiber reinforcements resulted in a systematic increase in the modulus of the obtained SMPs. This was because the incorporation of high flexural modulus fibers into matrix structure could increase the stiffness of SMP [16].

Figure 5.11 exhibited the plot of the flexural strength as a function of fiber contents. The flexural strength values at glassy state of benzoxazine-epoxy SMPs at 2-ply and 4-ply woven carbon fibers were 78.3, 81.3, 98.4, 119.9, 150.7 MPa and 741.2, 816.1, 875.3, 901.2, 1473.4 MPa at 30, 35, 40, 45, and 50vol% of fibers, respectively. Moreover, the flexural strength of the SMPs at 2-ply and 4-ply woven glass fibers were 92.7, 112.4, 178.7, 210.4, 249.9 and 293.3, 350.8, 371.4, 512.5, 847.3 MPa at the volume percentages of the woven glass fibers of 30, 35, 40, 45, and 50vol%, respectively. The flexural strength at glassy state of the benzoxazine-epoxy SMPs increased with increasing of the fibers contents. This enhancement in flexural strength was because of high young's modulus of woven fibers could lead to effective stress transfer within the reinforced polymer matrix, leading to high composite strength.

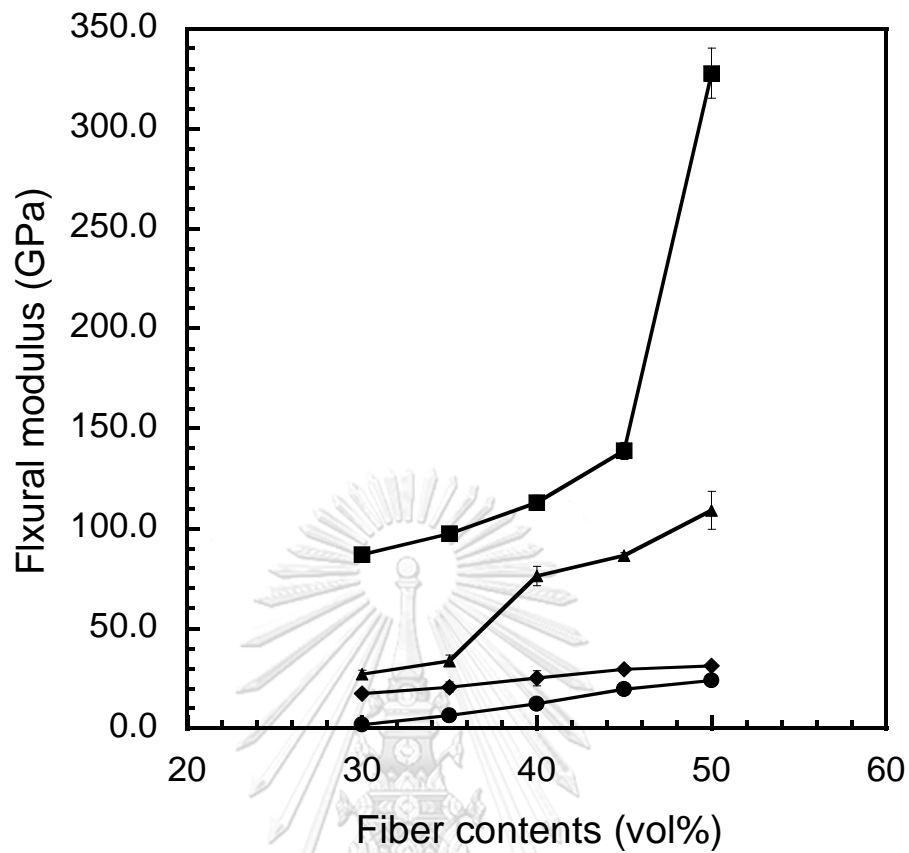


Figure 5.10 Relationship between flexural modulus at room temperature and fiber contents at various number of ply of woven carbon fiber (CF) and glass fiber (GF): (●) 2-ply CF (■) 4-ply CF, (◆) 2-ply GF, (▲) 4-plyGF.

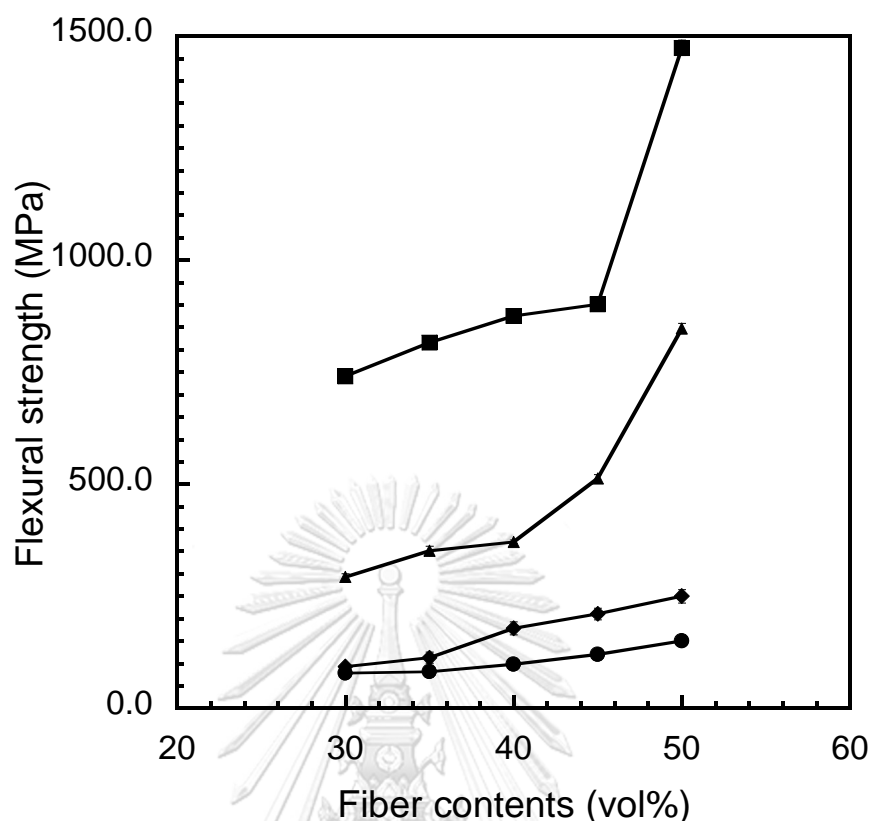


Figure 5.11 Relationship between flexural strength at room temperature and fibers content at various number of ply of woven carbon fiber (CF) and glass fiber (GF): (●) 2-ply CF (■) 4-ply CF, (◆) 2-ply GF, (▲) 4-ply GF.

5.3.2 Flexural Properties at Rubbery State

Mechanical properties of SMPs at a rubbery state are also important parameters that affect utilization of SMPs. The flexural properties of the woven fiber reinforced benzoxazine-epoxy SMPs were measured using three-point bending tests. A forced air convective environmental chamber was used for the tests at elevated temperatures. The test was conducted at rubbery state of the SMPs ($T_g+20^\circ\text{C}$). Figure 5.12 show the plots of the flexural modulus of the woven fiber reinforced benzoxazine-epoxy SMPs as a function of the fibers contents, respectively. The flexural modulus values at 30, 35, 40, 45 and 50vol% of woven carbon fiber reinforced SMPs were 0.7, 1.4, 2.4, 2.6, 4.3 GPa with 2-ply and 12.1, 17.5, 23.9, 30.4, 48.4 GPa with 4-ply, respectively. In addition, the flexural modulus of the woven glass fibers reinforced SMPs were 6.6, 9.5,

11.6, 13.9, 14.7 GPa with 2-ply and 7.5, 11.6, 15.2, 22.7, 25.4 GPa with 4-ply at the volume percentages of the woven glass fibers of 30, 35, 40, 45, and 50vol%, respectively. The results showed that increasing woven fiber contents cause higher flexural modulus because increasing stiffness of SMPs due to high young's modulus of woven fibers.

Figure 5.13 exhibits the plot of the flexural strength as a function of fiber contents. The flexural strength values at rubbery state of benzoxazine-epoxy SMPs reinforced of woven carbon fibers were 20.0, 24.7, 33.1, 47.6, 56.9 with 2-ply and 37.6, 59.8, 72.7, 142.3, 148.79 MPa with 4-ply at 30, 35, 40, 45 and 50 vol%, respectively. Furthermore, the flexural strength of the woven glass fiber reinforced SMPs were 17.5, 21.7, 36.1, 41.9, 65.6 MPa with 2-ply and 60.3, 65.9, 77.7, 92.9, 121.5 MPa with 4-ply at the volume percentages of the woven glass fibers of 30, 35, 40, 45, and 50vol%, respectively. The flexural strength at rubbery state of the benzoxazine-epoxy SMPs increased with increasing of the fibers contents. This increment in flexural strength was due to the same reason of that observed in increasing flexural modulus at glassy state, i.e. high young's modulus of woven fibers reinforcement could lead to effective stress transfer and high composite strength.

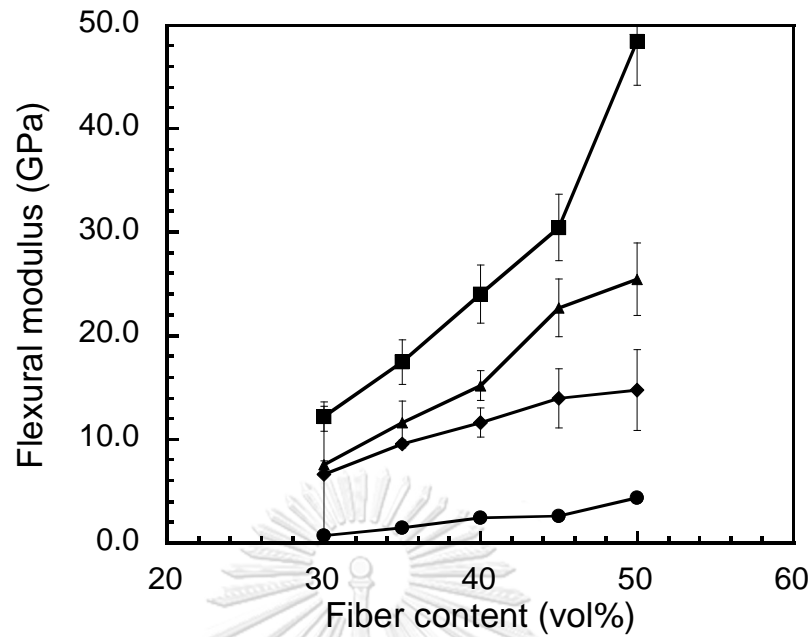


Figure 5.12 Relationship between flexural modulus at $T_g + 20$ degree Celsius and fibers content at various number of ply of woven carbon fiber (CF) and glass fiber (GF): (●) 2-ply CF (■) 4-ply CF, (◆) 2-ply GF, (▲) 4-ply GF.

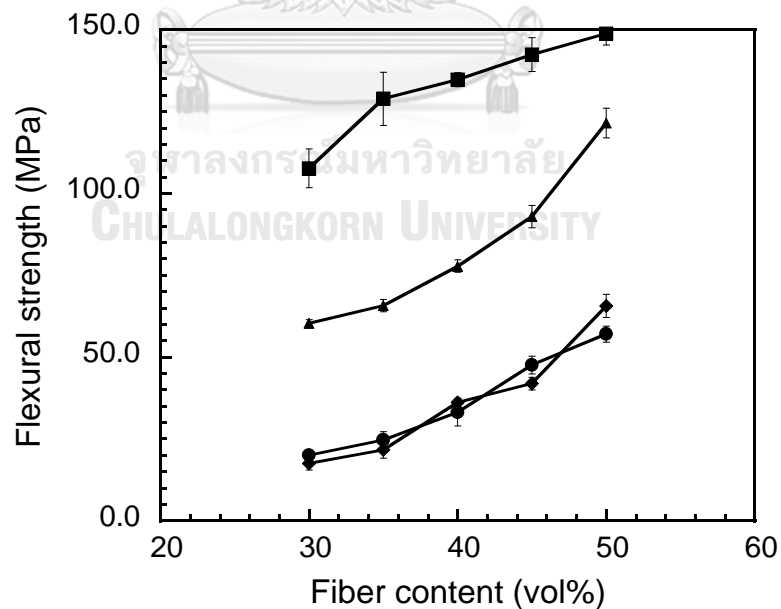


Figure 5.13 Relationship between flexural strength at $T_g + 20$ degree Celsius and fibers content at various number of ply of woven carbon fiber (CF) and glass fiber (GF): (●) 2-ply CF (■) 4-ply CF, (◆) 2-ply GF, (▲) 4-ply GF.

5.4 Shape Memory Properties

5.4.1 Shape Fixity of Woven Carbon and Glass Fibers Reinforced Benzoxazine-Epoxy SMPs

Shape memory behavior of the sample was evaluated by three parameters. Shape fixity is one parameter indicating the ability to remember the temporary shape or fixed shape of a polymer sample. The shape fixity was measured using flexural tests and a forced air convective environmental chamber was used for elevated-temperature tests. The flexural load was applied to deform and fix a sample. Then, unload step was conducted to measure shape fixity value. The shape fixity of 2-ply and 4-ply woven carbon reinforced benzoxazine-epoxy SMPs are illustrated in Figure 5.14 and Figure 5.15, respectively. For the 2-ply woven carbon reinforced benzoxazine-epoxy SMPs, the shape fixity (R_f) values of specimens were in range 99.6 to 100% with 1% strain, 98.5 to 99.7 with 3% strain, 97.5 to 99.4 with 5% strain and 91.0 to 95.1 with 7% strain, respectively. The 4-ply of woven carbon reinforced benzoxazine-epoxy SMPs on shape fixity were in range 99.2 to 99.9 with 1% strain, 97.3 to 98.7 with 3% strain and 94.6 to 96.3 with 5% strain, respectively. In addition, the shape fixities of 2-ply and 4-ply of woven glass fiber reinforced benzoxazine-epoxy SMPs are illustrated in Figure 5.16 and Figure 5.17, respectively. As can be seen from Figure 5.16, the shape fixity (R_f) values of the 2-ply specimens were in range 99.3 to 99.9 with 1% strain and 91.7 to 98.7 with 3% strain, and 85.5 to 89.7 with 5% strain, respectively. Moreover, shape fixity values of 4-ply specimens were 99.1 to 99.9 and 91.2 to 97.5, respectively. From the experiment, an increase in percentage of strain of the woven carbon and glass fibers at 2-ply and 4-ply in the benzoxazine-epoxy matrix resulted in a slight decrease in the composite's shape fixity. However, the shape fixities of all specimens were observed to be greater than 85%, which were high enough for a typical shape memory performance and significantly higher than those of some other shape memory composites [21]. Furthermore, as the woven fibers content increased, the shape fixity (R_f) were slightly increased. The presence of woven carbon fiber in composites improved structural

rigidity and stable polymer network. The strong stable network could prevent the chains from moving freely. Hence, the R_f values increased.

The shape fixity at the same percentage of strain of the woven carbon fiber reinforced SMPs was greater than that of woven glass fiber reinforced SMPs because the better interfacial adhesion between woven carbon fibers and the polymer matrix that facilitates the fixing of temporary shape.

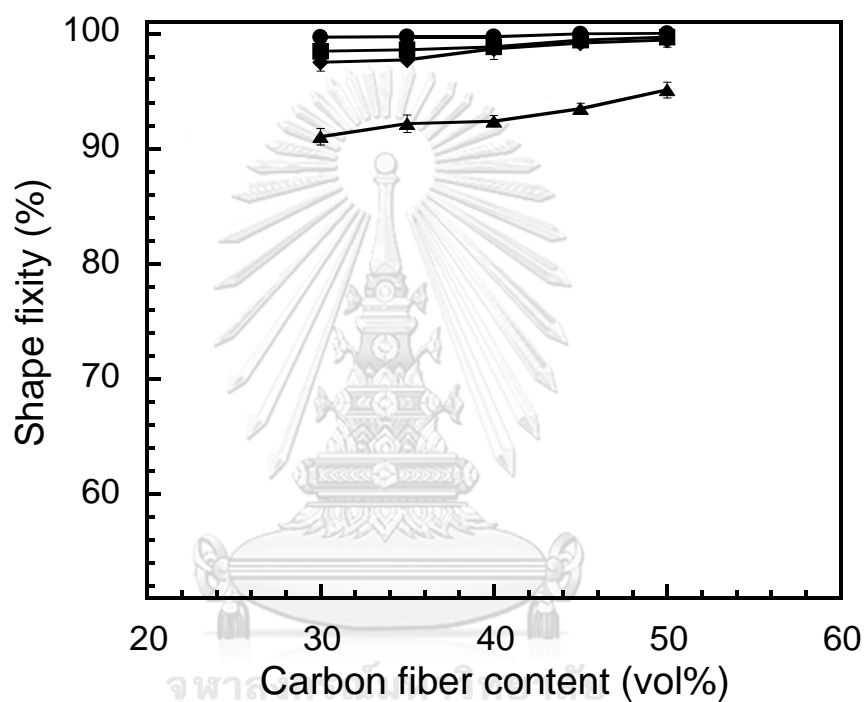


Figure 5.14 Effects of carbon fiber contents and various percentages of strain ((●) 1%, (■) 3%, (◆) 5%, and (▲) 7%) and on shape fixity of 2-ply woven carbon fiber reinforced benzoxazine-epoxy SMPs.

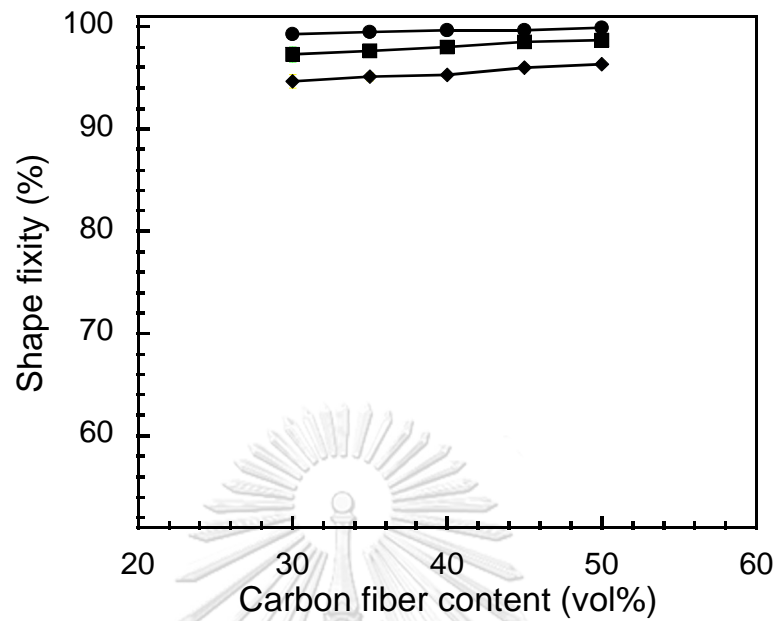


Figure 5.15 Effects of woven carbon fiber contents and various percentages of strain ((●) 1%, (■) 3%, (◆) 5%, and (▲) 7%) on shape fixity of 4-ply woven carbon fiber reinforced benzoxazine-epoxy SMPs.

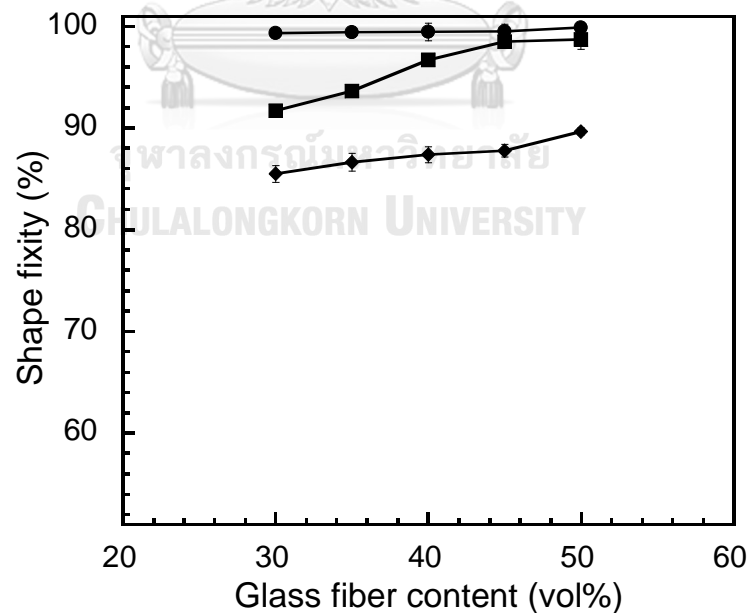


Figure 5.16 Effects of glass fiber contents and various percentages of strain ((●) 1%, (■) 3%, (◆) 5%, and (▲) 7%) on shape fixity of woven carbon fiber reinforced benzoxazine-epoxy SMPs.

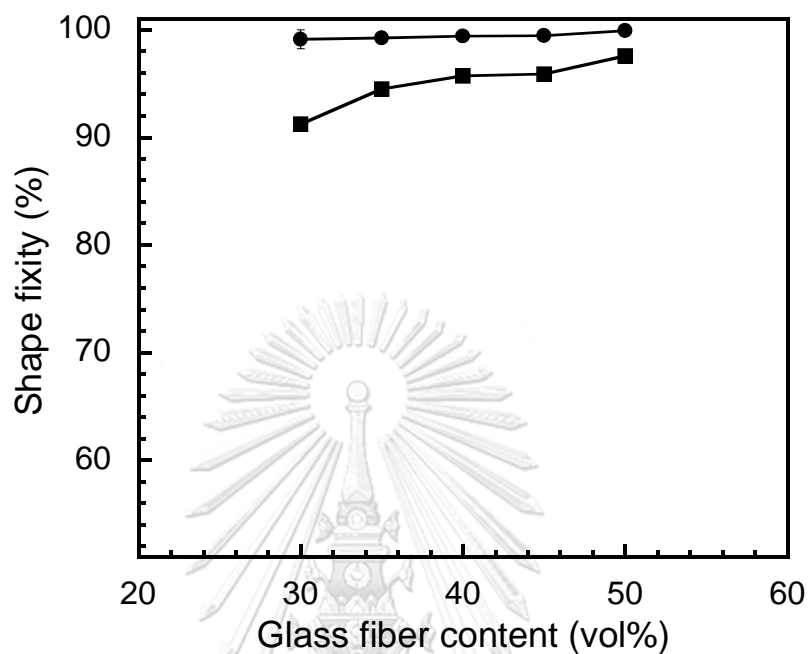


Figure 5.17 Effects of glass fiber contents and various percentages of strain ((●) 1% and (■) 3%) on shape fixity of 4-ply woven glass fiber reinforced benzoxazine-epoxy SMPs.

5.4.2 Shape Recovery of Woven Carbon and Glass Fibers Reinforced Benzoxazine-Epoxy SMPs

Shape recovery (R_r) is another parameter that is measured after a recovery of a fixed temporary shape. The effects of woven carbon fibers and woven glass fibers on shape recovery of the sample are illustrated in Figure. 5.18 – Figure 5.21. In Figure 5.18, the shape recovery values of 2-ply woven carbon fiber reinforced benzoxazine-epoxy SMPs decreased with increasing woven carbon fiber contents. It was because woven carbon fiber obstructed a polymeric chain mobility. The shape recovery values of 2-ply woven carbon fiber reinforced SMPs decreased from 100 to 99.3 with 1% strain, 99.4 to 99.0 with 3% strain, 99.2 to 98.2 with 5% strain and 93.8 to 87.2 with 7% strain. The 4-ply woven carbon reinforced benzoxazine-epoxy SMPs exhibited shape recovery

values of 99.9 to 99.5 with 1% strain and 99.5 to 98.6 with 3% strain, and 98.0 to 96.3 with 5% strain, respectively. For the 2-ply woven glass fiber reinforced SMPs, the shape recovery values were 99.6 to 99.1 with 1% strain, 99.5 to 99.0 with 3% strain, and 98.9 to 98.0 with 5% strain. The 4-ply woven glass fiber reinforced SMPs showed the shape recovery values of 99.6 to 99.2 with 1% strain and 99.4 to 97.9 with 3% strain. It can be seen that shape recovery values of all samples decreased with increasing reinforced fiber contents. The proportion of hard segments in SMPs increased with woven carbon fiber contents and thus the polymeric chain movement was hindered. Therefore, the shape recovery process was interfered. In addition, an increase in percentage of strain of the woven carbon fibers at 2-ply and 4-ply in the benzoxazine-epoxy matrix resulted in a slight decrease in the composite's shape recovery. The shape recovery values of all specimens were observed to be greater than 96%. In addition, these values were higher than other carbon fiber reinforced shape memory polymer composites [21].

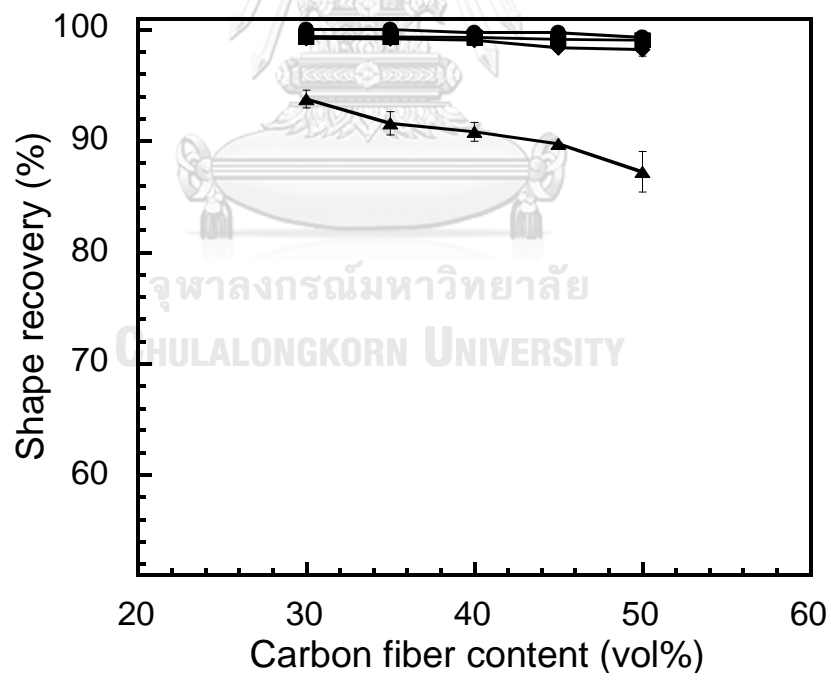


Figure 5.18 Effect of carbon fiber contents and various percentages of strain ((●)1%, (■) 3%, (◆)5%, and (▲)7%) and on shape recovery of 2-ply woven carbon fiber reinforced benzoxazine-epoxy SMPs.

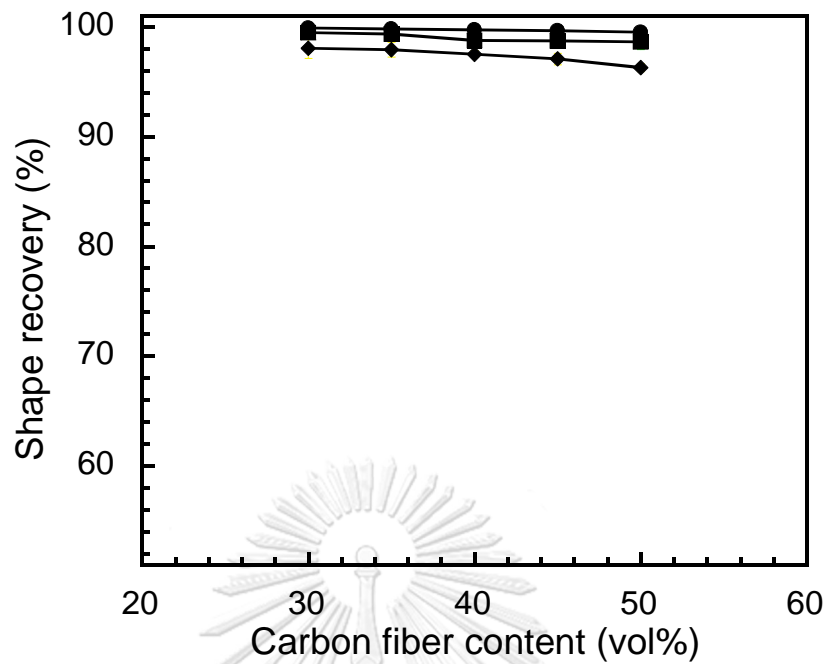


Figure 5.19 Effect of carbon fiber contents and various percentage of strain ((●) 1%, (■) 3%, and (◆) 5%) on shape recovery of 4-ply woven carbon fiber reinforced benzoxazine-epoxy SMPs.

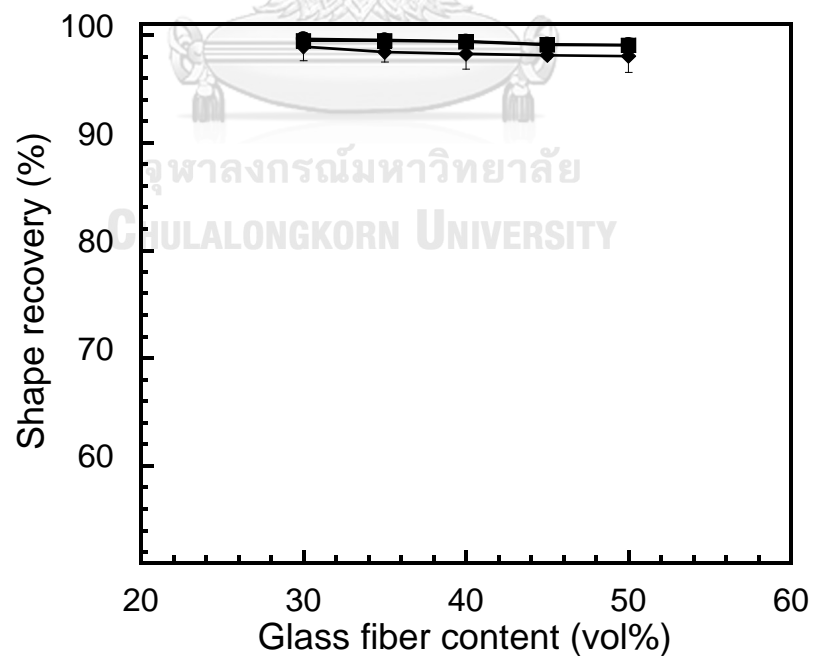


Figure 5.20 Effect of glass fiber contents and various percentages of strain ((●) 1%, (■) 3%, and (◆) 5%) on shape recovery of 2-ply woven glass fiber reinforced benzoxazine-epoxy SMPs.

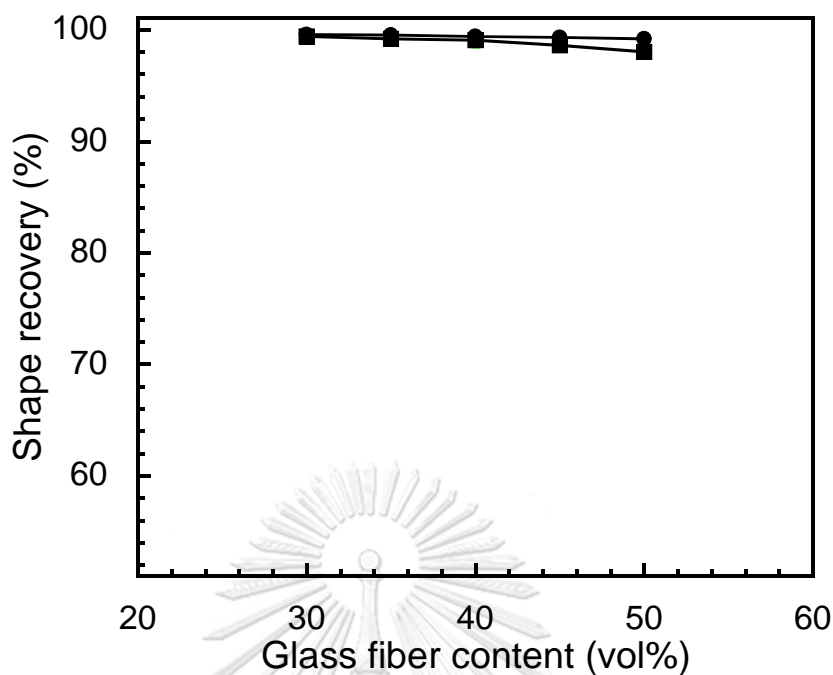


Figure 5.21 Effect of glass fiber contents and various percentage of strain ((●) 1%, (■) 3%, and (◆) 5%) and on shape recovery of 4-ply woven glass fiber reinforced benzoxazine-epoxy SMPs.

The shape recovery at the same percentage of strain of the woven carbon fiber reinforced SMPs was greater than that of woven glass fiber reinforced SMPs. E. Fitzer *et al.* reported that a direct correlation between the amount of carboxylic groups on the carbon fiber surface and the phenolic reinforcements. In addition, the oxide groups on carbon fibers exhibited a good interfacial adhesion with the polymer matrix [42]. Therefore, the shape recovery values of the carbon fiber reinforced SMPs was greater than those of the glass fiber reinforced SMPs.

5.4.3 Shape Recovery Time of Woven Carbon and Glass Fibers Reinforced Benzoxazine-Epoxy SMPs

The recovery time in SMP is an important property in many applications. The shape recovery time of the woven carbon and glass fibers reinforced benzoxazine-

epoxy SMPs were obtained using a universal testing machine equipped with an environmental chamber.

Figure 5.22–5.25 illustrate recovery time as a function of woven fiber contents. The recovery time were determined at maximum recovery for each specimen. The recovery time of 2-ply woven carbon fiber (Figure 5.22) were in the range of 1.7 to 7.1 seconds with 1% strain, 11.8 to 28.5 with 3% strain, 18.5 to 36.0 seconds with 5% strain, and 21.3 to 37.7 seconds with 7% strain. In addition, the recovery time of 4-ply woven carbon fiber (Figure 5.23) were in range of 2.9 to 8.7 seconds with 1% strain, 23.0 to 39.3 seconds with 3% strain, and 35.6 to 50.4 seconds with 5% strain. Figure 5.24 showed the recovery time of 2-ply woven glass fiber reinforced SMPs. The values were in range of 2.9 to 9.9 seconds with 1% strain, 22.9 to 42.8 seconds with 3% strain, and 55.2 to 61.2 with 5% strain. The recovery time of 4-ply woven glass fiber reinforced SMPs (Figure 5.25) were in range of 5.2 to 7.2 seconds with 1% strain and 45.3 to 121.2 seconds with 3% strain. The recovery time decreased with increasing percentage of strain. Increasing percentages of strain might trigger the damage within the polymer matrix and the recovery time was extended. It can be seen that the recovery time increased with increasing woven fiber contents. The addition of woven fibers into SMP effected directly on the proportion of hard segments SMPs and the original shape recovery was more difficult. However, the recovery time in this composite systems at 1% strain was less than those observed in reported woven glass fiber reinforced epoxy shape memory composites [16]

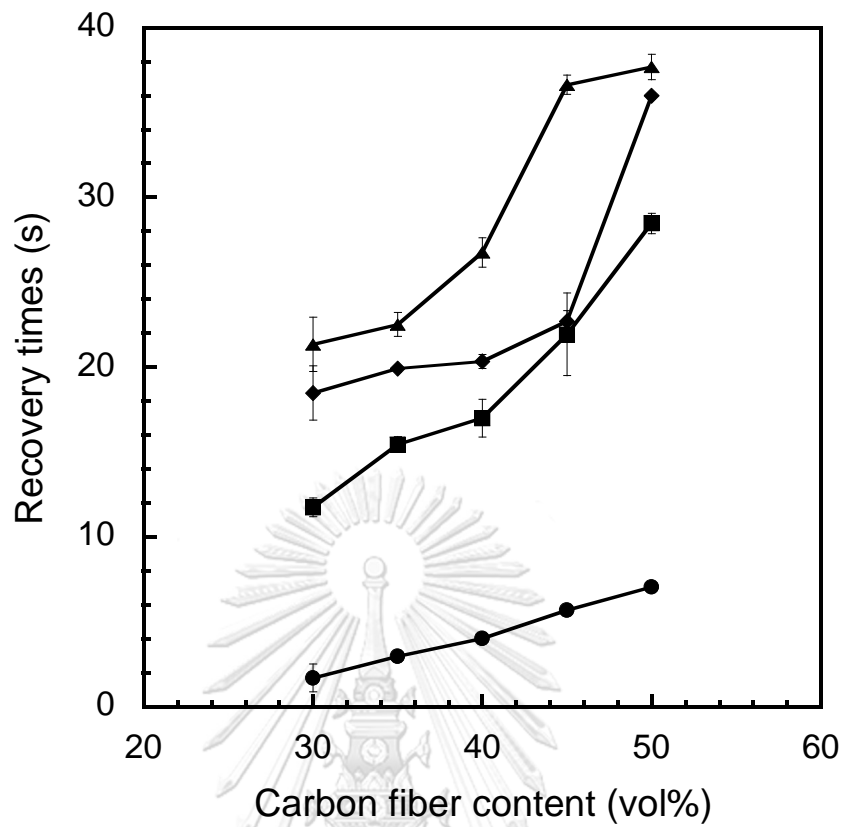


Figure 5.22 Shape recovery time as a function of woven carbon fiber contents at various percentages of strain ((●) 1%, (■) 3%, (◆) 5%, and (▲) 7%) of 2-ply woven carbon fiber reinforced benzoxazine-epoxy SMPs.

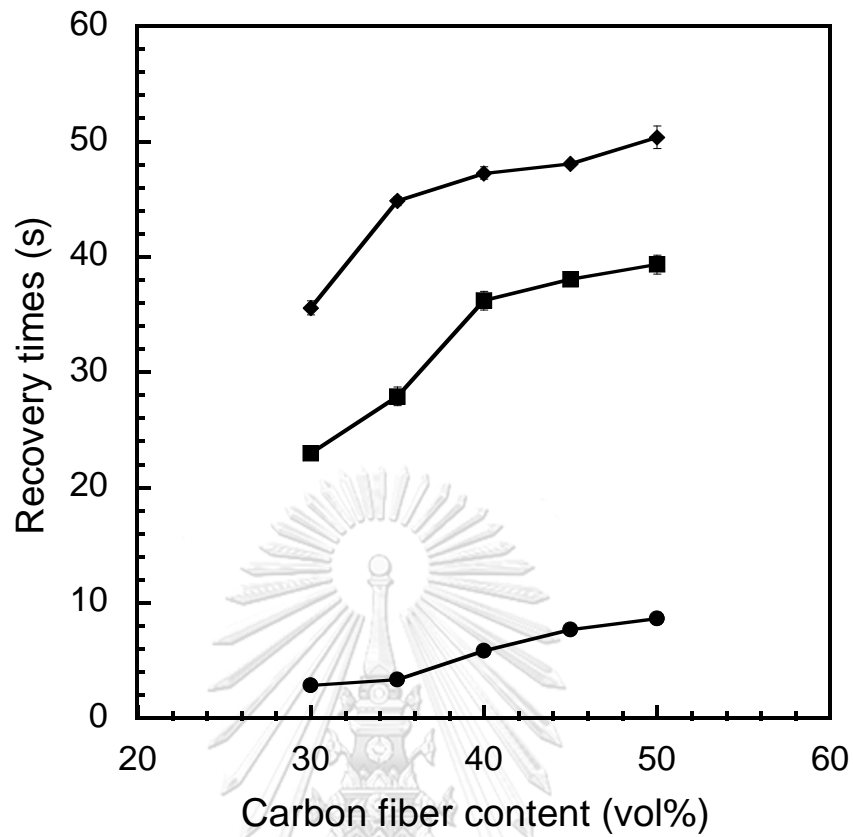


Figure 5.23 Shape recovery time as a function of woven carbon fiber contents at various percentages of strain ((●) 1%, (■) 3%, and (◆) 5%) of 4-ply woven carbon fiber reinforced benzoxazine-epoxy SMPs.

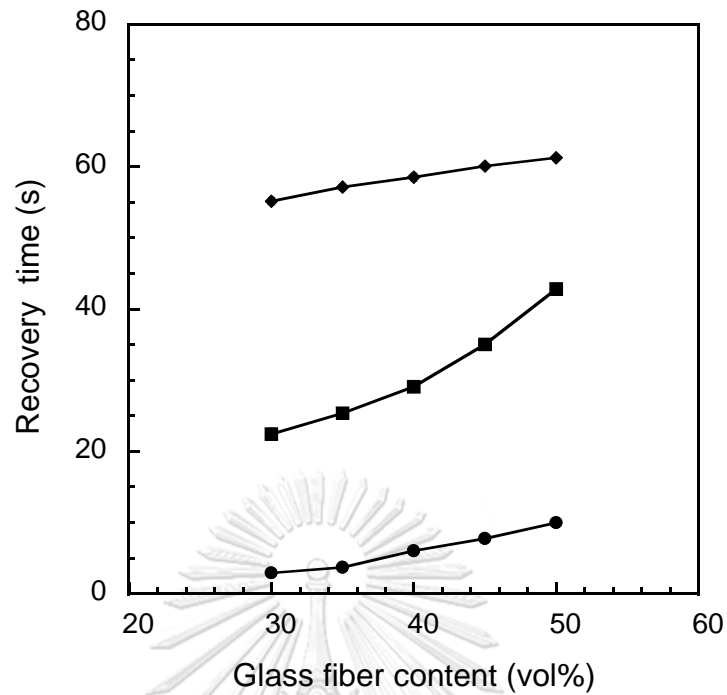


Figure 5.24 Shape recovery time as a function of woven glass fiber contents at various percentages of strain ((●) 1%, (■) 3%, and (◆) 5%) of 2-ply woven glass fiber reinforced benzoxazine-epoxy SMPs.

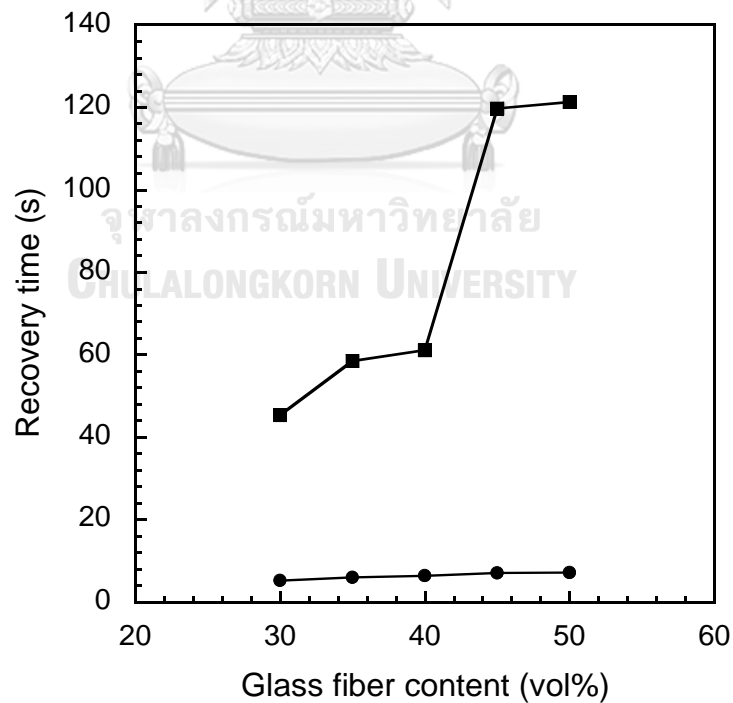


Figure 5.25 Shape recovery time as a function of woven glass fiber contents at various percentages of strain ((●) 1%, and (■) 3%) of 4-ply woven glass fiber reinforced benzoxazine-epoxy SMPs.

The recovery time of the woven carbon fiber reinforced SMPs was less than that of woven glass fiber reinforced SMPs at the same thickness and volume percentage of the fibers. The polymer matrix that was interfacially adhered to the fibers played an important role in the shape memory behavior of the composites. The smaller dimensions of the woven carbon fibers facilitated the shape recovery process and thus shortened the recovery time, whereas the larger dimensions of woven glass fibers impeded the shape recovery process.

5.4.4 Effect of Woven Carbon and Glass Fibers Reinforced Benzoxazine-Epoxy SMPs on Recovery Stress

The recovery stress is crucial property for smart material applications involving deployable structures. The recovery stress of SMPs is defined from the elastic stress in deformation procedure. When the SMPs were heated above T_g , the SMPs were deformed and the elastic stress was generated. 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 a recovery stress [23].

The recovery stress process for woven carbon and glass fibers reinforced benzoxazine-epoxy SMPs consists of four stages. In the initial stage, a sample is in an original rectangular shape. In the deformed state, the sample is bended at various percentage of strain. Then, the sample is fixed by cooling below T_g to get a temporary shape. At the final stage, the sample is heated and the bent shape of sample is subsequently recovered. The recovery stress of SMPs was measured from transition stage of the shape-fixed stage to the recovery shape stage [9]. The recovery stresses versus time of the woven carbon and glass fiber reinforced benzoxazine-epoxy SMPs are illustrated in Figure 5.26–5.33. The maximum recovery stress values of woven carbon fiber and glass fiber reinforced benzoxazine-epoxy SMPs at 2 plies and 4 plies are shown in Table 5.1–5.4. The woven carbon and glass fiber could improve the recovery stress of the benzoxazine-epoxy SMPs. The increase of the recovery stress of the SMPs was due to the presence of high elastic modulus reinforcing fibers [19].

Woven fibers were able to enhance elastic modulus of polymer composite and stiffen the stable network. As previously reported by M. Fejos *et al.* [16], the increase in the recovery stress value of woven glass fiber reinforced epoxy shape memory composites. It was found that the recovery stress was observed to be 42.3 MPa at 38vol% of glass fibers.

In addition, the recovery stress decreased with increasing percentage of strain. Increasing percentages of strain might trigger the damage within the polymer matrix and hindered the final shape recovery stage.

Table 5.1 Recovery stress values of the 2-ply woven carbon fiber reinforced benzoxazine-epoxy SMPs.

Woven carbon fiber contents (vol%)	Recovery stress at various percentage of strain (MPa)			
	1%strain	3%strain	5%strain	7%strain
30	45.2	38.9	34.1	30.2
35	41.4	34.2	30.9	24.6
40	32.4	32.3	28.8	24.4
45	25.0	21.0	18.5	13.6
50	22.4	21.9	18.9	15.4

Table 5.2 Recovery stress values of the 4-ply woven carbon fiber reinforced benzoxazine-epoxy SMPs.

Woven glass fiber contents (vol%)	Recovery stress at various percentage of strain (MPa)		
	1%strain	3%strain	5%strain
30	32.1	31.0	30.1
35	26.5	23.8	22.6
40	23.5	21.9	21.6
45	19.4	18.3	17.4
50	14.8	14.2	12.1

Table 5.3 Recovery stress values of the 2-ply woven glass fiber reinforced benzoxazine-epoxy SMPs.

Woven carbon fiber contents (vol%)	Recovery stress at various percentage of strain (MPa)		
	1%strain	3%strain	5%strain
30	138.8	127.7	87.7
35	88.0	77.8	76.5
40	60.1	58.3	53.4
45	47.4	37.6	32.7
50	38.2	35.1	28.1

Table 5.4 Recovery stress values of the 4-ply woven glass fiber reinforced benzoxazine-epoxy SMPs.

Woven glass fiber contents (vol%)	Recovery stress at various percentage of strain (MPa)	
	1%strain	3%strain
30	61.2	34.3
35	51.8	33.7
40	42.3	32.2
45	42.2	30.5
50	42.2	29.3

5.5 Optical Microscopy Investigations on Shape Memory Effect

The micrographs of the sample fracture surface were used to qualitatively evaluate the interfacial interaction between the fiber and the matrix. Figure 5.26–5.27 show the fracture surface of the 4-ply woven carbon fiber and 2-ply woven glass fiber reinforced SMPs at the same volume percentage of the fiber of 30vol%. Increasing percentages of strain might trigger the damage within the polymer matrix because the excessive strain. In addition, woven carbon fiber reinforced benzoxazine-epoxy SMPs displayed a lower extent of the fracture surfaces than that of the woven glass fiber reinforced SMPs because the higher strength of the carbon fibers than that of the glass fibers [40].

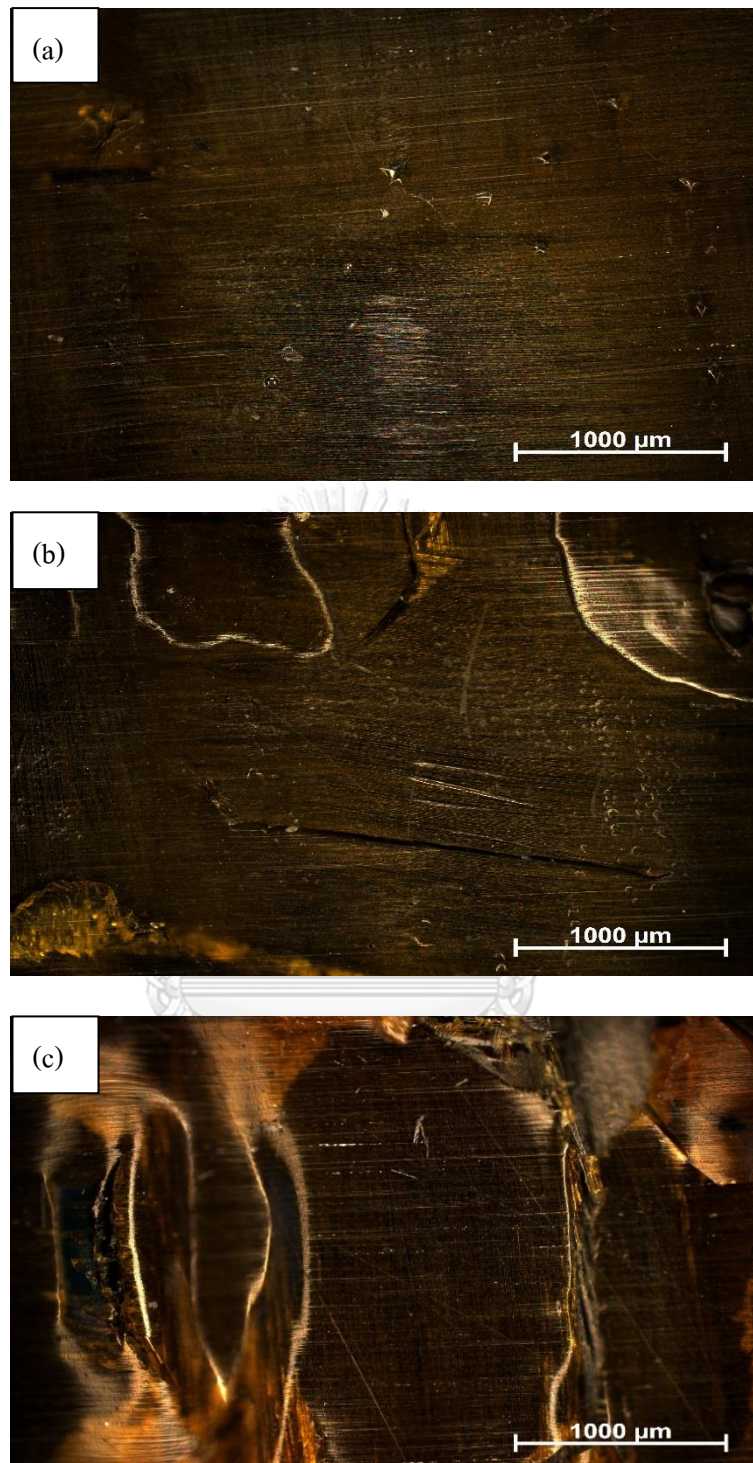


Figure 5.26 Optical micrographs of fracture surfaces of 4-ply woven carbon fiber reinforced benzoxazine-epoxy SMPs at various percentages of strain ((a) 1%, (b) 3%, and (c) 5%)

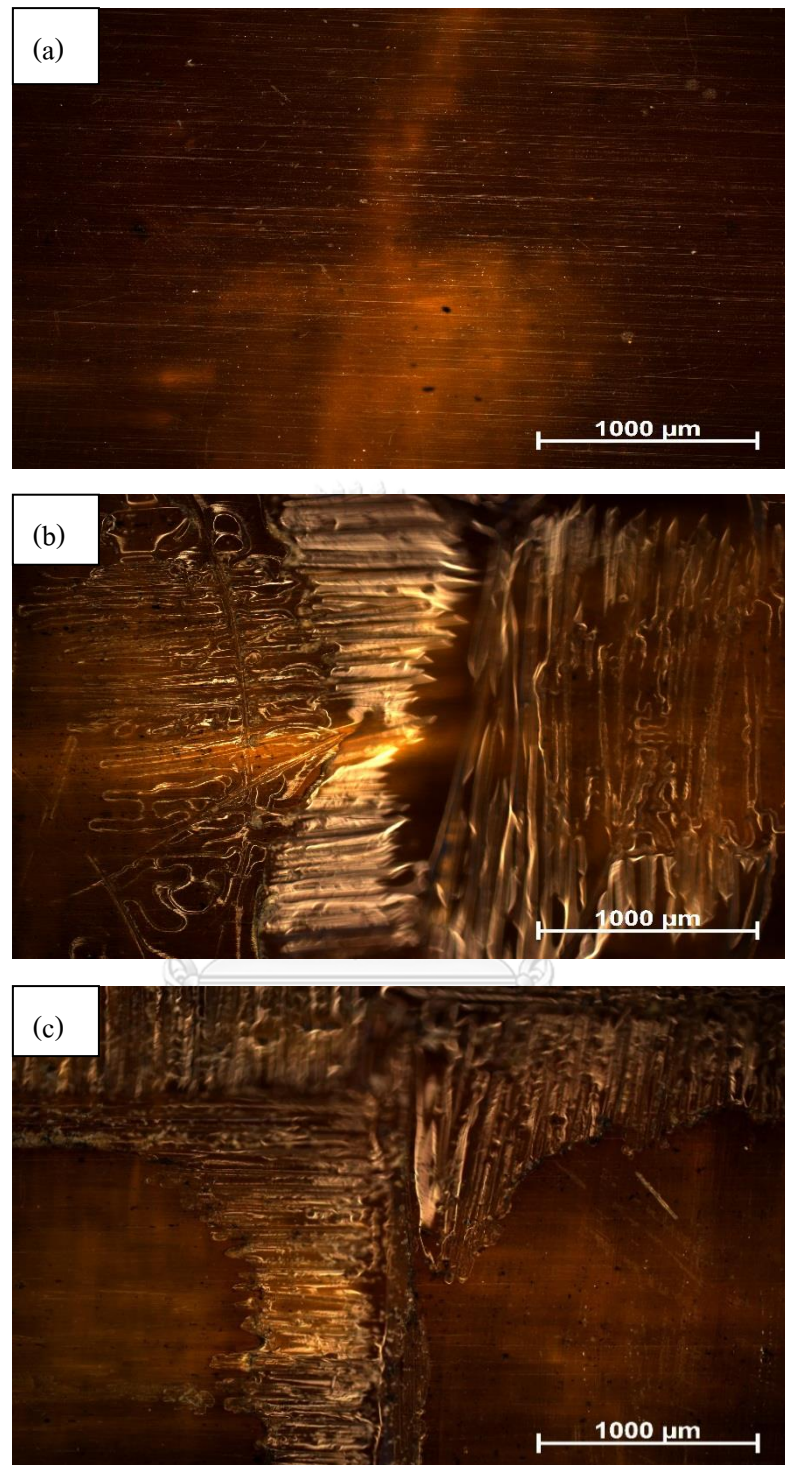


Figure 5.27 Optical micrographs of fracture surfaces of 2-ply woven glass fiber reinforced benzoxazine-epoxy SMPs at various percentages of strain ((a) 1%, (b) 3%, and (c) 5%).

5.6 Effects of Alternating Woven Carbon Fiber (CF) and Woven Glass Fiber (GF) Layers on Recovery Stress of Benzoxazine-Epoxy SMPs

Recovery stress are important parameters of shape memory properties. Figure 5.28–5.29 illustrate recovery stress as a function time of woven fiber reinforced benzoxazine-epoxy SMPs with 2-ply and 4-ply alternating woven carbon fiber and woven glass fiber layers, respectively. The percentage by volume of the woven fiber for each layer was 30vol%. From Figure 5.28, the recovery stress values of woven fiber reinforced benzoxazine-epoxy SMPs with 2-ply alternating woven carbon fiber and woven glass fiber layers were 26.5 with 1%strain, 20.8 with 3%strain, 19.8 with 5%strain, and 17.6 MPa with 7%strain. The recovery stress values of woven fiber reinforced benzoxazine-epoxy SMPs with 4-ply alternating woven carbon fiber and woven glass fiber layers were 56.1 with 1%strain, 44.3 with 3%strain, and 40.0 MPa with 5%strain (Figure 5.29). The recovery stress decreased with increasing percentage of strain. Increasing percentages of strain might trigger the damage within the polymer matrix. The SMP system with only one type of reinforcing fiber yielded higher the recovery stress than that the system with alternating fiber layers. As can be seen from the micrographs Figure 5.30–5.31, the SMP system with only one type of reinforcing fiber exhibited less surface fractures when compared to those of the SMP system with alternating reinforcing fiber layers. Therefore, recovery stress of the the SMP system with one type of reinforcing fiber was more than that of the SMP system with alternating reinforcing fiber layers.

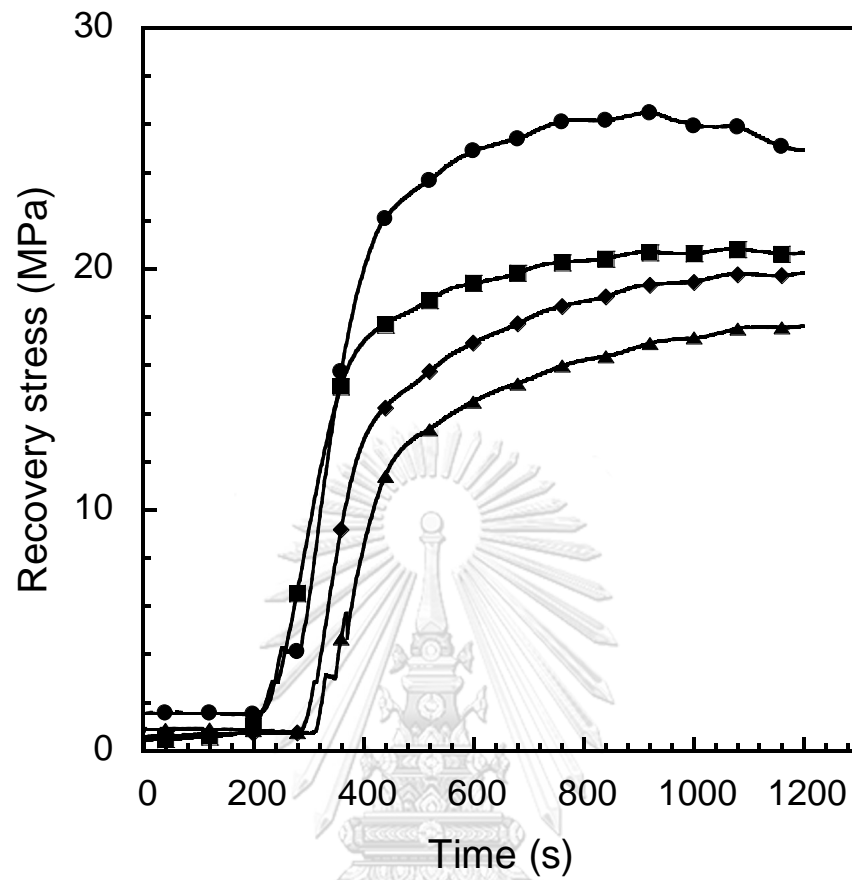


Figure 5.28 Recovery stress as a function of time at various percentages of strain ((●) 1%, (■) 3%), (◆) 5%, and (▲) 7%) of woven fiber reinforced benzoxazine-epoxy SMPs with 2-ply alternating woven carbon fiber and woven glass fiber layers. The percentage by volume of the woven fiber for each layer was 30vol%.

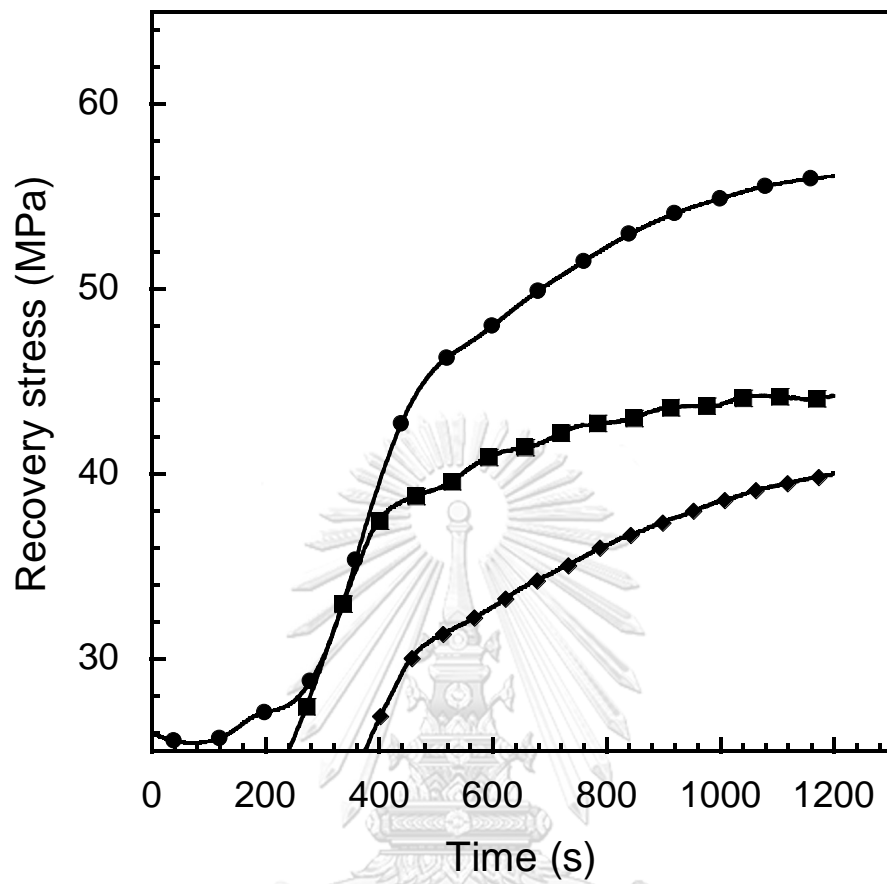
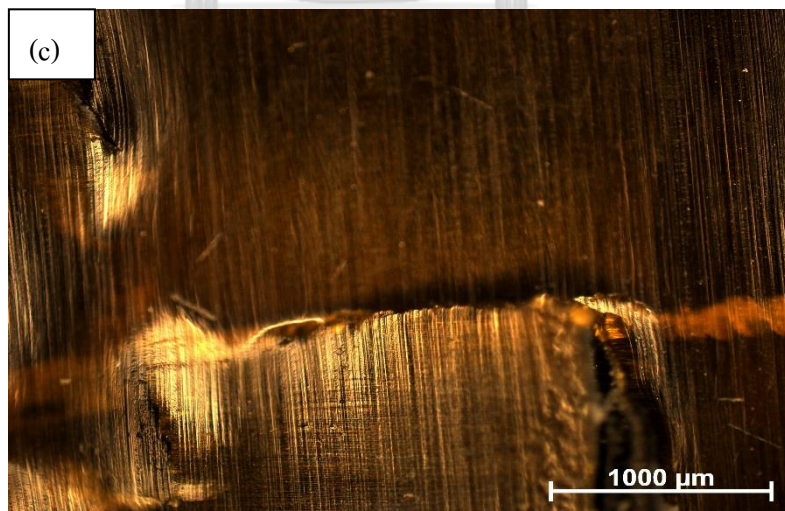
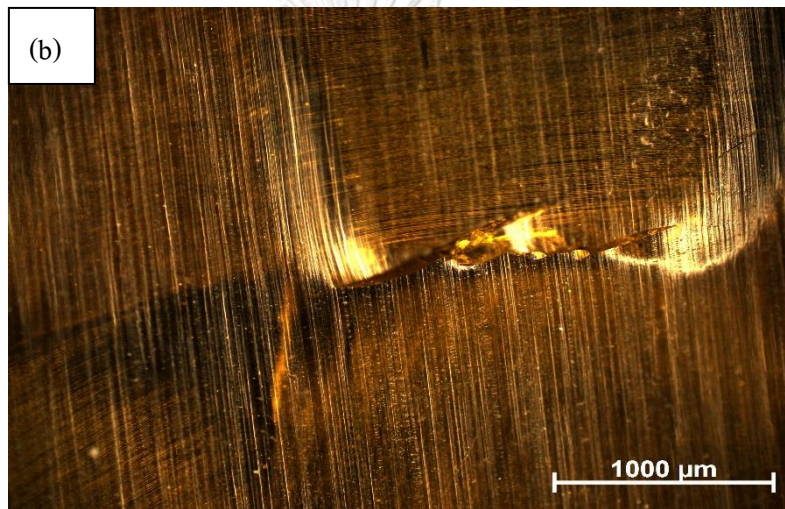
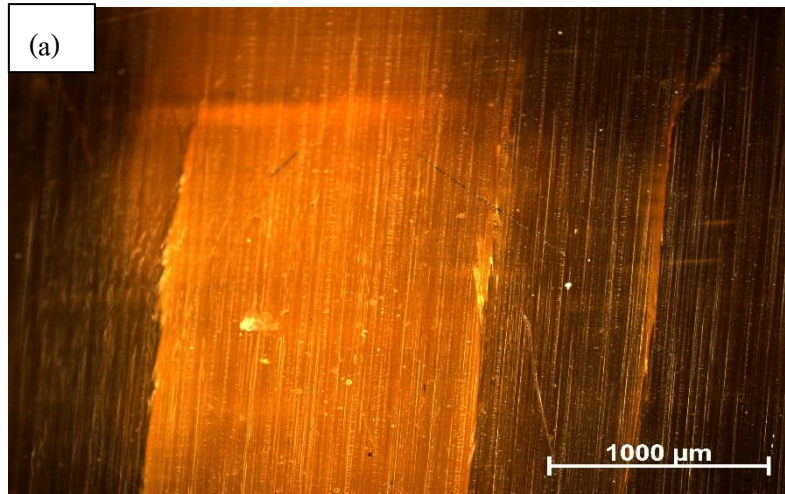


Figure 5.29 Recovery stress as a function of time at various percentages of strain (●) 1%, (■) 3%) and (◆) 5% of woven fiber reinforced benzoxazine-epoxy SMPs with 4-ply alternating woven carbon fiber and woven glass fiber layers. The percentage by volume of the woven fiber for each layer was 30vol%.



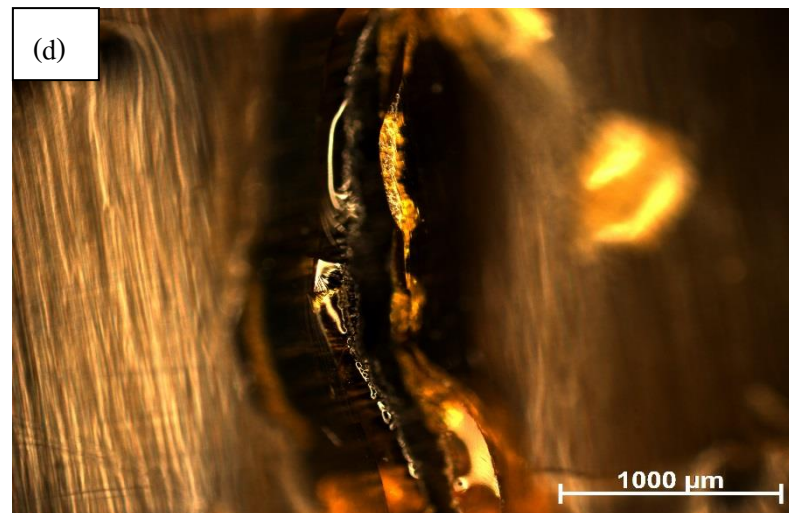


Figure 5.30 Optical micrographs of fractured surfaces at various percentages of strain ((a) 1%, (b) 3%, (c) 5%, and (d) 7%) of woven fiber reinforced benzoxazine-epoxy SMPs with 2-ply alternating woven carbon fiber and woven glass fiber layers. The percentage by volume of the woven fiber for each layer was 30vol%.

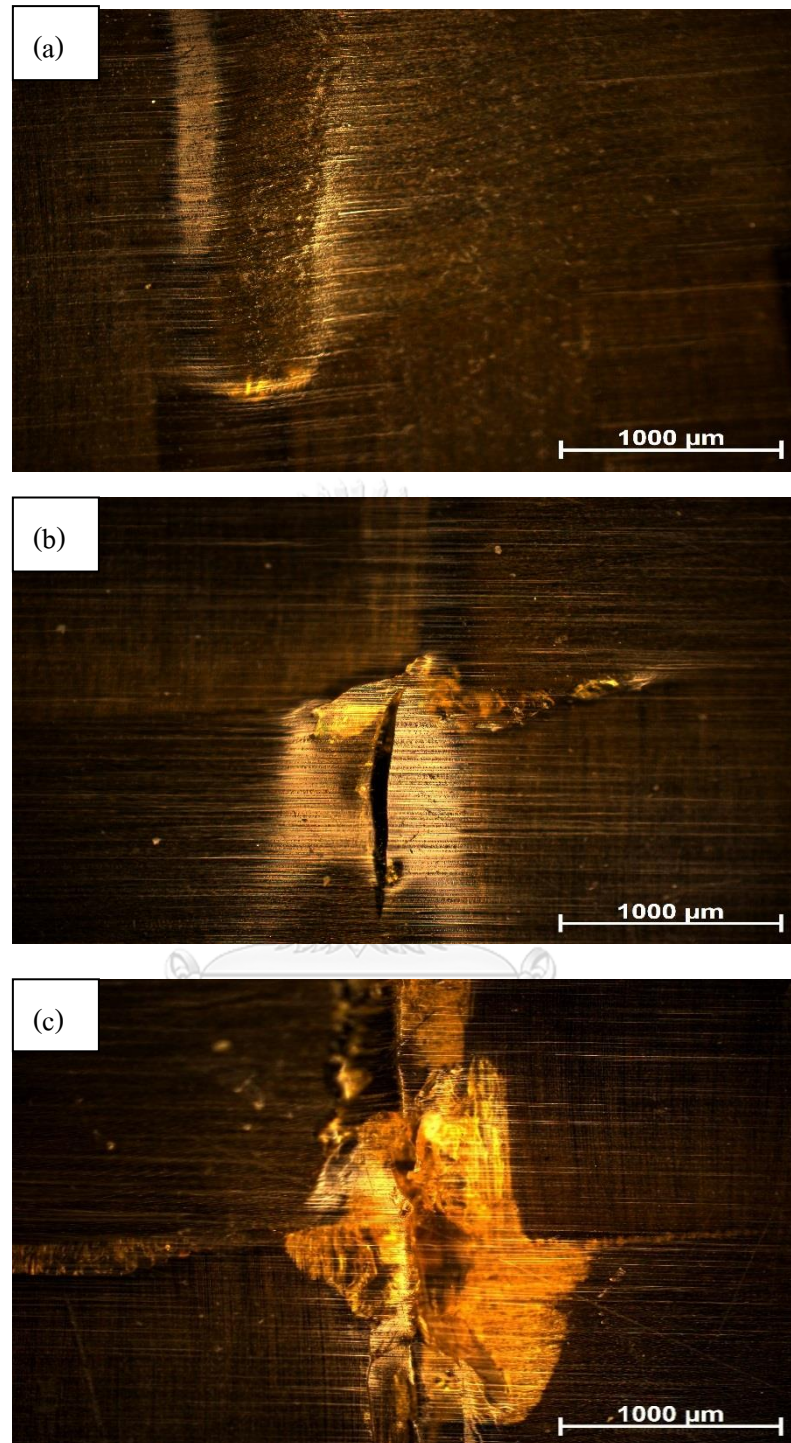


Figure 5.31 Optical micrographs of fractured surfaces at various percentages of strain ((a) 1%, (b) 3%, and (c) 5%) of woven fiber reinforced benzoxazine-epoxy SMPs with 4-ply alternating woven carbon fiber and woven glass fiber layers. The percentage by volume of the woven fiber for each layer was 30vol%.

CHAPTER VI

CONCLUSIONS

Woven carbon fiber and woven glass fiber reinforced benzoxazine-epoxy shape memory polymers (SMPs) was successfully developed. The woven fiber reinforced SMPs exhibited superior thermo-mechanical properties and shape memory performances. The storage modulus, flexural strength, and flexural modulus values at room temperature increased with increasing percentage by volume of the woven fiber contents and the number of composite layers. The storage modulus values increased from 1.9 GPa (the neat matrix) to 22.7 and 30.2 GPa for 4-ply woven glass fiber and woven carbon fiber reinforced SMPs at 50vol% of the fiber contents, respectively. The flexural strength values increased from 134.8 MPa (the neat matrix) to 847.3 and 1473.4 MPa for 4-ply woven glass fiber and woven carbon fiber reinforced SMPs at 50vol% of the fiber contents, respectively. The flexural modulus values increased from 4.7 GPa (the neat matrix) to 109.0 and 327.5 GPa for 4-ply woven glass fiber and woven carbon fiber reinforced SMPs at 50vol% of the fiber contents, respectively. The glass transition temperatures of woven fiber reinforced SMPs increased with the number of composite layers, while the values decreased with increasing percentage by volume of the woven fiber contents. The maximum glass transition temperatures achieved were 151°C and 162°C for the 4-ply woven glass fiber and woven carbon fiber reinforced SMPs with the percentage by volume at 30vol% of the fiber contents, respectively.

The developed woven carbon fiber and woven glass fiber reinforced benzoxazine-epoxy SMPs exhibited good shape memory performances. The shape fixity values in the range of 85–99% and the shape recovery values in the range of 96–100% were attained. The developed fiber reinforced SMPs exhibited the fast shape recovery with the recovery time in the range of 1.7–121 seconds. The best shape memory performances were obtained with the 2-ply woven carbon fiber reinforced benzoxazine-epoxy shape memory polymers with the percentage by volume at 30vol% of the fiber contents. This SMPs also exhibited the optimal thermo-mechanical properties.

The developed fiber reinforced SMPs particularly displayed high recovery stress values. The maximum recovery stress of 138.8 MPa was obtained with 4-ply woven carbon fiber reinforced benzoxazine-epoxy shape memory polymers with the percentage by volume at 30vol% of the fiber contents, while the neat matrix possessed the recovery stress of 3.5 MPa. The obtained SMPs are good candidates for applying as smart materials employed in a high recovery stress and modulus such as hinge or deployable structures.



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