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EFFECTS OF SILICON CARBIDE WHISKER ON SHAPE MEMORY POLYMERS FROM
BENZOXAZINE- EPOXY BINARY SYSTEMS

Mr. Chutiwat Likitaporn



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Recovery stress enhancement is one of the major research topics in shape memory polymers. One simple and practical way of enhancing recovery stress in SMPs is by making a reinforced composites using suitable reinforcing agent such as carbon nanotube or silicon carbide whisker. This research aims to study effects of silicon carbide whisker (SiC_w) on thermal, mechanical and shape memory properties of benzoxazine-epoxy SMPs particularly on recovery stress enhancement. The composition of SiC_w -filler in benzoxazine-epoxy SMPs is in a range of 5 to 20wt%. The SiC_w -filled benzoxazine-epoxy shape memory polymer was compression molded at 170°C , and pressure of 10MPa for 3 hours. The experimental results reveal that glass transition temperature of the composite samples increases with increasing SiC_w contents. The maximum glass transition temperature of benzoxazine-epoxy SMPs is 170°C at 20wt% of the filler. The flexural modulus and flexural strength at room temperature of the SMP samples are found to be 8.1 GPa and 178.0 MPa, respectively and those values of the SMP samples at rubbery stage are determined to be 174.1 and 10.9MPa, respectively. From shape memory test, benzoxazine-epoxy SMPs exhibit about 99% of shape fixity. The recovery time of benzoxazine-epoxy SMPs is in a range of 8 to 27 minutes. Furthermore, the incorporation of SiC_w in benzoxazine SMPs provides outstandingly high recovery stress up to 11.2MPa of benzoxazine-epoxy SMPs at 20wt% of the SiC_w . Recovery time of benzoxazine-epoxy shape memory composites under microwave heating is significantly shortened to be in a range of 3 to 5 minutes. These results suggest potential use of these materials as microwave responsive sensors and other medical devices.

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CHAPTER I

INTRODUCTION

1.1 Overview

Shape memory polymers (SMPs) belong to a family of smart materials. They demonstrate ability of memorizing their original or permanent shape after being deformed and fixed into a temporary one. Later they recover to the original shape if an external stimulus is applied [1]. They are stimuli-responsive materials with the ability to undergo a large recoverable deformation upon the application of an external stimulus such as light, humidity, solvents, electric or magnetic fields, ionic strength pH or most typically thermal activation [2]. Shape memory polymers (SMPs) have advantages over shape memory alloys (SMAs) [3] such as high elastic deformation, straining up to more than 200% for most of materials, low cost, light weight, ease of processing, simple design, good manufacturability, high shape deformability and easily tailorable glass transition temperature [4]. Especially, SMPs provide a broad range of transition temperatures which can be tailored to suit for their applications.

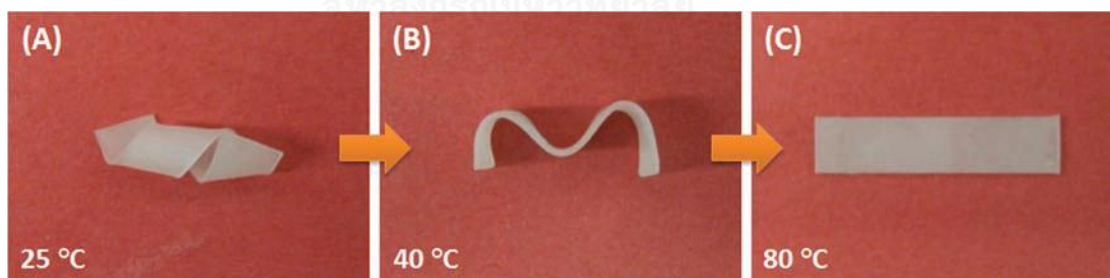


Figure 1.1 The sequential recovery of the epoxy/polycaprolactone composite (A) from a temporary shape, (B) to temporary shape b, and (C) to permanent shape c. [5].

Heat-activated SMPs can deform shape when material is heated above transition temperature (T_{trans}). It holds this temporary shape below the transition

temperature but being reheat up above T_{trans} , the material can recover to its original shape [6]. Figure 1.1 illustrates a typical recovery process of SMP.

Shape memory epoxies have attracted recently much attention from both academic and industrial researchers. The main reason for that different shape memory polymers such as polyurethane, polynorbonene, crosslinked polyethylene, styrene rubbers and acrylate systems have excellent thermal, thermo physical and mechanical properties along with ease of process ability into engineering components [7]. For example, shape memory polymeric systems from aromatic epoxy, aliphatic epoxy and curing agent (Jeffamine D230) have been reported to exhibit good shape fixity and they have complete shape recovery.

In principle, recovery stress is defined as the stress needed to hold a restrained sample at fixed temporary shape while the sample tries to undergo shape recovery upon the stimulus. However, the small recovery stresses presented by several kinds of polymeric systems over their alloy, ceramic, and glass counterparts are mainly because of their intrinsically lower modulus around their transition temperature used for shape recovery [8, 9]. This characteristic limits their use for many advanced applications, for example, clot removal devices, morphing of aircraft wings. Hence, increasing recovery stresses has been sought of, mainly, by increasing SMP's stiffness or their elastic modulus. This has been achieved by 1) incorporating more rigid molecular moieties into the SMP structure [10, 11] 2) by inclusion of reinforcing fillers to improve recovery stress such as by adding carbon nanotube, carbon fiber, glass fiber, silicon carbide nanoparticles [12-15], 3) by providing mesomorphic characteristics to SMPs [16] and 4) by enhancing crosslink density of the SMPs (i.e. thermosetting types) [9].

Benzoxazine resins (BA-a) are novel developed kind of thermosetting phenolic resin derived from ring-opening polymerization by thermal cure without a catalyst or curing agent and does not produce by-products during cure. The polymer possesses outstanding properties such as high thermal stability and outstanding mechanical properties thus showing high potential in many applications [17]. Notable properties of

polybenzoxazine have reported such as low melt viscosity before cure resulting in its high process ability, high thermal stability, and high glass-transition temperature (T_g), low melt viscosity before cure resulting in its high process ability, low water absorption. Furthermore, polybenzoxazine possess excellent mechanical performance and wide molecular design flexibility [18]. The resin has also been reported to act as a curing agent of epoxy. Moreover, synergism in some properties of copolymers from benzoxazine and epoxy was observed [19].

Moreover, in the recent study by Erden and Jana (2013), benzoxazine resin was selected for alloying with polyurethane for shape memory applications. The authors reported that the polybenzoxazine used can act as an additional hard phase of SMP due to its high glass transition temperature and much greater storage modulus than the soft segment phase of SMP. Secondly, benzoxazine resin can be ether chemically bonded with SMPU as a separate phase [10].

In addition, Rimdusit et al. (2013) developed shape memory polymer based on benzoxazine resin (BA-a) alloyed with aliphatic, aromatic epoxy and used Jeffamine D230 as the epoxy curing agent. Enhanced thermo-mechanical performance of the epoxy SMPs was achieved by an addition of the BA-a resin. The incorporation of the BA-a contributed to higher storage modulus in the glassy state, higher crosslink density, enhanced flexural strength and greater flexural modulus at room temperature. Moreover, their recovery stress was increased with increasing BA-a content up to 33 % by mole with the reported recovery stress of about 38 kPa comparing with 20.4 kPa of the unmodified shape memory epoxy [9]. Recently, Tanpitaksit et al. (2014) reported SMPs from binary mixtures based on benzoxazine-modified aliphatic epoxy. Still, it retains good thermomechanical and excellent shape memory properties with additional ease of sample preparation or processing [20]. The highest value of the recovery stress of these binary benzoxazine-aliphatic epoxy mixtures was reported to be up to 1.59 MPa [20].

In addition, the most common way of increasing elastic modulus and thus the corresponding recovery stress in SMPs is to include fillers in the polymer matrix [21]. A

certain amount of reinforcing fillers added has been reported to be able to improve the shape recovery stress and mechanical performance of SMPs [22]. Lui et al. studied silicon carbide (SiC) nanocomposite reinforcements in commercial thermosetting SMP epoxy systems. The authors reported an increase in recovery stress from 0.8 to 1.5 MPa with an addition of about 20 % by weight of SiC nanopowder. In this case, the SiC nanoparticles can substantially increase the modulus of the SMP material and thus the attainable recovery force [15]. Various types of the fillers have also been reported to significantly improve the elastic modulus and recovery stress of SMPs. In general, microfibers are found to be superior to micro- and nano-sized particles on reinforcing SMPs. Rod-shaped clay nanofillers have found to show better reinforcement effect than spherical nanoparticles as a result of their high aspect ratios but with the sacrifice of its handling and processing ability compared to the microfillers. Urayama et al. (2003) studied effect of shape of aluminum borate filler in form particle and whisker in poly (L-lactide). Whisker was reported affect to high mechanical properties of sample [23].

Moreover, Silicon carbide is chemically inert and strong MW absorbing material. Silicon carbide has been filled into PVA matrix to fabricate microwave induced shape memory polymer[24].

Accordingly, the purpose of this research is to study effects of silicon carbide whisker (SiC_w) on recovery stress of SMPs from benzoxazine modified aliphatic epoxy, in order to broaden their applications. It is expected the relatively high aspect ratio of the whisker as well as its outstanding mechanical properties should contribute to the substantial enhancement of the recovery stress of the obtained SMPs. Some essential properties, such as glass transition temperature, flexural modulus, flexural strength, shape recovery performance and recovery stress are also to be investigated.

1.2 Objectives

1. To develop silicon carbide whisker-filled composites based on binary system of aliphatic epoxy and benzoxazine resin for recovery stress enhancement.

2. To evaluate effects of silicon carbide whisker contents on shape memory properties, thermal stability and mechanical properties of shape memory polymers from benzoxazine- epoxy binary systems.

1.3 Scope of the study

1. Synthesis of BA-a typed benzoxazine resin by solventless synthesis technology.
2. Determination of the optimum composition of silicon carbide whisker filled benzoxazine-epoxy with 0-20% by weight of silicon carbide whisker content at benzoxazine resin (B)-cured aliphatic epoxy (E) at mole ratios of 50:50.
3. Preparation of shape memory polymers based on benzoxazine resin (B)-cured aliphatic epoxy (E) at mole ratios of B: E = 40:60, 50:50, and 60:40.
4. Property evaluation of silicon carbide whisker reinforced benzoxazine-epoxy SMPs as follows.
 - 4.1 Physical properties
 - Interfacial bonding by Scanning Electron Microscope (SEM)
 - 4.2 Thermal properties
 - Curing behaviors and glass transition temperature (Differential scanning calorimeter)
 - Thermal stability (Thermogravimetric analyzer)
 - 4.3 Mechanical properties
 - Dynamic mechanical properties (Dynamic mechanical analyzer)
 - Flexural properties (Universal testing machine)
 - 4.4 Shape memory properties
 - Shape fixity ratio
 - Shape recovery ratio
 - Deformation temperature
 - Recovery time
 - Recovery stress

1.4 Procedure of the study

1. Reviewing related literature.
2. Preparation of chemicals and equipment for this research.
3. Synthesis of benzoxazine resins (BA-a).
4. Preparation of benzoxazine-epoxy shape memory polymers.
5. Preparation of benzoxazine-epoxy/silicon carbide whisker composites.
6. Determination of physical, thermal, mechanical and shape memory properties of polybenzoxazine-epoxy/silicon carbide whisker composites.
7. Analysis of the experimental results.



CHAPTER II

THEORY

2.1 Shape memory polymers

Shape memory materials (SMMs) demonstrate a technologically class of stimuli-responsive materials for which the response change 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 [25]. Of all SMMs, shape memory alloys (SMAs) and shape memory polymers (SMPs) are by and large the most widely studied. More specifically, the conventional definition of an SMP is a polymer can be deformed and subsequently fixed into a temporary shape, which would remain stable unless it is exposed to an appropriate external stimulus that triggers the polymer to recover to its original (or permanent) shape. Accordingly, the associated behavior of SMP is called shape memory effect (SME) [2].

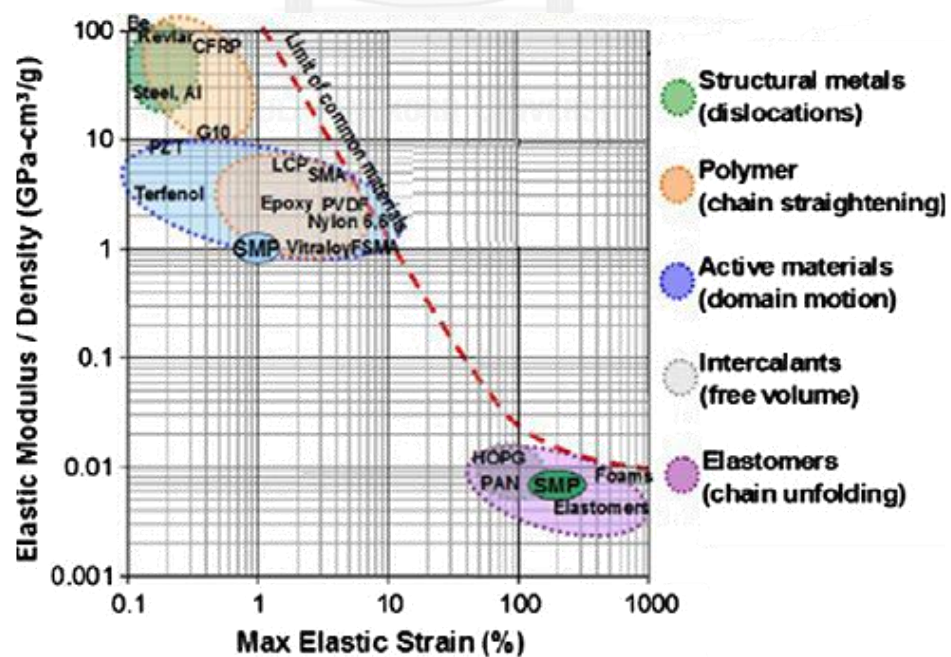


Figure 2.1 Comparison of mechanical properties among some typical materials [3].

The advantage of SMPs over SMAs relies mostly on their intrinsic properties such as lower cost, lower density, easier processing and larger attainable strains [3]. Figure 2.1 illustrate some comparison of mechanical properties among some typical materials, where SMPs perform a large strain but a relatively low stress.

2.1.1 Shape memory effects (SME)

Shape memory behavior can be observed in various polymer systems which are significantly different in molecular structure, morphology and processing method. Figure 2.2 shows shape-memory effects during a typical thermomechanical cycle. A temporary shape can be fixed after processing and the permanent shape subsequently can be recovered from the temporary shape when triggered by the external stimulus such as heating to a trigger temperature [26].

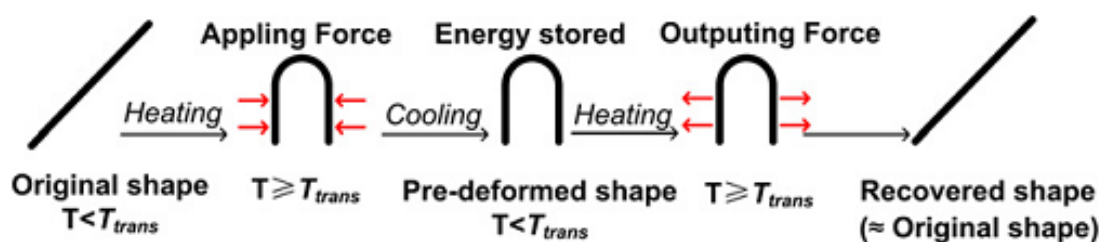


Figure 2.2 Schematic of shape-memory effects during a typical stimulus thermomechanical cycle [26].

2.1.1 Design principles of shape memory polymers

The two pre-requisites for the shape memory effect (SME) are a stable polymer network and a reversible switching transition of the polymer (see Figure 2.3). 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 lock in the network represents the reversible switching transition responsible for fixing the temporary shape, which can be crystallization/melting transition, reversible molecule cross-linking, linking, and supramolecular association/disassociation [22].

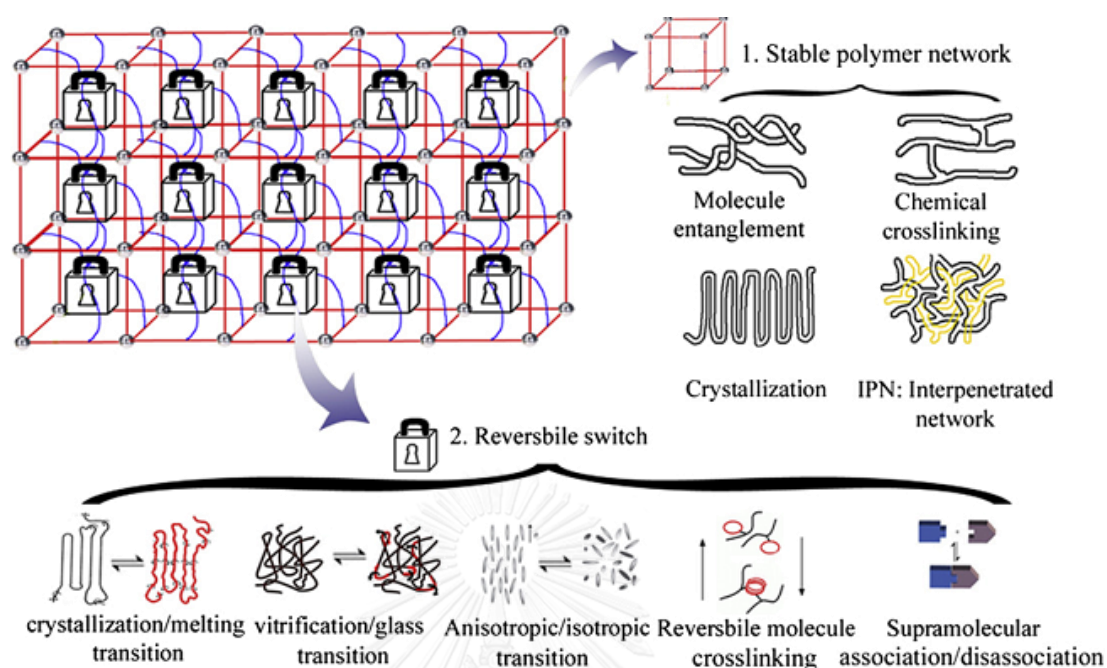


Figure 2.3 Various molecular structures of SMPs. A stable network and a reversible switching transition [22].

2.1.1.1 Shape memory polymers based on a melting transition

One possibility for the fixation of the second phase is its crystallization. The melting of this phase will lead to the shape recovery of the SMP. Often based on chemically cross-linked semi-crystalline networks or (multi)block copolymer systems these materials feature a higher stiffness than other SMP materials as well as a fast shape recovery [27]. However, generally T_m -based possess low thermal and mechanical properties.

2.1.1.2 Shape memory polymers based on a glass transition

Polymeric materials with a glass transition temperature (T_g) above room temperature can be utilized for T_g -based SMPs. These include chemically cross-linked glassy thermosets and physically cross-linked thermoplastics. Within this context a large variety of different materials have been investigated. In comparison to the T_m -

based SMPs, the T_g -based SMPs reveal a slower shape recovery due to the broad glass transition (representing a second order phase transition). Therefore, these SMPs are not best choice for applications where a sudden shape recovery is required. But on the other hand, the slow recovery makes them interesting candidates certain for biomedical applications [27]. Epoxy – as a classical thermoset– were also utilized as SMPs. Epoxy based on oligo(bisphenol A) diglycidyl ether and Jeffamines showed a SME [28]. Then, the aliphatic epoxy, aromatic epoxy modified by benzoxazine resin was investigated [9, 20]. Their system exhibited good in thermal, mechanical and shape memory properties.

2.1.2 SMPs characterization

Zhao et. al. compiled the study of shape memory polymer and summarize parameters for SMP. The parameters for SMP are shape memory transition temperature, shape fixity, shape recovery ratio and recovery stress [29]. Therefore the parameters should be able to define all of shape memory processes. In the end, the parameters should be able to consider the potential applications [30].

2.1.2.1 Shape fixity (R_f)

Shape fixity is parameter that described how well to fixed in temporary shape. The sample is first heated to a deformation temperature, normally (but not always) above T_{trans} , a force is then applied. When a shape memory polymer is activated to a temperature above the transition temperature for triggering typical shape memory behaviors such as T_g , it can develop large deformations which can be fixed by cooling to a low temperature. The shape fixity is the amplitude ratio of the fixed deformation to the total deformation, which is given by shape fixity related to both structures of polymers and the thermo-mechanical conditions of shape memorization. Compared to the macro structures of SMPs, the thermo-mechanical conditions play important roles in determining the shape fixity and other shape memory properties in polymer[30].

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

$$\text{Shape fixity} = 1 - \frac{E'r}{E'g}$$

$E'r$ = the rubbery modulus

$E'g$ = the glassy modulus

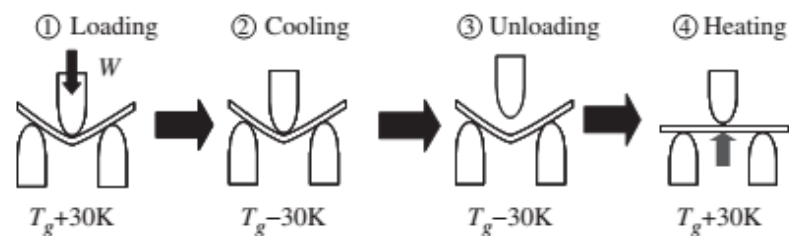


Figure 2.4 Experimental procedure in the shape fixity and recovery test [31].

2.1.2.2 Shape recovery (R_r)

Shape recovery is one parameter that describes how well recovered to original shape. Shape recovery characterizes the ability of an SMP to recover their shape to original shape. After shape fixity test, the specimen was reheated under no load. The deflection was measured. Similar to shape fixity, both the macro structures of polymers and the thermo-mechanical conditions determine shape recovery of shape memorization [21, 30].

2.1.2.3 Recovery stress

Recovery stress release in the recovery process. When SMPs are heated and deformed, while deforming the elastic stress is generated. Then elastic stress is stored when SMPs are cooled below T_g . When the deformed temporary SMPs are reheated above T_g , the SMPs recovered their shape and released 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 [30].

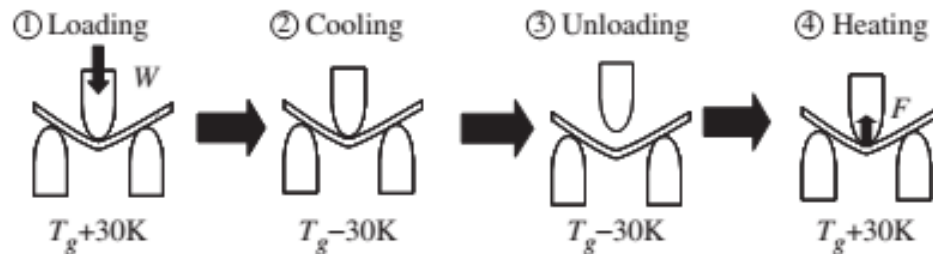


Figure 2.5 Experimental procedure in the recovery force test [31].

The stress relaxation is inevitable by all means if only the SMP is in a constrained state. Accordingly, in recovery stress investigation must control temperature in testing. Then the recovery stress was obtained from max stress release.

2.1.2.4 Recovery rate

Recovery rate is a dimension for describing the speed when a given SMP recovered from a temporary shape to its maximum recovery shape by being heated. The parameter can be measured qualitatively and quantitatively [30].

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

2.2 Shape memory polymer composites.

Since SMPs possess shape recovery stress and low mechanical performance. These troubles lead to largely restrict the applications. Reinforcing fillers are able to improve the shape recovery stress as well as mechanical performance of SMPs through physical blending, in-situ polymerization and chemical cross-linking [22]. The thermo mechanical behavior of SMPs can be designed by the addition of functional fillers into

the matrix polymer for multi-phase composites. The type of filler they employ in SMP composites can be classified as particle- or fiber- reinforced [3].

2.2.1 Particle-filled shape memory polymers

The SMP composites filled with particles (e.g., carbon black, carbon nanotubes, carbon nanofibers, SiC, Ni, Fe₃O₄, clay, and short or continuous fibers [14, 32-34]) may meet various requirements in practical applications. In general, the SMP composites filled with particles or short fiber develop some particular function, such as high electrical conductivity, magnetic-responsive performance, or high stiffness on the micro scale. Hence, multifunctional material is studied for this type of SMP composites [3]. Neat SMPs or particle-reinforced SMPs are not used as structural materials; however, they are mostly used as functional materials through the addition of some particular particle fillers. For instance, electrically conductive carbon black, carbon nanotubes, nickel powders and chopped carbon- fibers are incorporated into SMPs to develop electro-active SMPs. Ferromagnetic Fe₃O₄-filled SMPs can bring about magnetism induced SMPs [3]. Moreover, dielectric filler silicon carbide could be embedded into SMPs to develop microwave-induced SMPs [24].

2.2.2 Fiber-reinforced shape memory polymers

In general, SMP composite's reinforced with particles or short fibers cannot be used as good structural materials. In contrast, continuous fiber-reinforced SMPs offer a significant improvement in stiffness, strength and resistance against relaxation and creep, thereby providing preferable mechanical properties. As both a functional and structural material, these SMPs show good potential for many advanced applications. When used as actuator materials, they require no moving parts. Substantial interest has therefore been generated for the use of fiber-reinforced SMPs in deployable structures including antennas, trusses and solar arrays [3]. Epoxy SMP composites (Elastic Memory Composite, EMC) show outstanding potential for light weight deployable spacecraft structures applications. Composite Technology Development (CTD), Inc. firstly started

to comprehensively researched the EMC and the relevant practicable applications in deployable structures since the 1990s [3].

2.2.3 Applications of shape-memory polymers and their composites

SMPs currently cover a broad range of application areas ranging from automobiles to outer space. Recently, they are being developed and qualified especially for deployable components and structures in aerospace. The various applications include optical reflectors, trusses, booms, hinges and morphing skins. In addition, SMPs also present additional potential in the areas of smart textiles, automobile actuators and biomedicine [3]. In addition, there are many patents in relation to SMPs applications, such as intravascular delivery system, gripper, hood/seat assembly[35], tunable automotive brackets in vehicles and airflow control device [36]. The various application are very useful in numerous industry.

2.2.3.1 Deployable structures

The deployable structures widely use in the 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 difficulty for the conventional deployment devices, such as large volumes, massive mechanisms, complex assembling process as well as undesired effects during operation. In contrast, the deployment devices fabricated using SMPs and their composites maybe overcome certain inherent disadvantages [3].

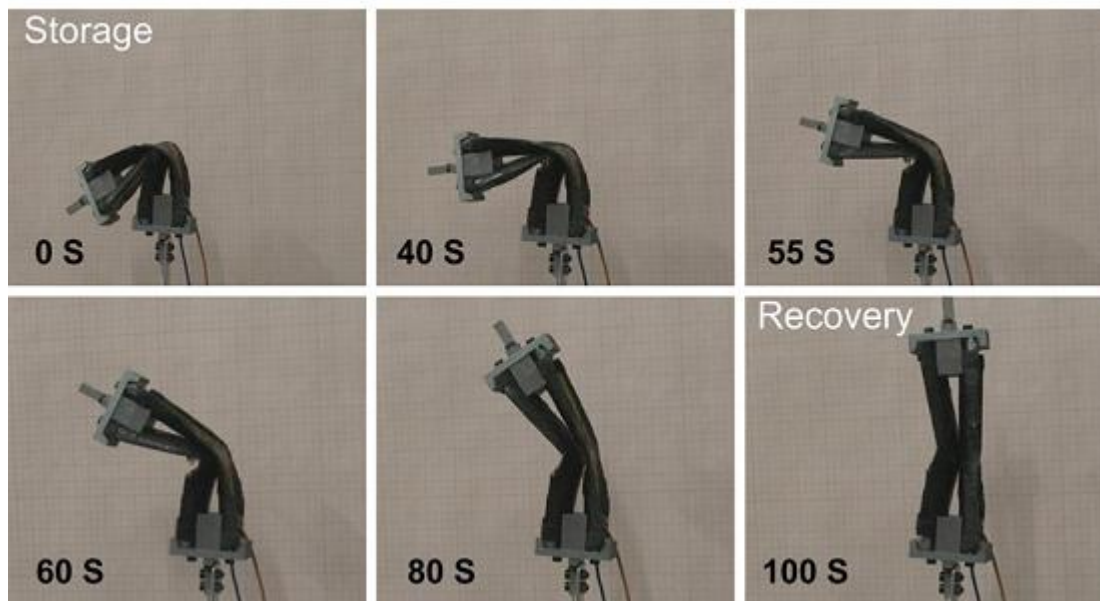


Figure 2.6 Shape recovery process of SMP-composite hinge [26].

2.2.3.2 Morphing structures

In morphing structures application can apply in some flight. The 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, many 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 low energy consumption, speed and dexterity [3]. For instance, the morphing structure technology to demonstrate radical shape changes was developed by Defense Advanced Research Projects Agency (DARPA). As illustrated in Figure 2.7, Lockheed Martin also achieves a z-shaped morphing change in flight model [37].

Typically, a wing skin is great necessary for a morphing aircraft. Researchers always focus their works on investigating suitable 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 morphing application. It becomes flexible when heated to a certain degree. Then it returns to a solid state when the external stimulus is terminated. Since SMPs holds the ability to change its elastic modulus, they could potentially be used in the mentioned concept morphing aircraft designs [3].

Although shape memory alloys are commercially available and found a wide range of different applications. However, SMPs have one decisive advantage, particularly considering applications in aerospace: Their weight. The weight of the applied materials is one of the most crucial issues in the design of new systems in aerospace (e.g., the newest Boeing 787 Dreamliner utilizes >50% polymer composites in the primary structure). Consequently, enormous efforts have been undertaken in the development of new SMPs for aerospace applications. The field for potential applications in this sector is huge [27].



Figure 2.7 Shaped morphing wings produced by Lockheed Martin [3, 37].

2.2.3.3 Automobile

SMPs have been developed to use in automobile engineering, and many interesting products. Some applications of SMPs include seat assemblies, reconfigurable storage bins, energy-absorbing assemblies, tunable vehicle structures, hood assemblies, releasable fastener systems, airflow control devices[36], adaptive

lens assemblies and automotive body molding. The SMP have many advantage such as easy manufacturing, high deformed strain and low cost [3].

2.2.3.4 Biomedicine and bioinspiration

An attractive application area for SMPs is use in medical device. SMPs show extensive interest in used for biomaterials and bio inspiration. For instant, 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 [3].

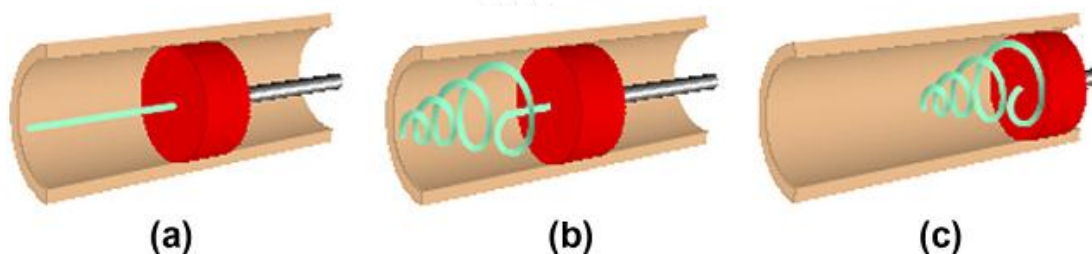


Figure 2.8 Depiction of removal of a clot in a blood vessel using the laser-activated SMP microactuator coupled to an optical fiber.(a) The temporary straight rod form. (b) The permanent corkscrew form by laser heating. (c) The deployed microactuator is retracted to capture the thrombus [25].

The same working principle can also be utilized for the design of vascular stents based on shape memory polymers. The state of the art is the utilization of stents made of stain-less steel or other metal containing materials (e.g., several alloys). Several drawbacks of these stents, such as too high stiffness for navigation.

2.3 Recovery Stress

Research of shape memory polymer composites (SMPCs) may be reinforcement of SMPs. Several kind of SMPs have intrinsic low mechanical strength and shape recovery stress, which have largely restricted the applications of SMPs [22].

The terminology of “shape memory” emphasizes the shape fixing and shape recovery and indeed reflects how SMPs had been exclusively used in the earlier days of development [2]. Recently, increasing attention has been paid to utilize the strain energy stored in a temporary shape to perform work. That is, after the completion of shape fixing, instead of allowing shape recovery under a free stress condition in the next step, the SMP is constrained such that the fixed shape is not allowed to change (i.e. an isostrain condition). Under such a condition, heating does not lead to shape change due to the external mechanical constraint, but the tendency of shape recovery generates a recovery stress (or force). In a typical stress recovery experiment, the recovery stress is monitored with respect to temperature and a maximum recovery stress at a certain temperature is typically observed. Often time the maximum recovery stress, which is simply referred to as the recovery stress, is reported for a given SMP [2].

Various strategies have been explored to enhance the recovery stress. Therefore, increasing recovery stresses has been sought by increasing SMPs stiffness or elastic modulus. This has been achieved by increasing crosslinking density, reinforcing polymer systems by inclusion of fillers, or by providing mesomorphic characteristics to SMPs. Moreover, including increasing the rubbery modulus by nanofillers reinforcement, raising the rubbery modulus through a higher crosslinking density, and deforming SMP at a relatively high modulus state instead of the rubbery region [2, 21].

2.4 Epoxy Resin

The epoxy, epoxide or oxirane group is a three-membered ring consisting of two carbon atoms and one oxygen atom. The nature of this three-membered ring makes it highly reactive. The structure for an epoxy resin is given in Figure 2.9. Chemically, an epoxy resin contain one or more epoxy (oxirane) groups per molecule which can be situated terminally, cyclically, or internally in a molecule and can be converted to a solid through a thermosetting reaction [38]. In addition, shape memory epoxy are unique thermoset shape memory polymer systems with excellent thermal,

thermophysical and mechanical properties along with ease of processability into engineering components. As epoxy polymers find extensive use as adhesives, coating, structural material, etc., additional function of shape memory will be a good aspect for extending their further applications [7].

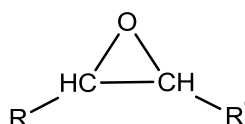


Figure 2.9 General structure of an epoxy resin [38].



Figure 2.10 Structure of Neopentyl glycol diglycidyl ether (NGDE) [9].

For some types of processing the viscosity of the uncured resin system needs to be lowered. When it is not advisably, as in the case of hand lay-up, to use volatile solvents as diluents, reactive diluents must be used. In this research used Neopentyl glycol diglycidyl ether (NGDE) as diluents. They are low viscosity liquids containing epoxide groups (see in Figure 2.10)

2.4.1 Application

Electrical potting, encapsulation, impregnation

Flooring

Adhesives

Tooling

Neopentyl glycol diglycidyl ether 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 plus 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 [39].

2.5. Benzoxazine Resin

Polybenzoxazine is a phenolic polymer in which generated by the Mannich-like condensation of phenol, formaldehyde and amine. It can be prepared by using solventless synthesis technology [40, 41]. Benzoxazine resin can be polymerized by heating. They do not need catalyst or curing agent for polymer curing process.

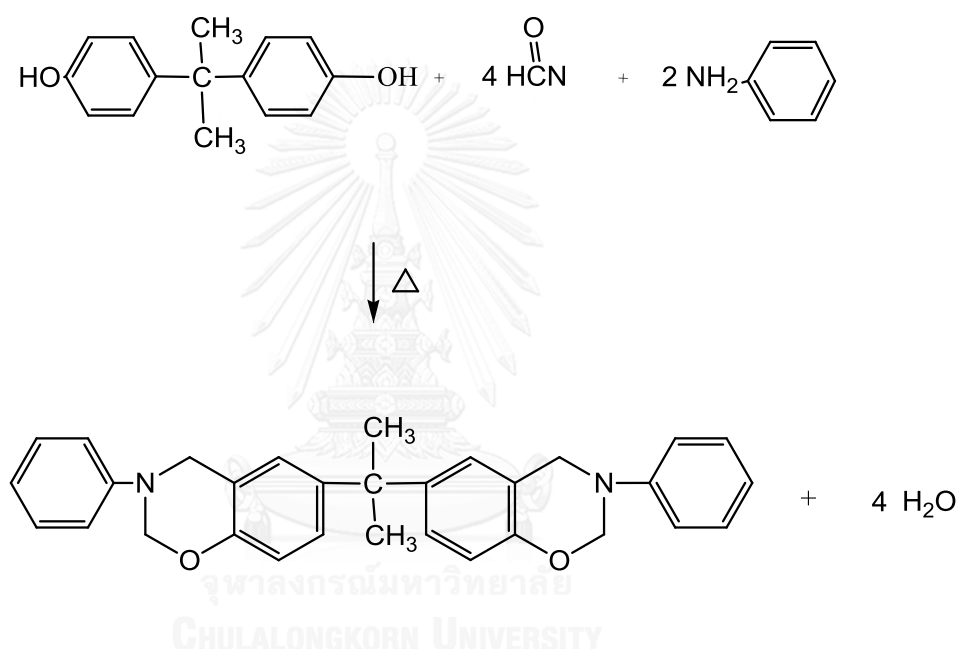


Figure 2.11 The reaction of benzoxazine formation.

Polybenzoxazine exhibits outstanding properties. First, thermal polymerization is easy to carry out. Second, a variety of reactants can be used to design desired molecular structures. Third, molten resin possess low viscosity that lead to easy processing condition. Fourth, benzoxazine polymerization does not produce any byproduct during processing. Consequently, benzoxazine can be easily processed to make void free products [42].

The polymer network structures are responsible for high modulus of polybenzoxazines based on bisphenol A compounds. Earlier, it was assumed that high flexural modulus (4.5 GPa) and near zero shrinkage upon polymerization are due to chemical crosslinking only [43]. However, more recent studies demonstrated that extensive hydrogen bonding networks also contribute substantially. The intra and intermolecular hydrogen bonding were found to establish large networks, which in turn prevent shrinkage and lead to higher modulus [42].

Furthermore, the benzoxazine resin was reported as a dual function of benzoxazine resin as a curing agent and a stable network segment in epoxy SMP system [9, 20]. The effect of benzoxazine content in aliphatic epoxy based SMPs on mechanical properties, thermal stability, and shape memory properties were characterized. An incorporation of the benzoxazine resin in the aliphatic epoxy based SMP resulted in an increase of glass transition temperature, storage modulus, crosslink density and recovery stress of the SMPs.

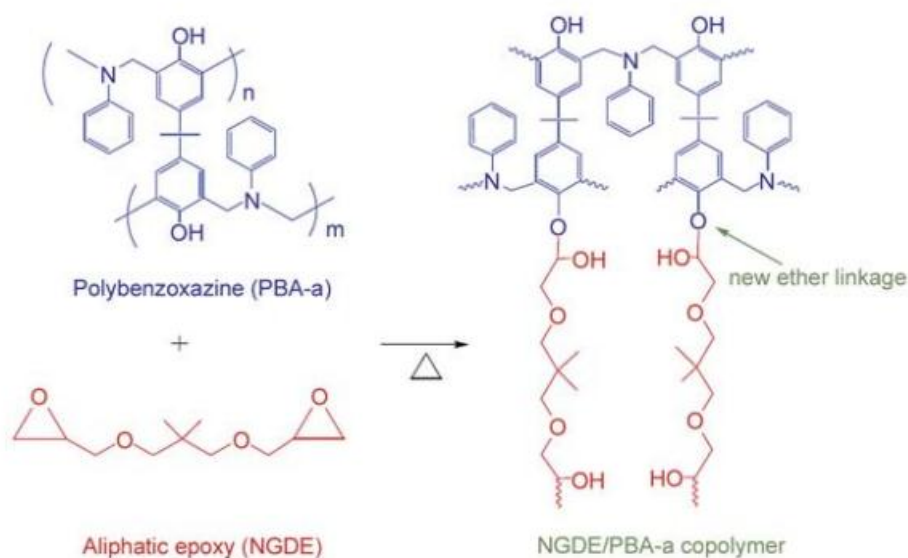


Figure 2.12 A possible chemical reaction between PBA-a and aliphatic epoxy (NGDE) [20].

2.6. Silicon Carbide Whisker (SiC_w)

The term “whisker” is commonly used to describe a small single-crystalline rod. SiC whiskers can be synthesized by various methods, such as sol-gel, plasma deposition, chemical vapor deposition, and pyrolysis of agricultural waste. The latter method seems to be preferred for industrial-scale production of Silicon carbide whiskers. Generally, agricultural waste containing both silica (SiO_2) and carbon is used. Waste sources include rice hulls, sugarcane leaf, and rice straw. Silicon carbide whiskers can also be fabricated from mixtures of silica and carbon powders, carbon and silicon halides, polymer precursors, or other materials like silicon nitride. In addition to silicon carbide whiskers, the synthesis process also usually produces some amount of (usually unwanted) non-whisker silicon carbide particles which varies depending on processing details [44]. Moreover, SiC is chemically inert and strong MW absorbing material. Moreover, it has strongly high temperature stability and low thermal expansion coefficient [24].

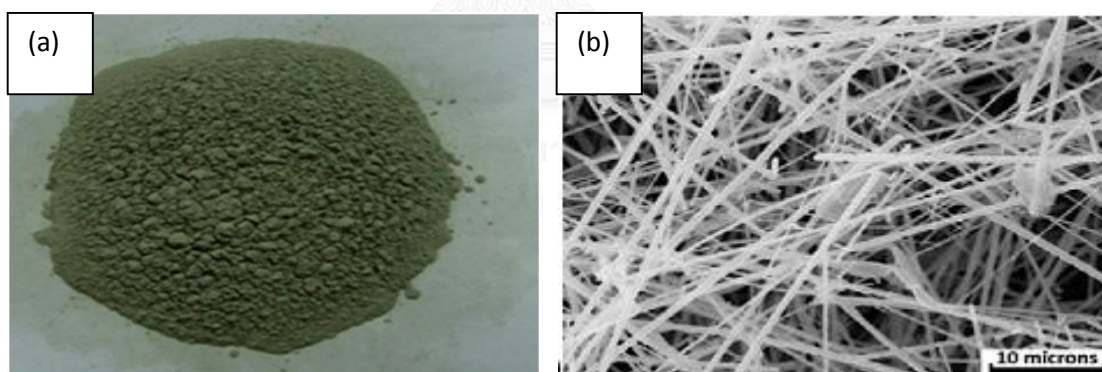


Figure 2.13 Silicon carbide whisker (SiC_w): (a) Photograph of SiC_w (b) SEM of SiC [44].

2.7 Microwave Heating Mechanism

Microwave as the special heat source provides a route to greatly shorten the heat exchange time. The potential utility of microwave in stimulus responsive materials is expected in the future. The microwave can heat material with interactions between

the polar molecules or dielectric materials .and the microwave electromagnetic field enable the microwave energy to be absorbed by samples. The alternating magnetic field make the random polar molecules orientation arrangement. In this process, the friction loss induced by polar molecules steering frequently converted the electromagnetic energy into heat [45]. From attractive useful of microwave heat, it was studied to be actuation of many active materials such as SMP[24].

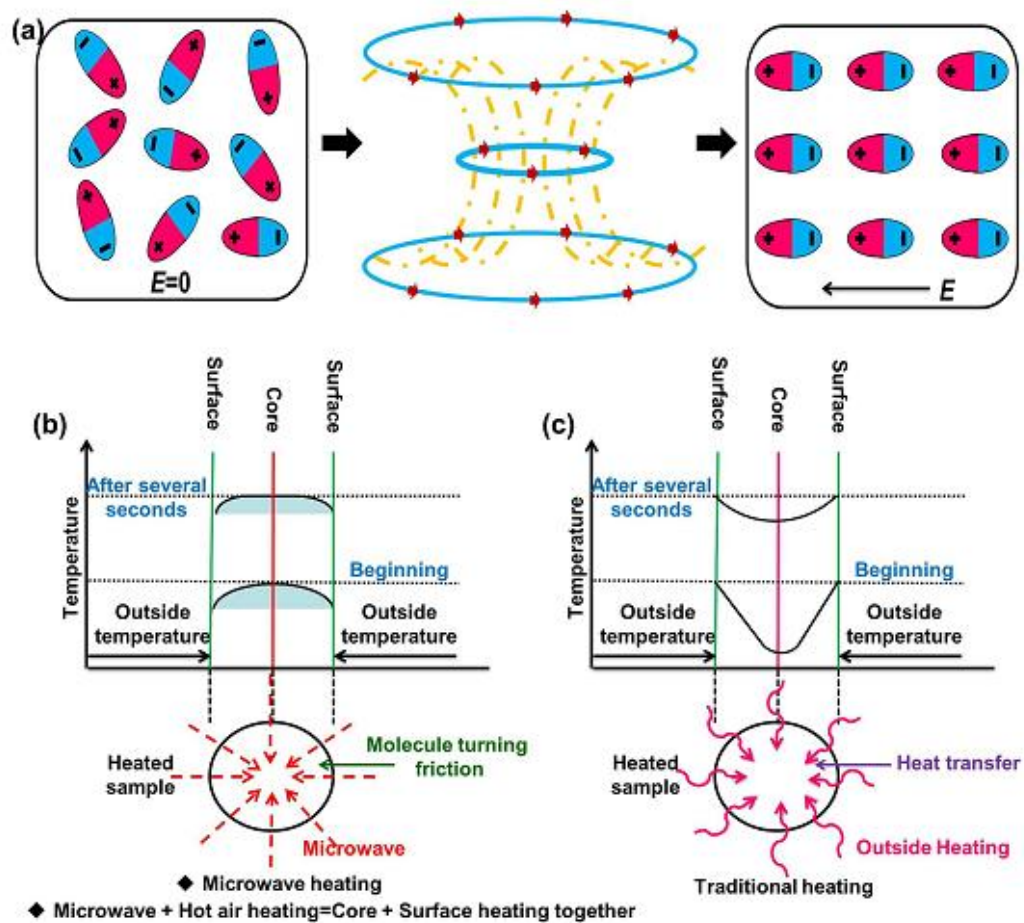


Figure 2.14 Mechanism of microwave heating (a), (b), and traditional heating (c) [45].

CHAPTER III

LITERATURE REVIEW

Xie and Rousseau (2009) investigated shape memory polymer from epoxy based. Starting with an amine (Jeffamine D230) cured aromatic epoxy (diglycidyl ether of bisphenol A epoxy monomer) system, epoxy polymers were synthesized by either reducing the crosslink density by substituting the diamine curing agent with a monoamine such as decylamine (DA) or introducing flexible by replacing the EPON 826 with a flexible aliphatic epoxy (NGDE). Table 3.1 reported molar compositions of all epoxy synthesized [28].

All the other epoxy polymers in Table 3.1 show typical shape memory properties, with shape fixity above 90% and shape recovery around 100%. The shape fixities for all sample are different. That can be correlated to the difference in glassy modulus and rubbery modulus for each individual sample. However, in sample NGDE4. Which can't exhibit shape memory polymer behavior. It's due to T_g is too low because remove stable network (aromatic epoxy).

Table 3.1 Compositions, shape fixity, and shape recovery of the epoxy samples [28].

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

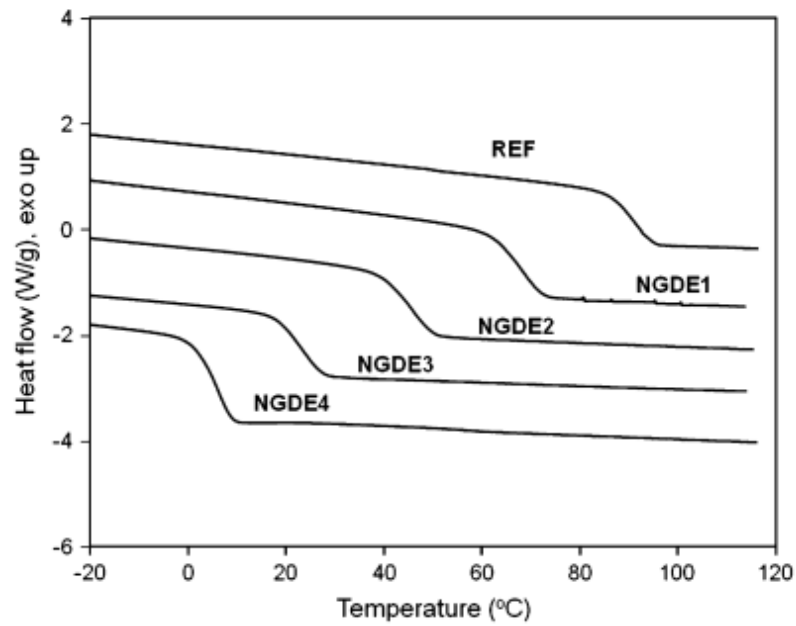


Figure 3.1 DSC curves for the NGDE epoxy series. [28]

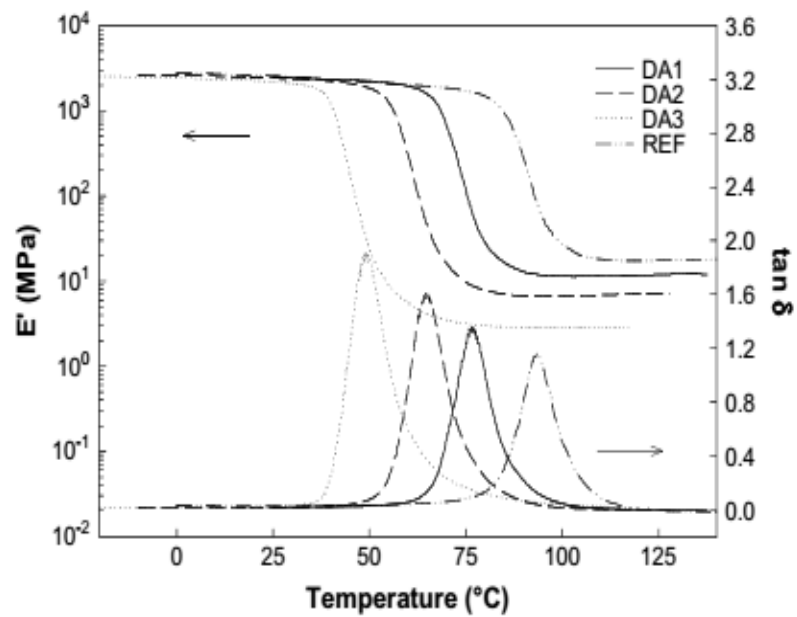


Figure 3.2 DMA curves for the NGDE epoxy series [28].

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. For examples,

Erden and Jana (2013) investigated the properties of polyurethane-polybenzoxazine based shape memory polymers by using DSC, DMA, universal testing machine (tensile mode) etc. SMP was synthesized from 4,4'-methylenebis phenyl isocyanate (MDI), polytetramethylene glycol (PTMG), 1,4-butanediol (BD) and benzoxazine (BA-a). Molar ratio of ingredients and weight percent hard segment (HS) are shown in Table 3.2 [10]. It is clearly the addition mole of benzoxazine resin also increase weight percent hard segment.

Table 3.2 Corresponding molar ratio of raw materials [10].

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 it is evident that all three materials exhibited a single peak of $\tan\delta$, indicating a single value of T_g , respectively, 51, 65, and 91 °C for sample I to III, respectively. Also the increasing of T_g is due to the increasing amount of benzoxazine in the samples. In table 3.3, the values of elastic modulus, shape recovery ratio and transition temperature were found to increase with an increasing of BA-a resin contents. The elastic modulus were 228, 258 and 475 MPa with 0, 9.4 and 17.5 wt% of BA-a contents. Then, the transition temperature were increase with glass transition temperature. The shape fixity were measured values are given as follows: 93.5, 96.6 and 99.3 % with sample I, II and III, respectively. This is due to an instantaneous shrinkage of a very small portion of polymer chains that cannot preserve the imposed strain with more BA-a.

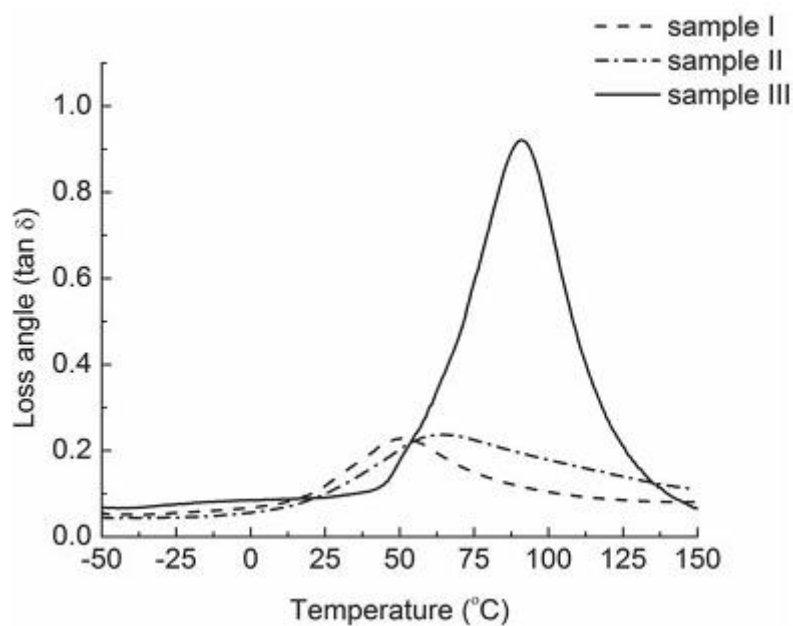


Figure 3.3 loss tangent as a function of Temperature heating rate $4\text{ }^{\circ}\text{C min}^{-1}$, frequency 1 Hz [10].

Table 3.3 Corresponding molar ratio of raw materials

BA-a contents (wt%)	Young's modulus (MPa)	Shape recovery (%)	Shape fixity (%)	Transition temperature ($^{\circ}\text{C}$)
0	228	72	93.5	71
9.4	258	84	96.6	85
17.5	475	93	99.3	110

Moreover, the recovery stress had been observed as the results in Figure 3.4 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 and 13 MPa, respectively [10].

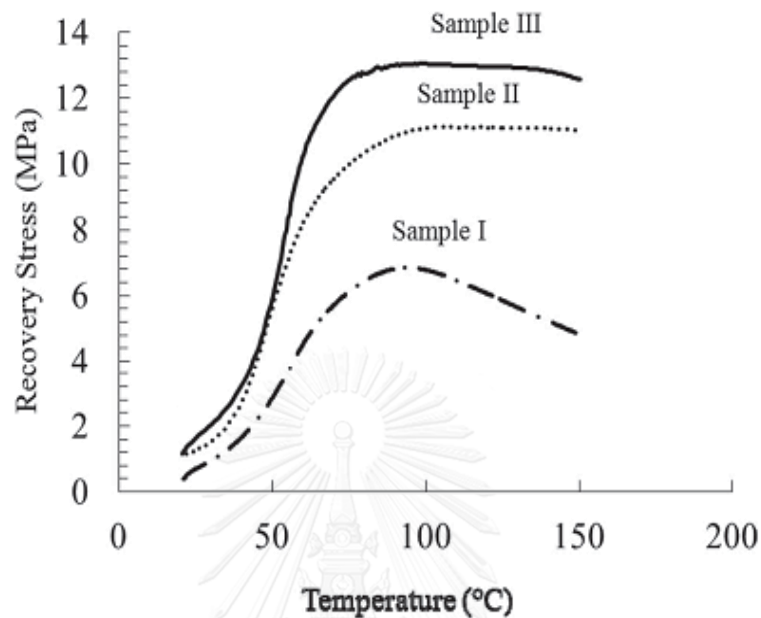


Figure 3.4 Recovery stress behaviors of 100% strained samples. Heating rate was 4°C/min and stretching rate was 50 mm/min [10].

Rimduisit et al. (2013) studied the effects of benzoxazine resin and Jeffamine D230 mol ratios on glass transition temperature, mechanical and shape memory properties of SMP epoxy system. They investigated shape memory polymer from epoxy-benzoxazine system. As show in table 3.4, EPON 826, NGDE, Jeffamine D230 and BA-a were represented by E, N, D, B, respectively. The digits after the notation give the molar ratio of the monomer in the same order. The increasing of storage modulus and crosslink density were found when add more BA-a in the alloys as a result of the more rigid characteristics of the BA-a resin. Moreover, the glass transition temperature also increases when increasing of BA-a content [9].

Table 3.4 Properties of benzoxazine-modified epoxy SMP samples from DMA [9].

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 3.5. 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 [9].

As can be seen in Table 3.4. The cross-link density, glass transition temperature and storage modulus were successful increased with an increasing benzoxazine resin in system. The resulted in an increase of the T_g with increasing BA-a fraction in the alloys. The author explained this may be due to the more rigid molecular structure and possibly much higher intramolecular and intermolecular forces in the polybenzoxazine compared with the epoxy [9]. Then, this increasing affects to important shape memory properties like stress recovery.

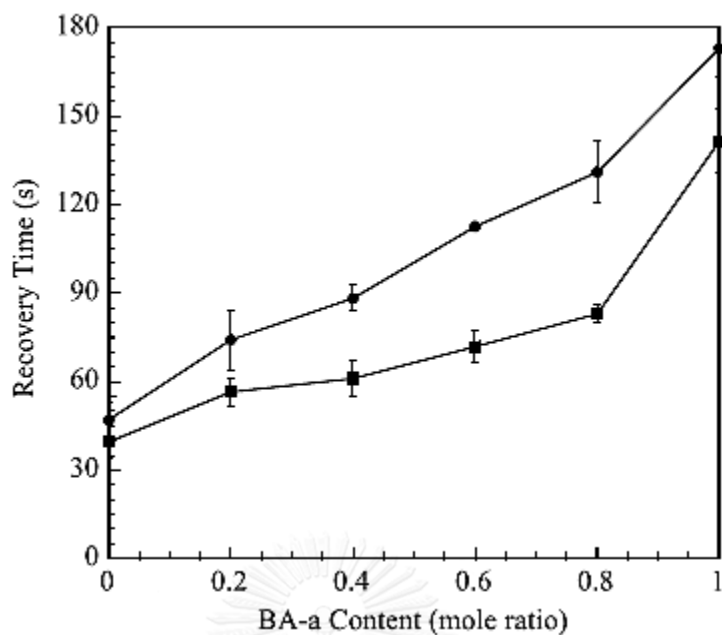


Figure 3.5 Recovery time as a function of BA-a content of the benzoxazine-modified epoxy SMP samples at various composition: (●) T_g , (■) $T_g+20^\circ\text{C}$ [9].

The recovery stress under flexural mode of the SMPs was measured from the transition stage of the shape-fixed stage to the recovery shape 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 of 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 3.6. Based on their results, the benzoxazine resin can substantially improve the recovery stress of epoxy-based SMPs. This is due to the fact that the BA-a may be able to store elastic strain energy [9].

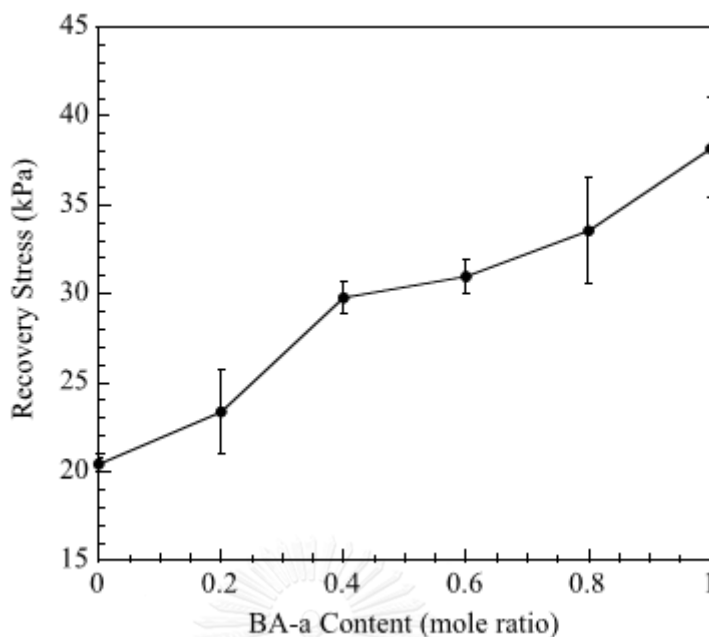


Figure 3.6 Recovery stress as a function of BA-a content of the benzoxazine-modified epoxy SMP samples at various compositions [9].

Tanpitaksit et al. (2015) 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 curing agent. Moreover, this system used no aromatic epoxy which was replaced by the BA-a resin. In other words, the BA-a resin was used both as the epoxy curing agent and as rigid segments in the resulting SMPs. Still, the SMP system retains good thermomechanical and excellent shape memory properties with additional ease of sample preparation or processing. In Figure 3.7, it was observed that recovery stress under flexural mode could be increased with increasing BA-a contents from 0.25 MPa at 30 mole% to 1.59 MPa at 50mol%. The phenomenon was attributed to an increase in crosslink density with the addition of the BA-a benzoxazine resin 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 3.8 while the shape fixity slightly decreased with increasing BA-a content [20].

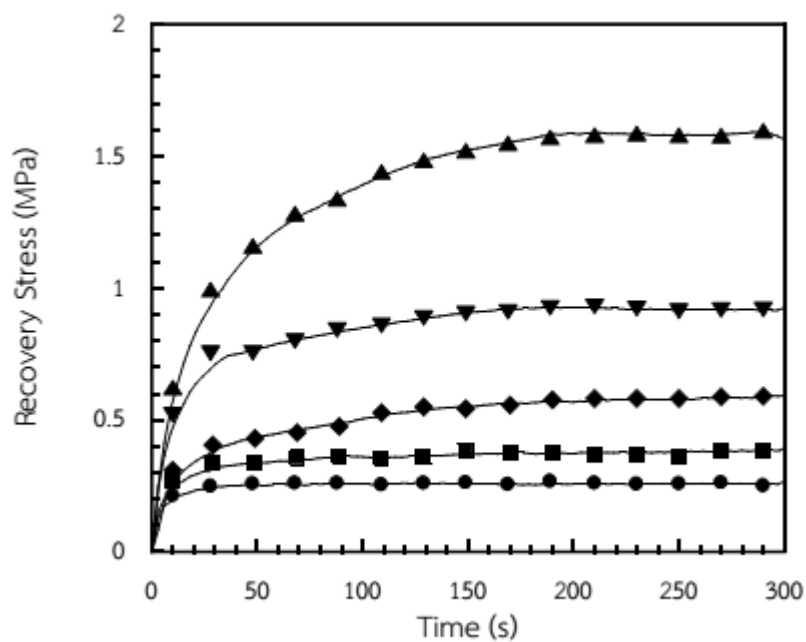


Figure 3.7 Recovery stress versus time of aliphatic epoxy/benzoxazine SMPs at various mole percents of the BA-a: (●) 30 mol%, (■) 35 mol%, (◆) 40 mol%, (▼) 45 mol% and (▲) 50 mol% [20].

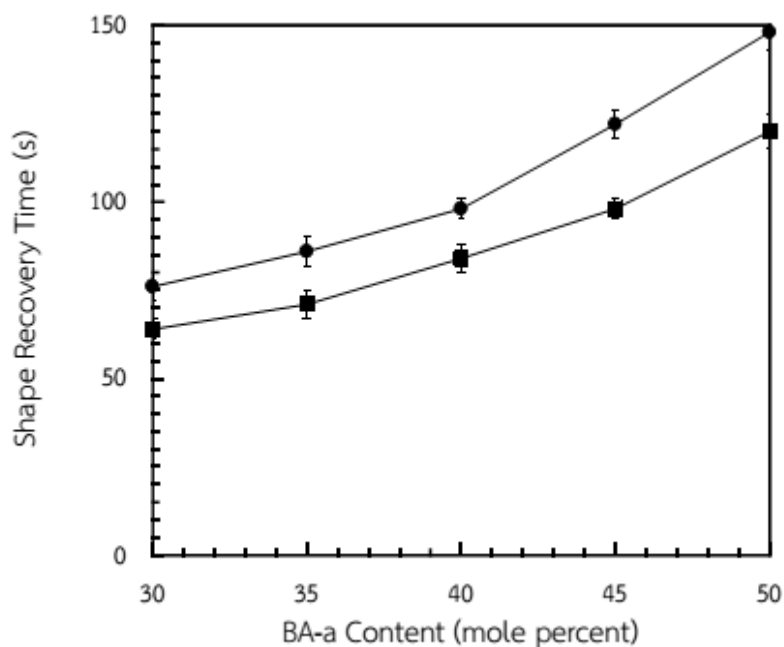


Figure 3.8 Recovery time as a function of BA-a contents of the aliphatic epoxy/benzoxazine SMP samples at various temperatures: (●) T_g and (■) T_g+20 °C [11].

Miaudet et al. (2007) studied fibers that contain a large fraction of CNTs embedded in polyvinyl alcohol (PVA). They are obtained by a particular coagulation spinning process that allows a homogeneous distribution of the CNTs within the fibers.

It is observed that the maximal recovery stress (under tension mode) generated by the fiber is close to 150 MPa. This value is about one to two orders of magnitude greater than the stress generated by conventional shape memory polymers. The recovery stress is closer to the stress generated by shape-memory metallic alloys, which ranges between 200 and 800 MPa for NiTi alloys under tension [12].

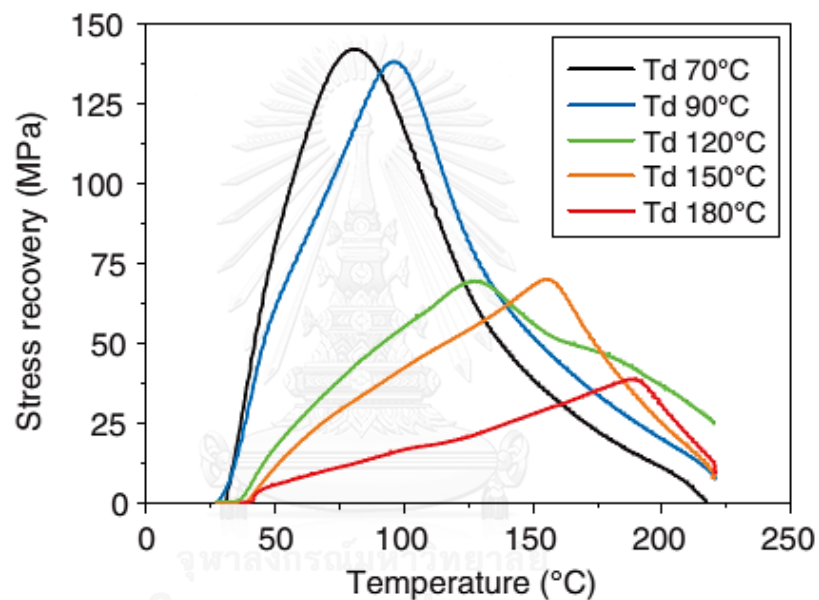


Figure 3.9 Stress generated by a nanocomposite fiber when it is reheated [12].

Gall et al. (2002) fabricated shape memory polymer nanocomposites from thermoset epoxy filled with silicon carbide nanopowder. Electron microscopy showed that the nanoparticulate reinforcements were well dispersed throughout the shape memory polymer matrix [46].

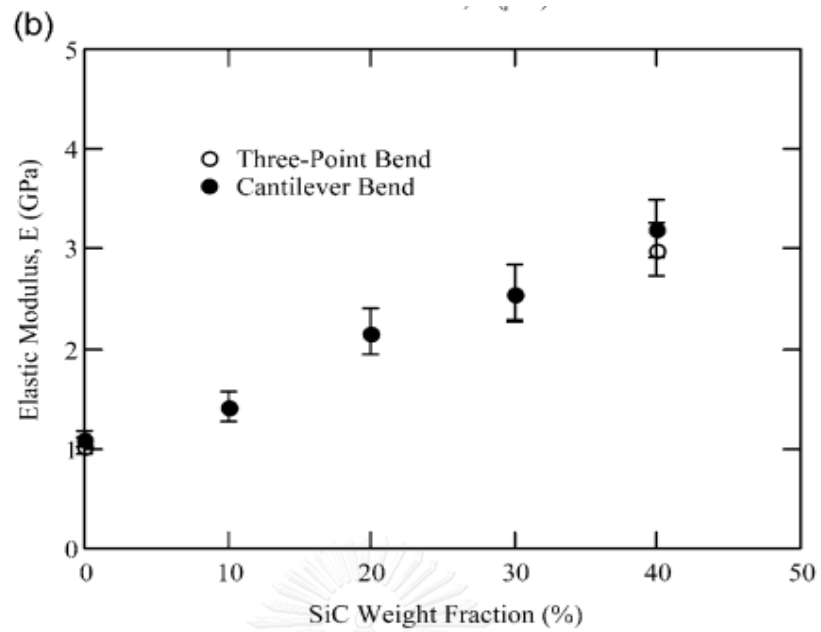


Figure 3.10 Elastic modulus as a function of the weight fraction of SiC as determined by micro bend test [46].

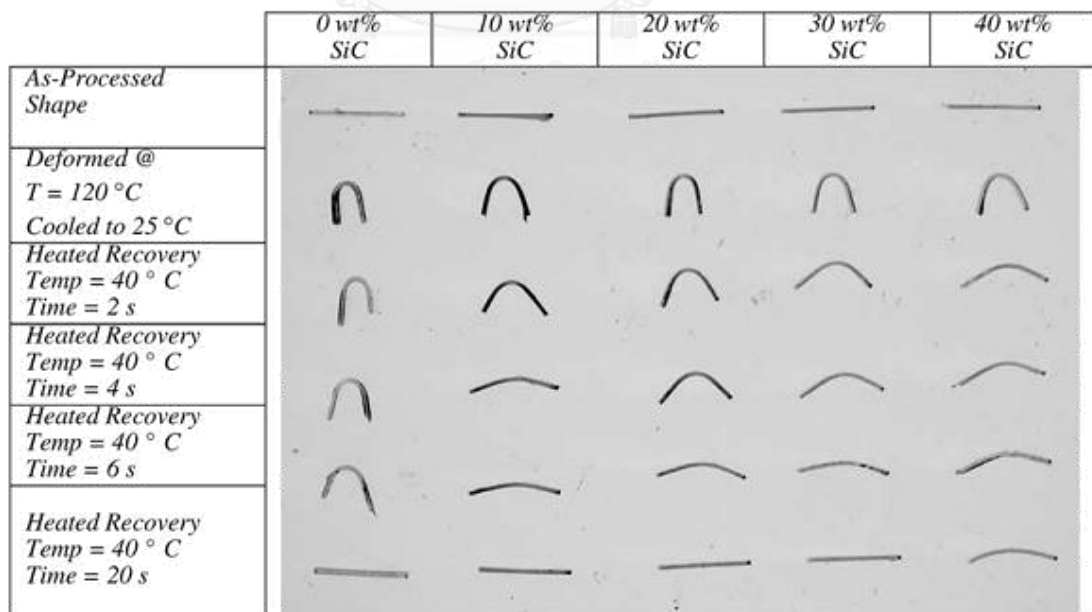


Figure 3.11 Image demonstrating the unconstrained bend recoverability as a function of SiC fraction and time at temperature [46].

Lui et al. (2004) studied the thermo mechanics and shape memory properties of a SMP polymer and its composites made by adding nano-scale silicon carbide (SiC) reinforcements. Figure 3.12, the glass transition temperature (T_g) for the SMP is about 88°C. Above 118°C ($T_g + 30^\circ\text{C}$), the storage modulus is almost constant and the rubbery state of the SMP is obtained. With the addition of 20 wt. % silicon carbide nanoparticles, T_g increased by approximately 10°C. The storage modulus of the SMP at 26°C ($E_r=1230$ MPa) is about two orders of magnitude larger than that at 118°C ($E_r= 10:4$ MPa). Storage modulus for the SMP nanocomposites at 26 and 118°C is higher than that of the SMP resin. Isothermal quasi-static stress–strain tests under flexure were also conducted at 26 and 118°C for the SMP and SMP nanocomposites [15].

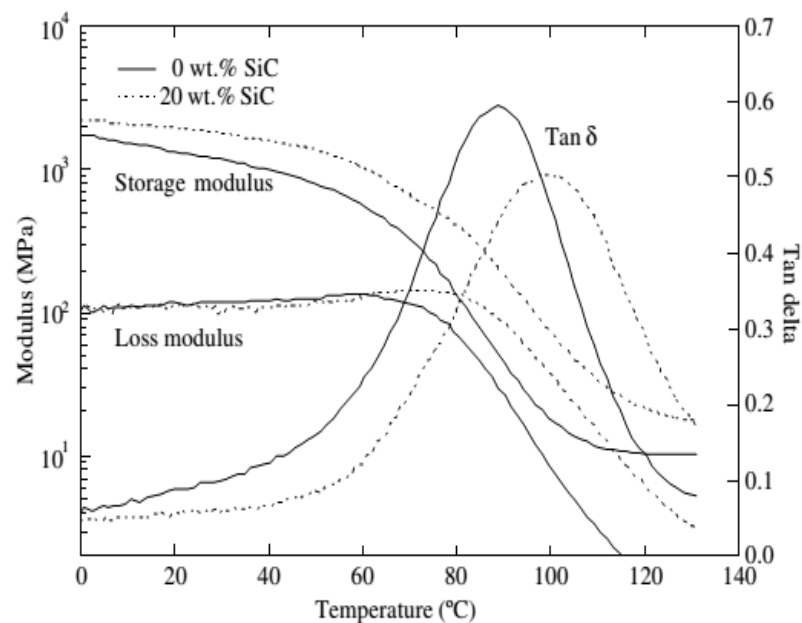


Figure 3.12 Storage modulus, loss modulus and tangent δ of the SMP and SMP nanocomposites [15].

Stress recovery tests of the SMP and SMP nanocomposite were pre-deformed at 118°C. In the stress recovery tests (Fig. 3.13), the solid lines represent the response of the SMP while the dashed lines represent the SMP nanocomposite. Only the cooling

(Step 2) and the stress recovery (Step 3a) curves are drawn. After heating to 118°C, the specimens were pre deformed to a strain of 11%. The SMP nanocomposite starts at a higher stress level for the same pre-deformation strain. Stress recovery of SMP nanocomposite was clearly observed to be higher than non-nanocomposite [15].

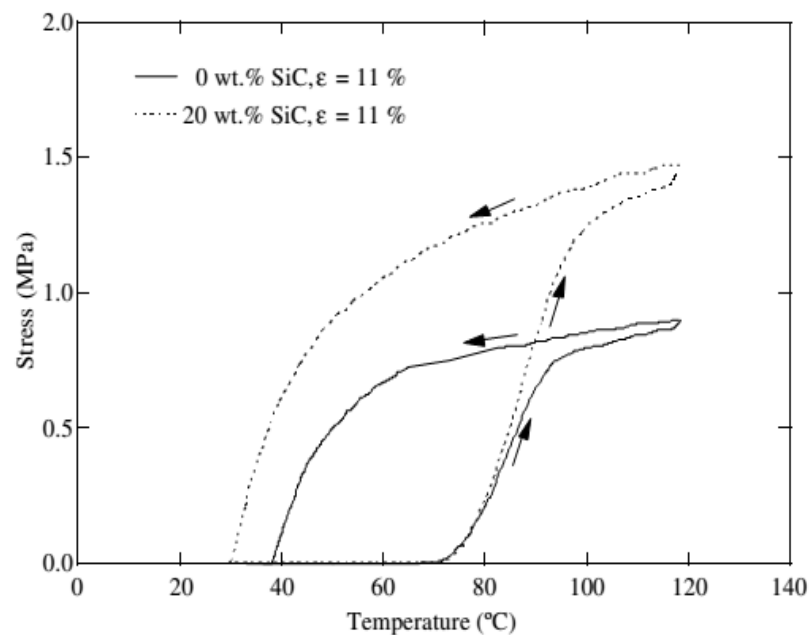


Figure 3.13 Stress recovery of the SMP and SMP composite under strain constraint [15].

Inorganic whiskers have been found to be an ideal filler for use in polymer-based composites. A whisker is a rod-shaped single-crystal inorganic fiber with a high aspect ratio. Due to the perfect crystal structures and small diameters of the whiskers, these fibers exhibit a high tensile strength and Young's modulus [47].

Wang et al. (2011) studied shape memory polymer from poly (L-lactide-co- ϵ -caprolactone) (PLLCA) filled with 5, 10, 20, and 30 wt% of CaCO_3 whiskers. They assessed the influence of the CaCO_3 whisker content on the mechanical and thermal properties of the PLLCA/ CaCO_3 whisker composites [47].

Figure 3.14 also shows a comparison of the Young's moduli of the neat PLLCA and the composites. The Young's modulus of neat PLLCA was <5 MPa at the test

temperature of 23°C. As the CaCO₃ whisker content of the composite increases, the Young's modulus increases from 4.2 MPa to 28.2 MPa.

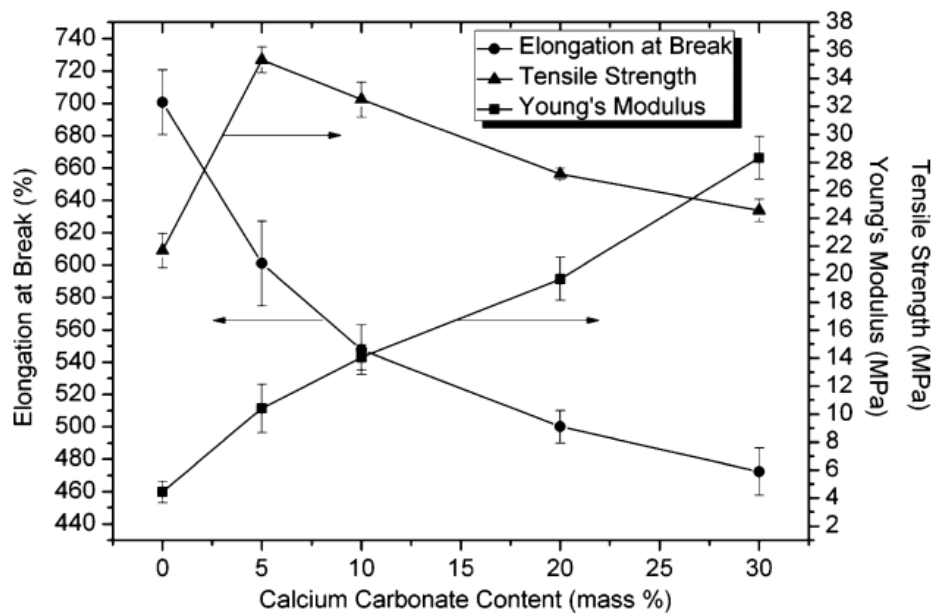


Figure 3.14 Mechanical properties of neat PLLCA and all of the composites [47].

Rimdsut et al. (2007) studied variable power input was investigated as a tool to facilitate the curing reaction of benzoxazine-epoxy-phenolic molding compound i.e., BEP893. Dielectric filler for microwave coupling was silicon carbide whisker (SiC_w). The effect of SiC_w loading on dynamic mechanical properties of the fully cured BEP893 composites is shown in Figures 3.15 and 3.16 depicts the effect of the whisker loading (in the range of 0–20% by weight) on the storage modulus of the composites. From the plot, the presence of a high modulus SiC_w (400 GPa) was found to significantly enhance both the glassy state modulus and the rubbery plateau modulus of the neat BEP893 matrix due to the reinforcing effect of the filler. Furthermore, the glass transition temperature (T_g) of the sample obtained from the peak position of the loss modulus as shown in Figure 3.15 was also found to increase with increasing the SiC_w content. The enhancement of the modulus and the T_g implies a relatively good adhesion between this filler and the BEP893 matrix [48].



Figure 3.15 Effect of SiCw loading on storage modulus of fully cured BEP893 composites: (●) 20 wt %, (■) 15 wt %, (◆) 10 wt %, (▲) 5 wt %, and (▼) 0 wt % [48].

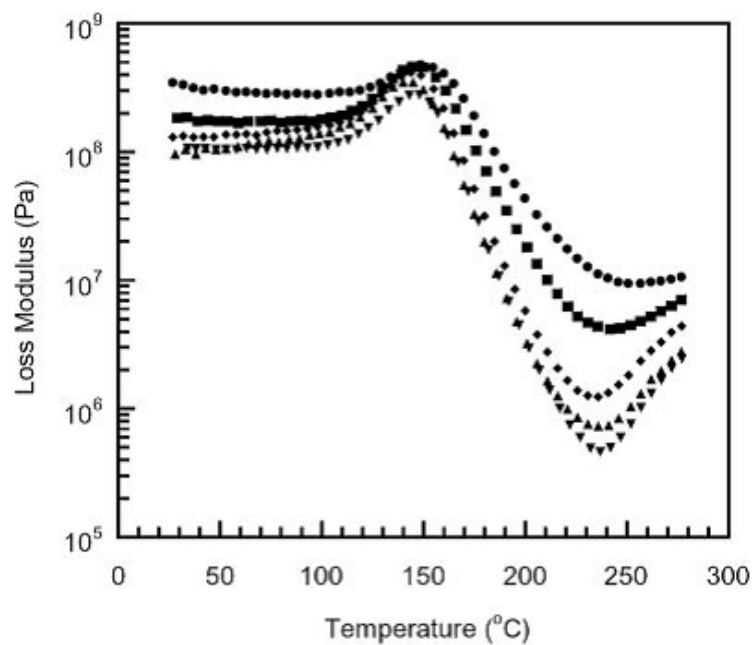


Figure 3.16 Effect of SiCw loading on loss modulus of fully cured BEP893 composites: (●) 20 wt %, (■) 15 wt %, (◆) 10 wt %, (▲) 5 wt %, and (▼) 0 wt % [48].

In recently, **Du et al.** (2015) used solution casting method to prepare shape-memory composites based on poly (vinyl alcohol) with silicon carbide (SiC). Figure 3.17, the result reveal the silicon carbide content has effect on the microwave induced shape recovery property. The required shape recovery time decreases with an increasing silicon carbide content. It indicates the more silicon carbide is filled in composite the more heat generated, which leading to the fast recovery under the same irradiation condition [24].

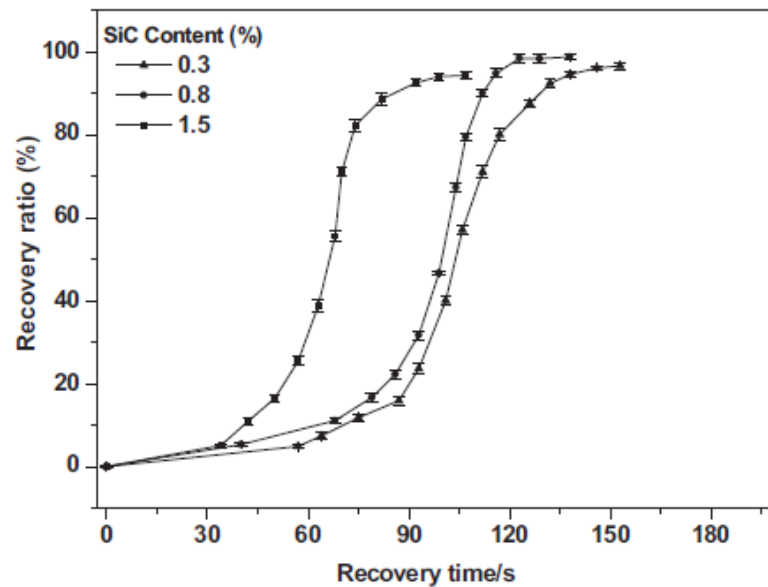


Figure 3.17 Effect of SiC content on Shape-memory behavior of SM-PVA composites under 300 W of microwave irradiation [24].

CHAPTER IV

EXPERIMENTAL

4.1 Raw Materials

The materials used in this research are benzoxazine resin, aliphatic epoxy and silicon carbide whisker. Benzoxazine resin is based on bisphenol-A, aniline and formaldehyde. The bisphenol-A (polycarbonate grade) was provided by Thai Polycarbonate Co., Ltd. (TPCC). Para-formaldehyde (AR grade) was purchased from Merck Company and aniline (AR grade) was contributed by Panreac Quimica S.A. Company. The neopentyl glycol diglycidyl ether (NGDE) was available from Aditya Birla Chemical (Thailand). Silicon carbide whisker from Tokai Carbon Co., Ltd. (Tokyo, Japan), having average diameter of 0.5 μ m and average length of 30 μ m, was used as a filler for this investigation. All chemicals were used as received.

4.2 Specimen Preparation

4.2.1 Benzoxazine Resin Preparation

Benzoxazine resin (BA-a) synthesized by using bisphenol-A, formaldehyde and aniline at the mole ratio of 1:4:2. The mixture was heated to 110 °C in an aluminum pan and was stirred until a homogeneous mixture was obtained for approximately 30 minutes to yield a light yellow liquid monomer product, according to the patented solventless method in the U.S. Patent 5,543,516 [41]. The resulting benzoxazine monomer is solid at room temperature with transparent yellow color. The as-synthesized monomer was ground into fine powder and taken for material characterization.

4.2.2 Preparation of Silicon Carbide Whisker-Filled Benzoxazine-Epoxy SMP

Samples

The BA-a resin was mixed with aliphatic epoxy (NGDE) at 50 mole percent of BA-a, later which was varied between 40-60 mol%. The mixture was heated at 70-80 °C in an aluminum pan. Then, the mixture was mechanically stirred for about 20 minutes to yield a homogeneous mixture. The molten resin was thermally cured at 80 °C for 2 h in vacuum oven and 130 °C/ 12 h respectively, in an air circulated oven. Then, the filler was added in benzoxazine-epoxy mixture, which was varied 5 to 20 wt%. The filler was mechanically stirred to achieve uniform dispersion in benzoxazine-epoxy mixture at about 140°C. For thermal-cured specimen, the compound was compression-molded by hot pressing. The thickness was controlled by using a metal spacer. The hot-press temperature of 160°C was applied for 20 minute and 170°C for 3 hours using a hydraulic pressure of 10 MPa. All samples were air-cooled to room temperature in the open mold and were cut into desired shapes before testing.

4.3 Characterization Methods

4.3.1 Differential Scanning Calorimetry (DSC)

Curing condition of benzoxazine-epoxy matrix were investigated by a differential scanning calorimeter (DSC) model 2910 from TA Instruments. We sealed each sample with a mass in a range of 3–5 mg in an aluminum pan with lid. The sample temperature was systematically scanned from room temperature to 320 °C under nitrogen purging with 10 °C/min of heating rate. The purge nitrogen gas flow rate was maintained to be constant at 50 ml/min.

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

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

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

4.3.2 Dynamic Mechanical Analysis (DMA)

The dynamic mechanical properties: storage modulus (E'), loss modulus (E'') and loss tangent ($\tan\delta$), that are investigated by dynamic mechanical analyzer (NATZSH, model DMA 242). The sample, with a dimension of $10 \times 50 \times 3 \text{ mm}^3$, was tested using a three-point bending mode at the frequency of 1 Hz and heating rate of $2 \text{ }^\circ\text{C}/\text{min}$ from room temperature to the temperature beyond the glass transition temperatures (T_g) of each sample. The glass transition temperature was observed as the maximum peak on loss tangent.

4.3.3 Universal Testing Machine (Flexural Mode)

Universal testing machine (model 5567) from Instron Co., Ltd was used for determined mechanical properties of the polymers or polymer composites. The flexural mode was used for test method on three-point loading with the supporting span of 32 mm and tested at a crosshead speed 1.0 mm/min. A dimension of a specimen is $10 \times 50 \times 2 \text{ mm}^3$. Flexural properties were determined based on ASTM D 790M. The flexural strength and the modulus were calculated by the following equations:

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

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

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 Recovery Performance

The shape recovery performance is an essentially important characteristic of SMPs. Therefore, a systematic shape recovery test of benzoxazine-epoxy SMPs and their composites under bending load was performed. The procedure for the thermo-mechanical bending of the SMPs includes the following steps: First, the sample in its permanent shape was kept in an oven for 20 min at T_g+20 °C; then the SMPs was bent to a storage angle θ_0 in a "U" shape with the radius of 4-5 mm in the soft rubbery state, and then the SMPs were cooled and kept at room temperature with the external constraint to freeze the elastic deformation energy for 20 min. The SMP sample fixed on the apparatus was immersed into air circulated oven at an elevated temperature, and then it recovered to an angle θ_N . The method used to quantify the precision of deployment is illustrated in Figure 4.1.

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

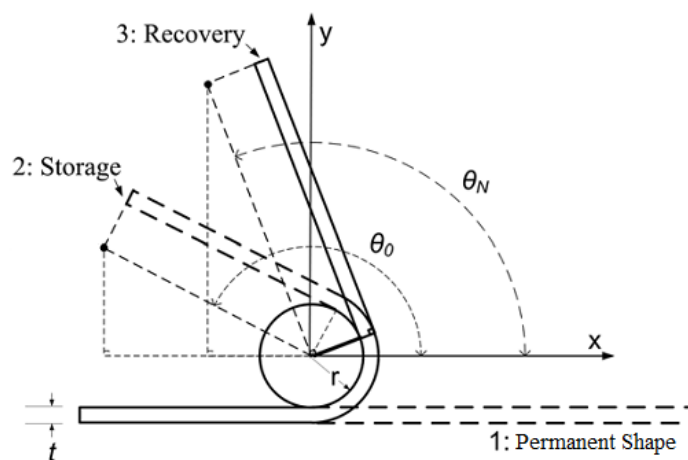


Figure 4.1 Schematic illustration of the setup for the shape recovery performance in U-shape deployment test [49].

$$R_N = \frac{\theta_0 - \theta_N}{\theta_0} \times 100 \quad (4.4)$$

4.3.5 Shape Fixity and Recovery Stress Test

The shape fixity and recovery stress of benzoxazine-epoxy SMPs and their composites were investigated by Universal testing machine under flexural test in three point bending mode. The experimental procedure for the shape fixity and recovery stress is shown in Figure 4.2. Firstly, a fixed shape was formed by applying the force to a sample ($10 \times 50 \times 2 \text{ mm}^3$) at $T_g + 20 \text{ }^\circ\text{C}$ and left to cool down to room temperature. The force was then removed perfectly to obtain a temporary shape. The deflection after unloading was measured, and rate of shape fixity (R_f) was determined. The sample was heated up to $T_g + 20 \text{ }^\circ\text{C}$ by keeping the fixed deflection content afterwards. Force release from specimen during heating was measured and the recovery stress was obtained [31].

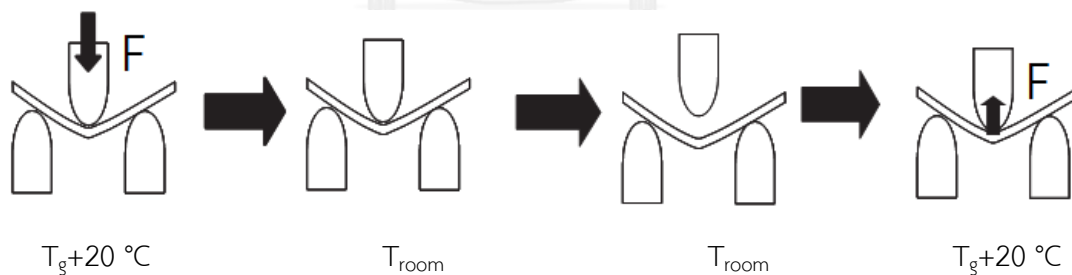


Figure 4.2 Experimental procedure in the shape fixity and recovery stress process.

4.3.6 Microwave Actuation for Shape Recovery

The SMP samples with original rectangular shape were heated and bended into U-shape. The temporary shape can be successfully fixed at room temperature. The fixed sample started to recover after microwave actuate, using video camera to record the

shape recovery process. The output power could be continuously at 900W. The recovery time determine at maximum recovery each specimen [45].

4.3.7 Scanning Electron Microscope (SEM)

To investigate interfacial bonding between the filler and the matrix used a JSM-6400 scanning electron microscope (SEM) at an acceleration voltage of 15 kV. All samples were coated with thin film of gold using a JEOL ion sputtering device (model JFC-1200) for 4 min to obtain a thickness of approximately 30 Å and the micrographs of the sample fracture surface were obtained. The micrographs of the sample fracture surface were used to qualitatively evaluate the interfacial interaction between the SiC_w filler and the matrix.



CHAPTER V

RESULTS AND DISCUSSION

5.1 Curing Condition Investigation of Benzoxazine-Epoxy Shape Memory Polymer

Figure 5.1 exhibits the curing exotherms of the neat benzoxazine-epoxy and the silicon carbide whisker (SiC_w)-filled benzoxazine-epoxy molding compounds at different SiC_w contents. The DSC thermograms revealed a maximum exothermic peak of all these molding compounds to be at about $248^\circ\text{C} - 250^\circ\text{C}$. The less changed exothermic peak position with an increment of the SiC_w content implies that SiC_w has few effect on curing reaction of the benzoxazine-epoxy binary system e.g. curing acceleration or curing retardation. No direct effect of SiC_w on curing reaction during process was found in SiC_w -filled benzoxazine resins [50]. However, the peak area was found to decrease with increasing the SiC_w content. The exothermic peak area are 482, 412, 330, 300 and 270 J/g at 0, 5, 10, 15 and 20 wt% of SiC_w , respectively. This phenomenon is correlated to the decreasing amount of benzoxazine-epoxy mixture in molding compounds with an increase of the SiC_w content. Furthermore, the reactions between the benzoxazine and NGDE were found to consist of at least two major reactions. The first is attributed to the polymerization reaction of benzoxazine monomer at the two overlap peak, another exothermic peak at higher temperature is reaction between the phenolic hydroxyl group of the polybenzoxazine (PBA-a) and epoxide group of the NGDE. This phenomenon is in agreement with curing behaviors of aliphatic epoxy (NGDE)/benzoxazine resin (BA-a) [20].

Figure 5.2 exhibits the DSC thermograms of benzoxazine-epoxy resin with no addition of silicon carbide whisker for study curing conditions of the systems. From the experiment, the uncured benzoxazine-epoxy resin possesses a heat of reaction determined from the area under the exothermic peak to be 482 J/g and the value decreased to 429 J/g after step curing at $130^\circ\text{C}/12\text{hours}$ then curing at $160^\circ\text{C}/2\text{hours}$, $160^\circ\text{C}/3\text{hours}$, $170^\circ\text{C}/3\text{hours}$ and $180^\circ\text{C}/3\text{hours}$, respectively. The value decreased to

282, 242, 172 and 123.6 J/g. The degrees of conversions estimated by equation 5.1 were 11.0, 41.5, 50.0, 64.3 and 74.4%. The conversion with 64.3% was selected to be curing conversion. Owing to these values were corresponding to those of NGDE/PBA-a shape memory, i.e. Tanpitaksit et al. [20] reported approximately 60% conversion to cure all NGDE/ BA-a mixtures. Moreover, Liu et al. [51] suggested that the degree of conversion about 60 % of shape memory epoxy provided samples with good balance properties between shape memory performance and thermomechanical properties.

5.2 Dynamic Mechanical Analysis (DMA) of SiC_w-Filled Benzoxazine-Epoxy SMPs

Since polymeric materials are viscoelastic, dynamic mechanical analysis (DMA) is suitable to evaluate mechanical properties as a function of temperature, complex transition and relaxation phenomena when polymeric materials are presented. Figures 5.3, 5.4 and 5.5 illustrate dynamic mechanical properties of the SiC_w-filled benzoxazine-epoxy SMPs with the SiC_w ranging from 0 to 20wt%. Viscoelastic properties of the samples were investigated in flexural mode. Several parameters such as storage modulus and loss tangent were obtained as a function of temperature from room temperature up to 210 °C based on a heating rate of 2 °C/min. Figure 5.3 presents the storage modulus of SiC_w-filled benzoxazine-epoxy SMPs at its glassy state. The modulus values tended to increase significantly with increasing the SiC_w contents as a result of the more rigid characteristics of the composites. At initial temperature (30°C), the modulus of SiC_w-filled benzoxazine-epoxy SMP increased from 5.1 GPa (neat matrix) to 8.8 GPa of the 20% by weight of SiC_w composite. The phenomenon is contributed to the addition of the more rigid filler in the benzoxazine-epoxy SMPs. The results also suggested that the substantial interfacial adhesion between the SiC_w and the SMP matrix. The storage in rubbery state seems to further increase with increasing temperature suggesting further curing of the matrix during the DMA experiment.

Figure 5.4 illustrates loss modulus curves of SiC_w-filled benzoxazine-epoxy SMPs. The glass-transition temperatures (T_g s) were obtained from the maximum peak of the loss modulus of the SiC_w-filled benzoxazine-epoxy SMPs. The resulting T_g values of the

SMPs were observed to be in range of 136 to 151°C at 0-20 wt% of SiC_w contents. It could be seen that the T_g values increased with increasing SiC_w contents in the SMPs. This result also implies good adhesion between the filler and matrix which obstruct the polymeric chain movement, leading to increase in T_g values. The results are correlated to SiC_w on benzoxazine-epoxy-phenolic system [48].

Figure 5.5 exhibits α -relaxation peaks of the loss tangent ($\tan\delta$) of the SiC_w-filled benzoxazine-epoxy SMPs. From the figure, it was found that the peak maxima of the loss tangent were shifted to higher temperature in good agreement with the loss modulus peak. $\tan\delta$ curves, obtained from the ratio of energy loss (E'') to storage energy (E') in sinusoidal deformation, are shown in Figure 5.5. The peak positions of the $\tan\delta$ were used to also indicate the T_g of the specimens. As can be seen from Figure 5.5, the T_gs of SMPs were 154, 165, 165, 168 and 170°C at 0, 5, 10, 15 and 20 % by weight of SiC_w, respectively. The magnitude of $\tan\delta$ peak reflects the large scale mobility associated with α relaxation, while the width of $\tan\delta$ relates to the network homogeneity. The peak height of $\tan\delta$ found to decrease with increasing SiC_w contents. This is due to the reduction in segmental mobility chain with the presence of the rigid SiC_w. Finally, the width at half height of the $\tan\delta$ in SiC_w-filled benzoxazine-epoxy SMPs presented large width compared with neat matrix SMP. This indicates more network heterogeneity of the polymer composite system.

5.3 Thermal Degradation of SiC_w-Filled Benzoxazine-Epoxy SMPs

Degradation temperature (T_d) is one parameter used to determine temperature stability of polymeric materials. Figure 5.6 exhibits TGA thermograms of the neat SMP and SiC_w-filled benzoxazine-epoxy SMP at various SiC_w contents at heating rate of 20°C/min under nitrogen atmosphere. It was observed that pure SiC_w shows outstandingly high thermal stability. On the other hand, the benzoxazine-epoxy matrix possesses a degradation temperature at its 5% weight loss of 293°C and char residue at 800°C of 28%. From the thermograms, the degradation temperature at 5% weight

loss of the SiC_w-filled benzoxazine-epoxy SMPs increased with increasing SiC_w content as seen in the Figure 5.7. The degradation temperature at 5 % weight loss ($T_{d,5}$) was found to systematically increase from 293 to 303°C at 0 to 20wt% of silicon carbide whisker. This enhancement in the thermal stability of the SiC_w-filled benzoxazine-epoxy SMPs is attributed to the fact that the physical barrier effect of SiC_w can serve as a good thermal cover layer, which slows down the escape of pyrolysis products and then delays the further degradation of matrix [52]. This increment is correlated with degradation temperature at 10 % weight loss ($T_{d,10}$). Another feature in TGA thermograms is amount of residue at 800°C. The solid residue of SiC_w-filled benzoxazine-epoxy shape memory polymer was expectedly found to increase with increasing SiC_w contents. The solid residue of the shape memory polymer composites with 0, 5, 10, 15, and 20wt% of filler content were 28.1, 31.6, 34.8, 38.5 and 43.0%, respectively. The increase in solid residue content with the increasing SiC_w loading in the composites was found to correspond relatively well with a rule of mixture.

5.4 Effect of SiC_w on Mechanical Properties of SiC_w-Filled Benzoxazine-Epoxy SMPs

5.4.1 Flexural Properties at Room Temperature (Glassy State)

Mechanical properties of SMPs play important role on their practical utilization. In this work, the mechanical properties of the SMP samples were investigated at glassy state (room temperature) and rubbery state ($T_g+20^\circ\text{C}$). Generally, SMPs were commonly used over these temperatures.

Figures 5.8 and 5.9 show the plots of the flexural modulus and flexural strength of benzoxazine-epoxy SMPs and SiC_w-filled benzoxazine-epoxy SMPs at room temperature as a function of the SiC_w content, respectively. The flexural modulus are the ratio of stress to strain values at 0, 5, 10, 15 and 20 wt% are 4.7, 5.9, 6.6, 7.3 and 8.1 GPa, respectively. The addition of SiC_w resulted in a systematic increase in the modulus of the obtained SMP. This is because the addition of high flexural modulus of SiC_w [53] into matrix structure could increase the stiffness of SMP. Moreover, the enhancement in flexural modulus was due to a uniform dispersion and strong

interfacial bonding between ceramic filler and matrix. Figure 5.9 represents the flexural strength of SiC_w-filled benzoxazine-epoxy SMP increases ranging from 134.8 to 178.0 MPa. This increment in flexural strength is due to good interfacial bonding and dispersion between whisker filler and matrix. That leads to effective stress transfer and high composite strength.

5.4.2 Flexural Properties at Rubbery State

Mechanical properties of SMPs at a rubbery state are also important parameters that affect deploying ability of SMP. The flexural properties of the SiC_w-filled benzoxazine-epoxy SMPs was measured using three-point bending tests. A forced air convective environmental chamber was used for elevated-temperature tests. The test was conducted at the temperature of 20°C above T_g. Figure 5.10 exhibits the plot of flexural modulus as a function of the SiC_w. The addition of SiC_w also resulted in an increase of the modulus, i.e. 58.8, 75.5, 90.5 130.7 and 174.1 MPa at 0, 5, 10, 15 and 20 wt% of SiC_w, respectively.

Figure 5.11 exhibited the plot of the flexural strength as a function of SiC_w contents. The flexural strength at rubbery state values of SiC_w-filled benzoxazine-epoxy SMP were 3.4, 4.5, 6.2, 9.5 and 10.9 MPa at 0, 5, 10, 15 and 20 wt% of SiC_w. The flexural strength at rubbery state of the benzoxazine-modified epoxy SMPs increased with increasing of the SiC_w. This increment in flexural strength is due to the same reason of that observed in glassy state, i.e. good interfacial bonding and dispersion between whisker filler and matrix could lead to effective stress transfer leading to high composite strength.

5.5 Shape Memory Properties of SiC_w-Filled Benzoxazine-Epoxy SMPs

5.5.1 Effect of SiC_w on Shape Fixity and Shape Recovery of SiC_w-Filled Benzoxazine-Epoxy SMPs

Shape memory behavior of the sample was evaluated by three parameters. Shape fixity is one parameter that indicates the ability to remember the temporary shape or fixing shape of polymer sample. The shape fixity was measured using flexural tests, a forced air convective environmental chamber was used for elevated-temperature tests. The flexural load was applied to deformed and fixed sample. Then, unload step was conducted to measure shape fixity value. The effects of silicon carbide whisker on shape fixity of the sample are illustrated in Figure. 5.12. As can be seen from this figure, the shape fixity (R_f) values of all specimens were more than 98%. Furthermore, as the silicon carbide whisker content increases, the shape fixity (R_f) are slightly increases. Maintaining in shape fixity is possibly due to the presence of silicon carbide whisker in composites is mean improve rigid structure that affect to more strong stable polymer network. The strong stable network can prevent the chains from moving freely, which causes the R_f values increase. The increase of the shape fixity was similarly to the work of Li et al. [47] reporting that shape fixity of the PLLCA increase from 97 to 99 % with increase CaCO₃ content from 0 to 30 %. In addition, cycle fixing shape exhibits in Figure 5.14. It can be seen shape fixity value of benzoxazine-epoxy SMP slightly decrease with more cycles but shape fixity value of SiC_w-filled benzoxazine-epoxy SMP maintain until 5 cycles.

Shape recovery (R_r) is another parameter that is measured after fixed temporary shape. The effects of silicon carbide whisker on shape recovery of the sample are illustrated in Fig. 5.13. The shape recovery values of specimen were decreased with increasing SiC_w contents. It was because whisker obstructs chain mobility of polymeric chain. The shape recovery values were in range of 86-98%. However, these values were higher than SiC filled SMPPU [54]. Figure 5.15 exhibits shape recovery with more cycle. It can be seen that shape recovery value of all sample decrease with increasing recovery cycle. Moreover, more decreasing in shape recovery value was found in the sample with adding more filler. This is possibly due to when SMPs recover their shape

many times some filler particles are partly de-bonded from a matrix. The de-bonded filler might obstruct a shape recovery process of the polymer matrix.

5.5.2 Effect of SiC_w on Shape Recovery Time of SiC_w-Filled Benzoxazine-Epoxy SMPs

To evaluate the shape memory performances of the SiC_w-filled benzoxazine-epoxy SMPs, a fold-deploy shape memory was performed.

In this study, the shape recovery process of the bent samples was recorded by a video camera and their shape recovery angles were determined by measuring the angle between the straight ends of the specimens. The rectangular specimens were used to investigate the recovery phenomenon [9]. Figure 5.16 illustrates shape recovery angle as a function of time. The recovery time were determine at maximum recovery each specimen. The recovery time was in range of 26.5 to 8.5 minutes with 0 to 20 wt% of SiC_w filler. It can be seen that the recovery time decreased with increasing SiC_w contents. The recovery in this composite systems is less than those observed in styrene-based SMP filled hybrid filler between carbon black and short carbon fiber [33]. This is due to the addition of high elastic modulus filler (SiC_w) into SMP, effecting on the SMPs to spring back like elastic materials. The recovery time in SMP is important property in many application that require various time for use. Moreover, recovery angle was determined in recovery ratio. The shape recovery ratio each specimen were correlated shape recovery in shape fixity and shape recovery test.

5.5.3 Effect of SiC_w on Recovery Stress of SiC_w-Filled Benzoxazine-Epoxy SMPs

The recovery stress is crucial property for smart material applications to apply a specific motion or force to a product or process. The recovery stress of SMPs defined from the elastic stress in deformation procedure. When the SMPs were heated above T_g, the SMPs were deformed and generated the elastic stress. This elastic stress was stored when the SMPs were cooled below T_g. Then, the SMPs were reheated above T_g again, the stress stored in the SMPs was released as recovery stress [30].

The recovery stress process for SiC_w-filled benzoxazine-epoxy SMPs consists of four stages. Initial stage is a sample in an original rectangular shape. In the deformed state, the sample is bended at the maximum deflection (y_{max}) of 10 mm. Then, the sample was fixed by cooling below T_g to get a temporary shape. At final stage, the sample was heated then the bent shape of sample was recovered. The recovery stress of SMPs was measured from transition stage of the shape-fixed stage to recovery shape stage [9]. The recovery stress versus time of the SiC_w-filled benzoxazine-epoxy SMPs is illustrated in Figure 5.17. The maximum recovery stress values of each samples were observed to be 3.4, 4.1, 6.0, 10.1, 11.2 MPa at 0, 5, 10, 15, 20 wt% of SiC_w contents, respectively. As the result, it could be seen that the SiC_w could improves the recovery stress of the benzoxazine-epoxy SMPs. It was seem that the increase of the recovery stress of the SMPs was due to the presence of high elastic modulus filler [21]. SiC_w, was able to enhance elastic modulus of polymer composite and stiffen the stable network. As previous reported by Liu et al. [15], the shape memory epoxy nanocomposites was observed in increase of the recovery stress value. It was found that the recovery stress was observed to be 1.5 MPa at maximum filler loading (20 wt%), i.e. 1 time greater than that of the neat epoxy SMP with the recovery stress value about 0.8 MPa. Interestingly, compared to our system that the recovery stress was observed to be 11.2MPa at SiC_w maximum loading (20 wt%).

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5.5.4 Effect of Benzoxazine Resin Contents on Dynamic Mechanical Properties

Interfacial Adhesion of SiC_w-Filled Benzoxazine-Epoxy SMPs

The effect of the benzoxazine resin (BA-a) compositions on dynamic mechanical properties of SiC_w-filled benzoxazine-epoxy SMPs at 20 wt% of SiC_w is presented in Figure 5.18, 5.19 and 5.20. The storage modulus of SiC_w-filled benzoxazine-epoxy SMPs as seen in in Figure 5.18 that tend to increase with increasing amount of benzoxazine resin. This is due to more rigid or stiffness of benzoxazine resin compared with epoxy used. The storage modulus at room temperature exhibits value about 7.8, 8.7 and 9.6 GPa at 40, 50 and 60 mol% of BA-a, respectively. The glass transition temperature were observed by loss modulus and loss tangent peak as can be seen in Figure 5.19 and

5.20. Figure 5.19 exhibits glass transition temperature value about 133, 151 and 174°C at 40, 50 and 60 mol% of BA-a, respectively. Figure 5.20 exhibits same increasing trend in glass transition temperature. This is due to more thermal stability of benzoxazine resin compared with epoxy used.

Figures 5.21 (a), (b) and (c) illustrate fracture surface of 40, 50 and 60 mol% of BA-a in SiC_w-filled benzoxazine-epoxy SMP. As seen in the figures, the SiC_w was well dispersed for all sample at various BA-a contents in matrix. However, the figure also shows different whisker pull-out length. The samples at 60 mol% of benzoxazine content in matrix show shorter whisker pull-out length compared to the sample at lower content. This is due to good interfacial adhesion of filler and benzoxazine, which could explain the enhancement in glass transition temperature and mechanical properties [48].

5.5.5 Microwave Induced Shape Memory Effect

The SMP samples with original rectangular shape were heated and bended into U-shape. The temporary shape can be successfully fixed at room temperature. The fixed sample started to recover after microwave actuates, using a video camera to record the shape recovery process. The output power could be continuously at 900W. The recovery time determines a maximum recovery each specimen. In Figure 5.22 exhibits the recovery time of SiC_w-filled benzoxazine-epoxy SMPs that was in a range of 5min. 5sec. (at 5 wt% of SiC_w) to 3min. 25sec. (at 5 to 20 wt% of SiC_w). Moreover, microwave actuate has no effect on the neat SMP as observed from the Figure 5.22. The temporary shape recovered to the maximum recovery shape was achieved, confirming that microwave radiation enabled the SiC_w-filled benzoxazine-epoxy SMP to be rapidly actuated. Moreover, the actuation efficiency was improved by using microwave in comparison with other heating methods. This is attributed to the fact that microwave treatment provides uniform heating to sample from inside to outside.

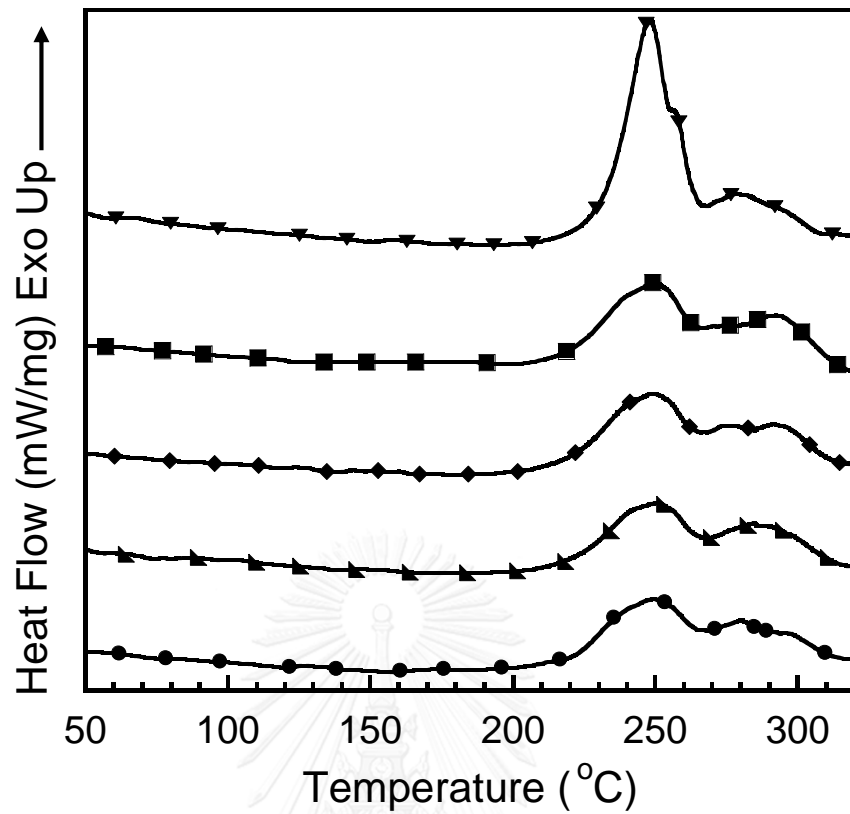


Figure 5.1 DSC thermograms of benzoxazine-epoxy molding compound at different silicon carbide whisker contents: (▼) neat matrix, (■) 5wt%, (◆) 10wt%, (▲) 15wt%, (●) 20wt%.

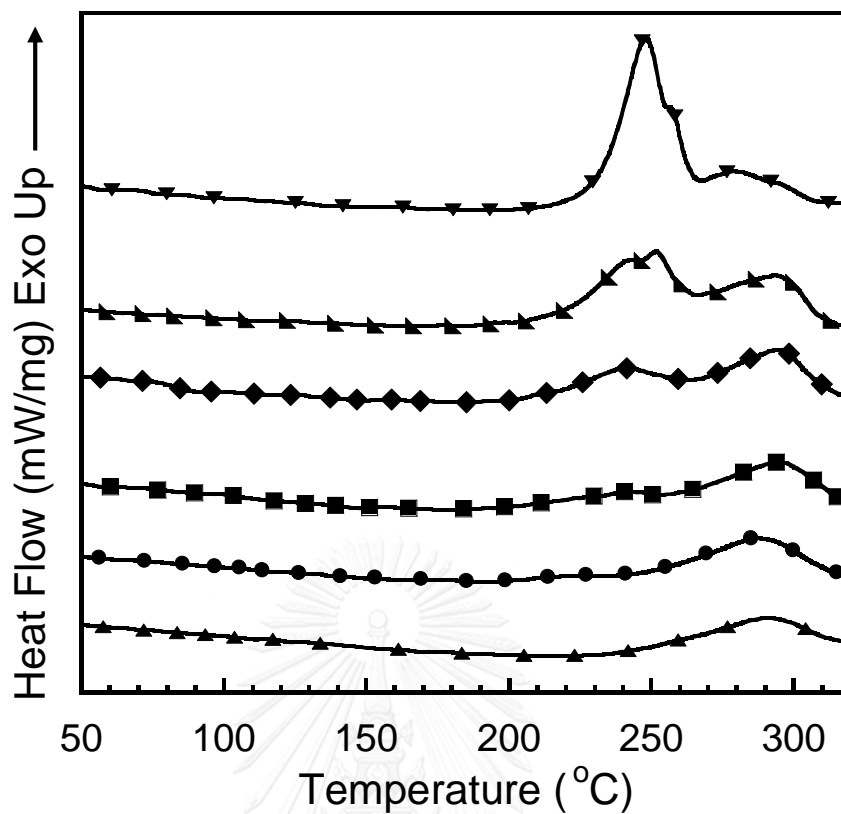


Figure 5.2 DSC thermograms of benzoxazine-epoxy SMP sample at various curing times: (▼) uncured, (▲) 130°C/12 hours, (◆) 130°C/12 hours + compress 160°C/2 hours, (■) 130°C/12 hours + compress 160°C/3 hours, (●) 130°C/12 hours + compress 170°C/4 hours, (▲) 130°C/12 hours + compress 180°C/3 hours.

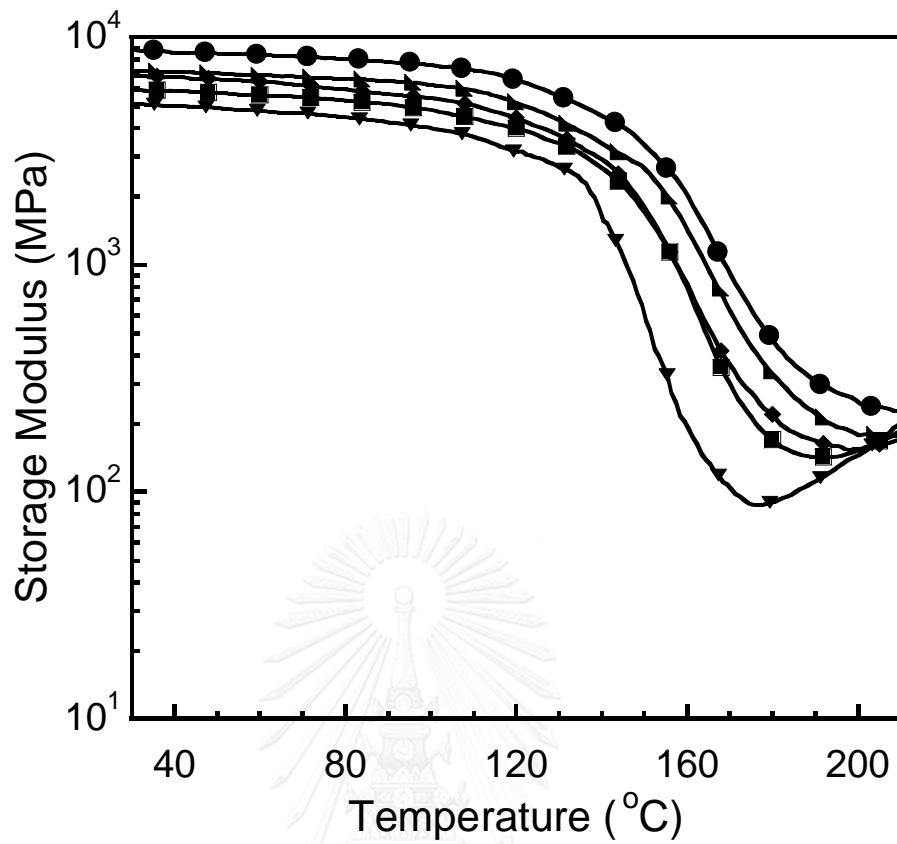


Figure 5.3 Storage modulus of silicon carbide whisker-filled benzoxazine-epoxy SMPs at various silicon carbide whisker contents: (\blacktriangledown) 0wt%, (\blacksquare) 5wt%, (\blacklozenge) 10wt%, (\blacktriangle) 15wt%, (\bullet) 20wt%. **CHULALONGKORN UNIVERSITY**

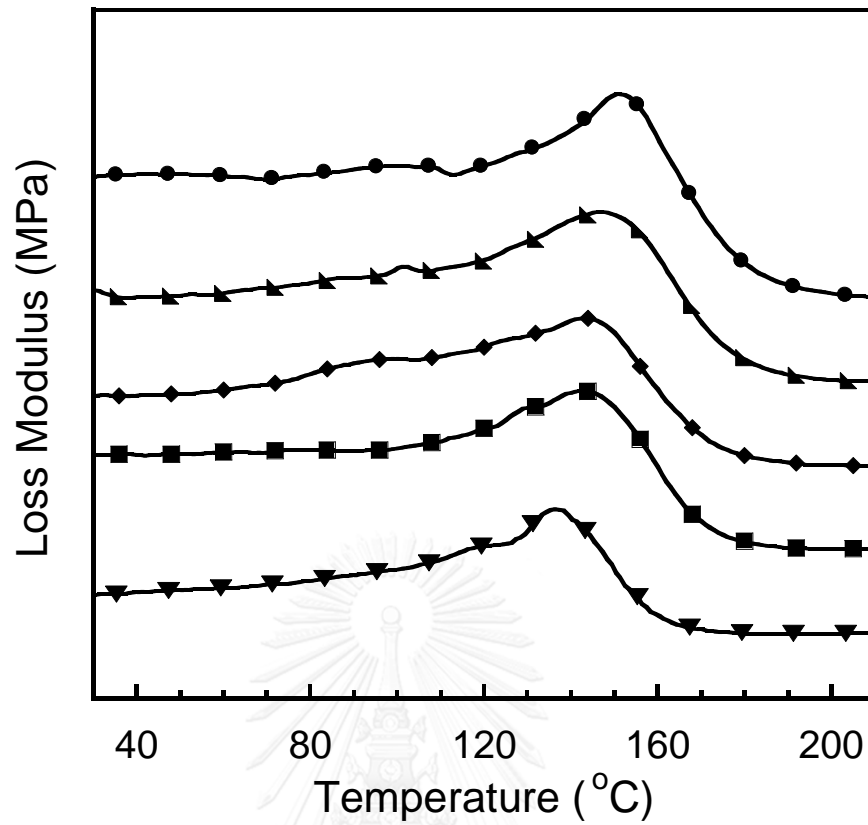


Figure 5.4 Loss modulus of silicon carbide whisker-filled benzoxazine-epoxy SMPs at various silicon carbide whisker contents: (▼) 0wt%, (■) 5wt%, (◆) 10wt%, (▲) 15wt%, (●) 20wt%.

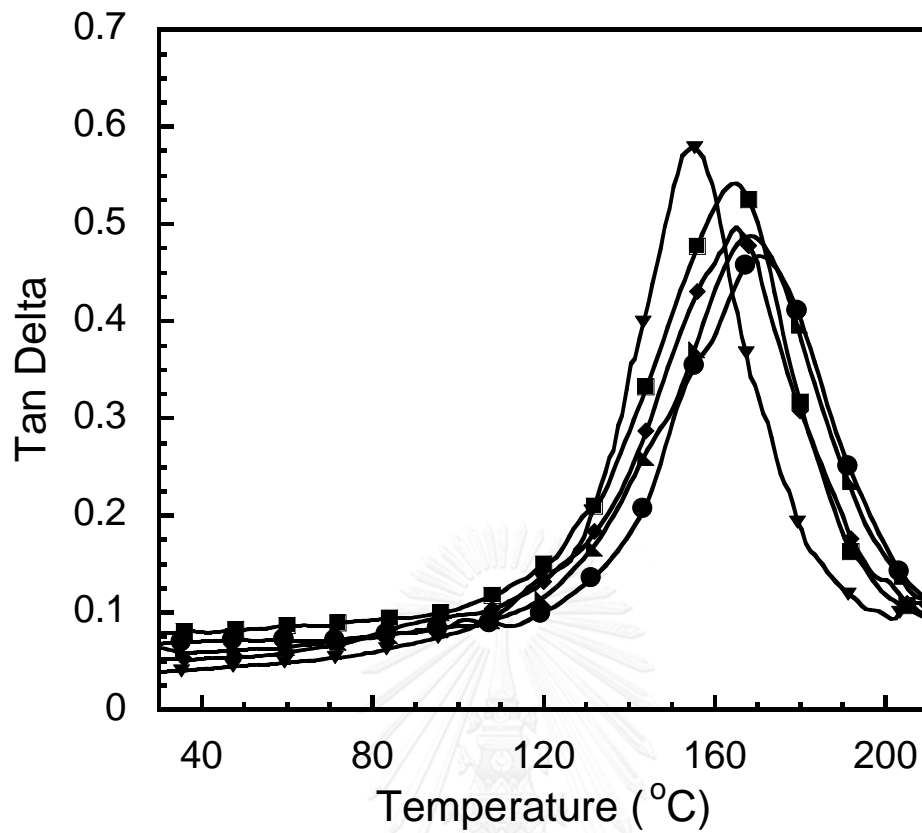


Figure 5.5 Loss tangent of silicon carbide whisker-filled benzoxazine-epoxy SMPs at various silicon carbide whisker contents: (\blacktriangledown) 0wt%, (\blacksquare) 5wt%, (\blacklozenge) 10wt%, (\blacktriangle) 15wt%, (\bullet) 20wt%.

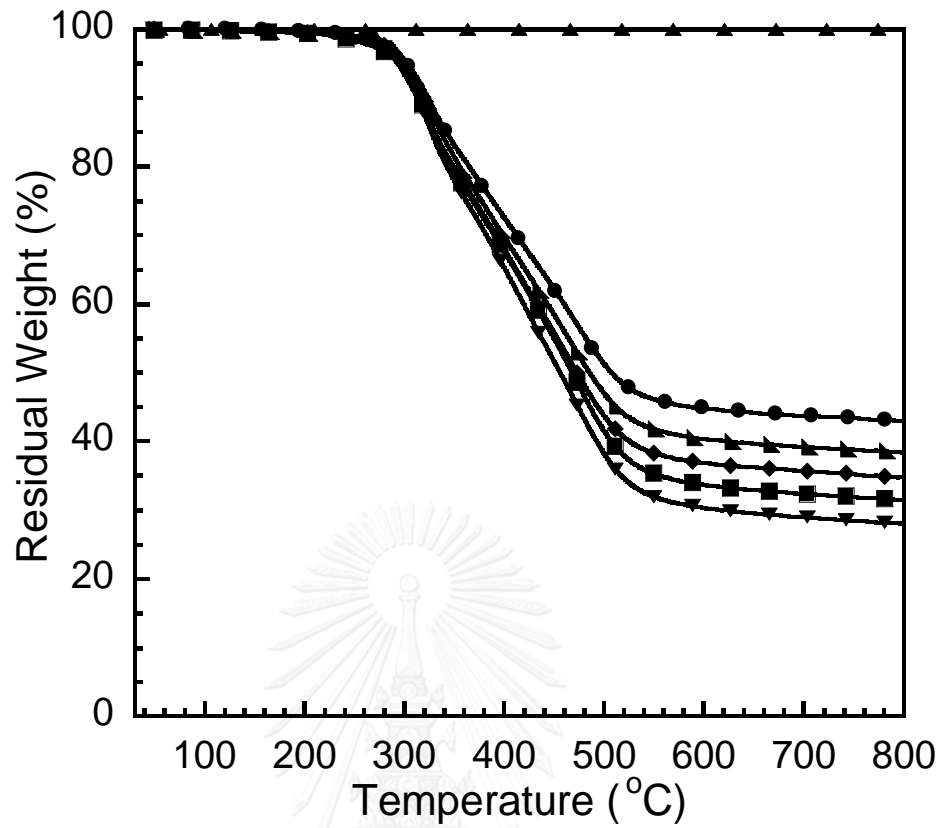


Figure 5.6 TGA thermograms of silicon carbide whisker-filled benzoxazine-epoxy SMPs at various silicon carbide whisker contents: (▼) 0wt%, (■) 5wt%, (◆) 10wt%, (▲) 15wt%, (●) 20wt%.

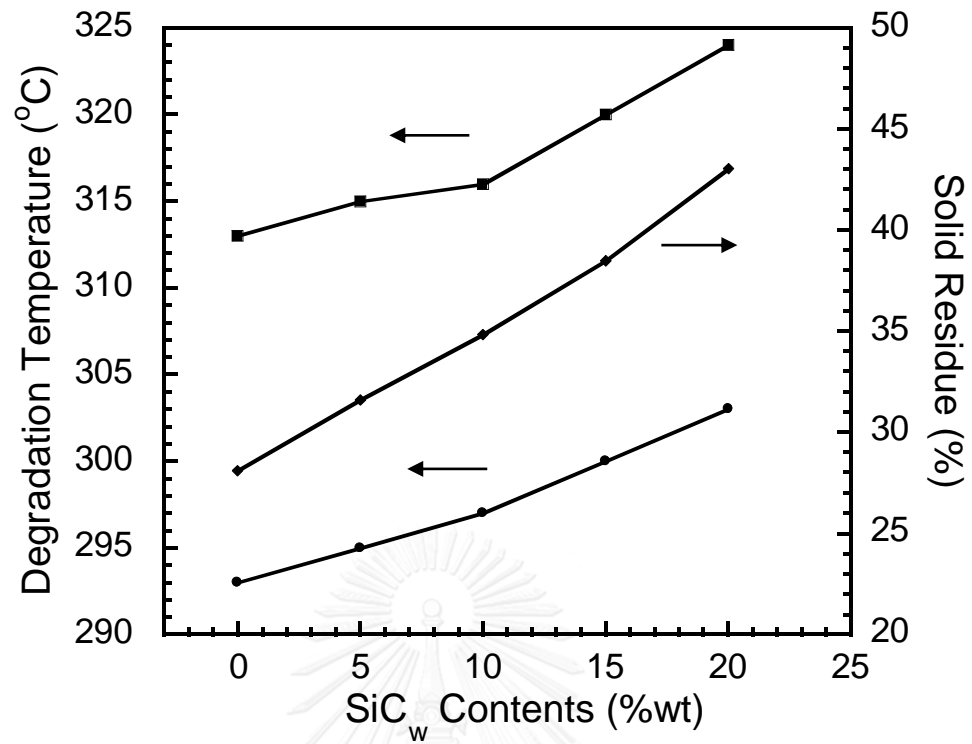


Figure 5.7 (●) Degradation temperature (5% weight loss) of silicon carbide whisker-filled benzoxazine-epoxy SMPs, (■) Degradation temperature (10% weight loss) of silicon carbide whisker-filled benzoxazine-epoxy SMPs, (◆) solid residue at 800°C.

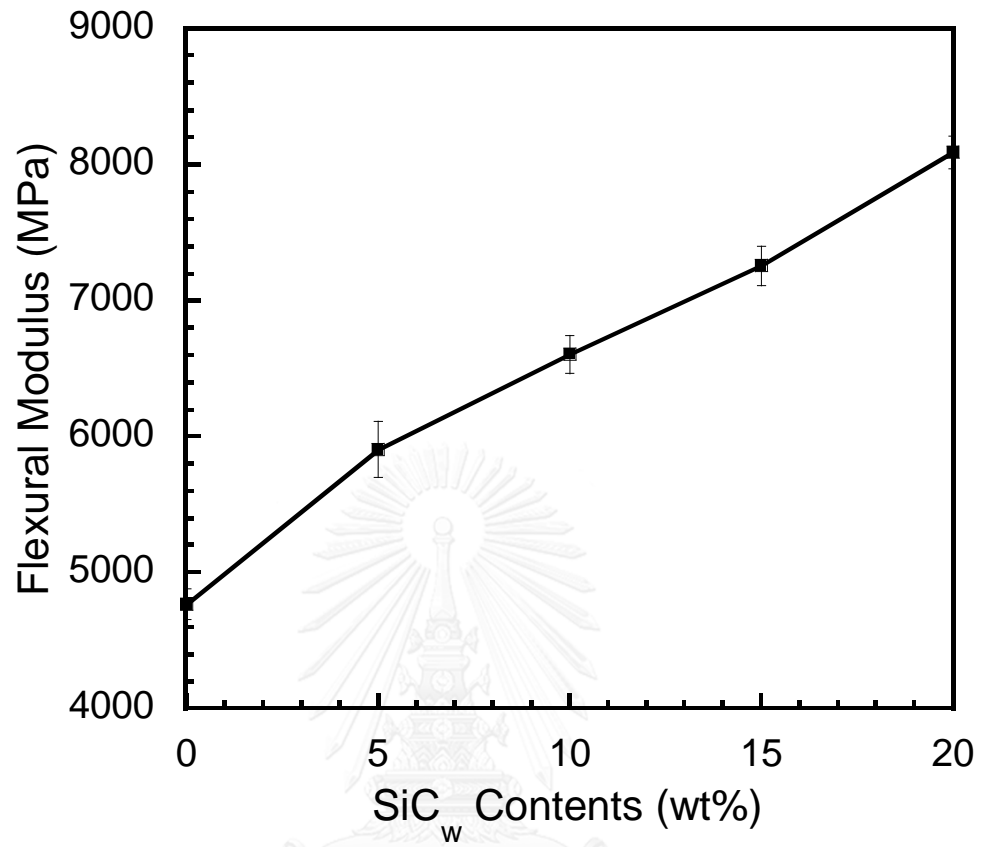


Figure 5.8 Relation between silicon carbide whisker content and the flexural modulus at room temperature of silicon carbide whisker-filled benzoxazine-epoxy SMPs.

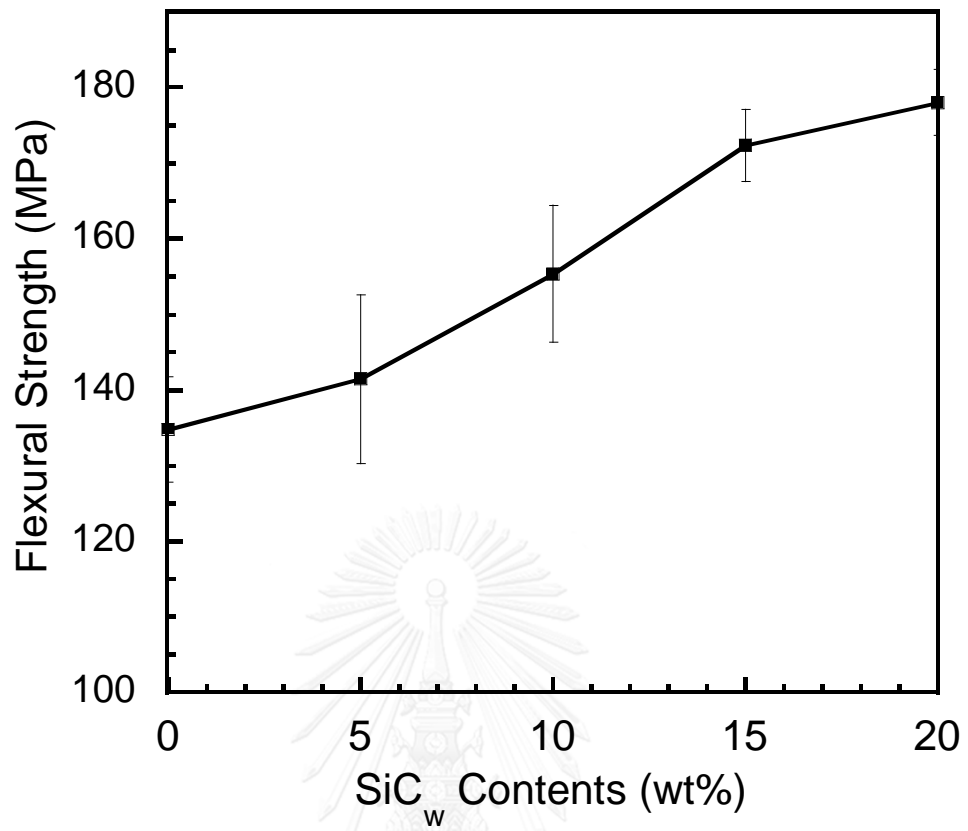


Figure 5.9 Relation between silicon carbide whisker content and the flexural strength at room temperature of silicon carbide whisker-filled benzoxazine-epoxy SMPs.

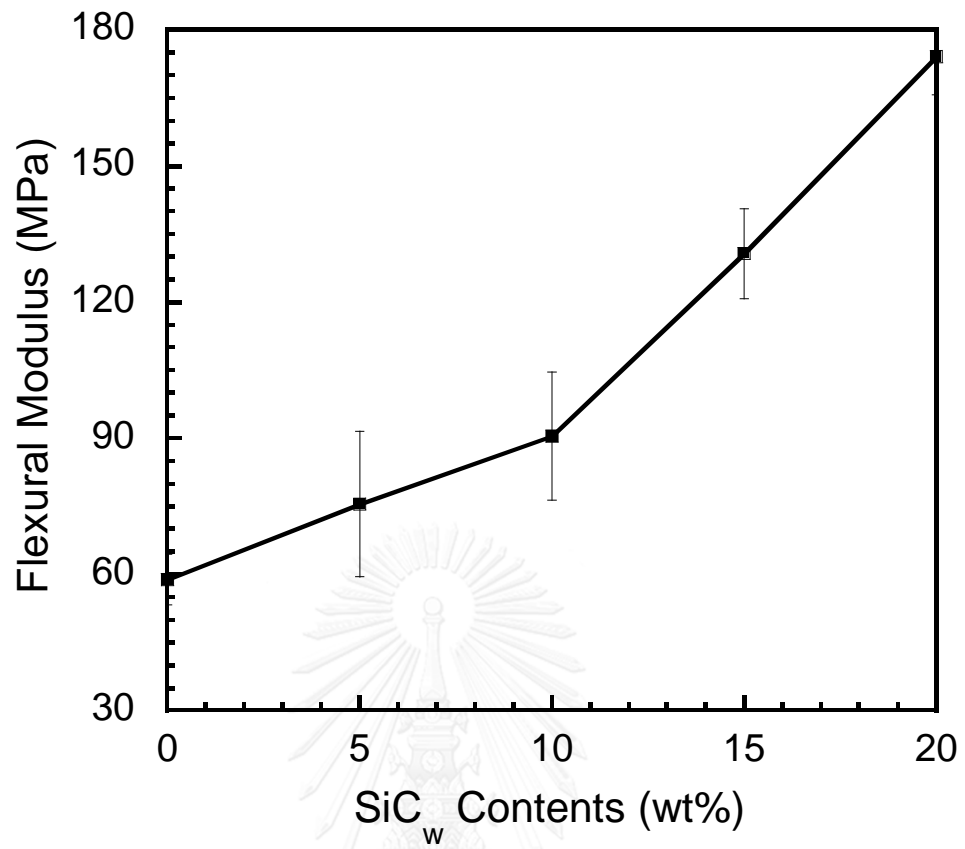


Figure 5.10 Relation between silicon carbide whisker content and the flexural modulus at $T_g + 20$ of silicon carbide whisker-filled benzoxazine-epoxy SMPs.

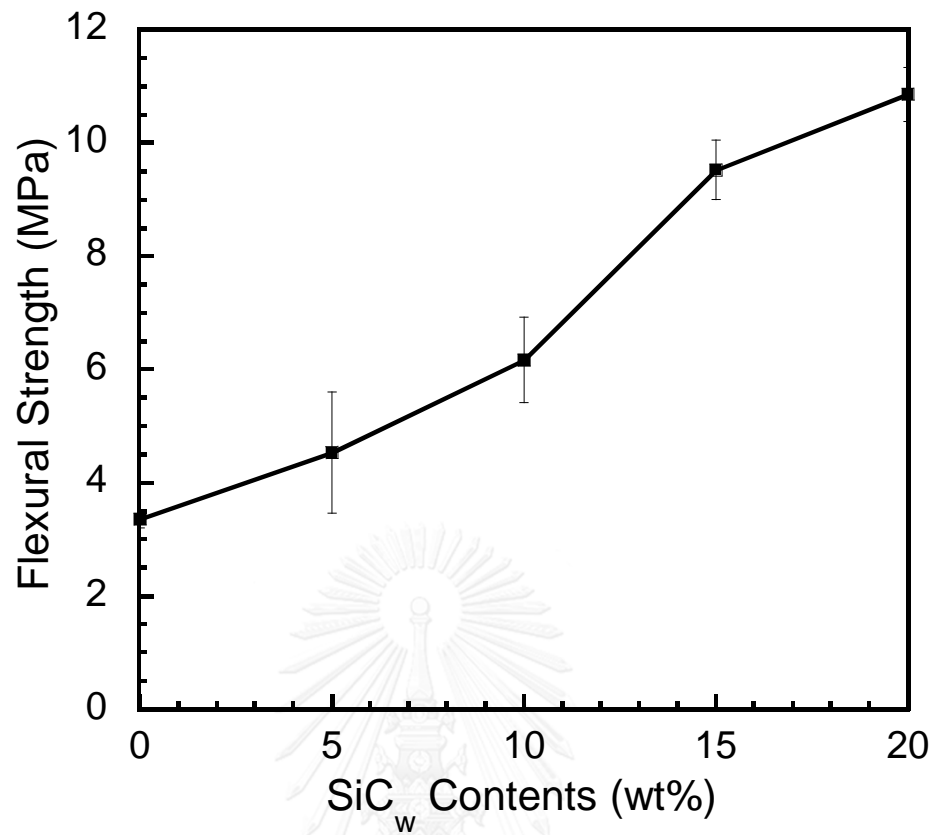


Figure 5.11 Relation between silicon carbide whisker content and the flexural strength at $T_g + 20$ of silicon carbide whisker-filled benzoxazine-epoxy SMPs.

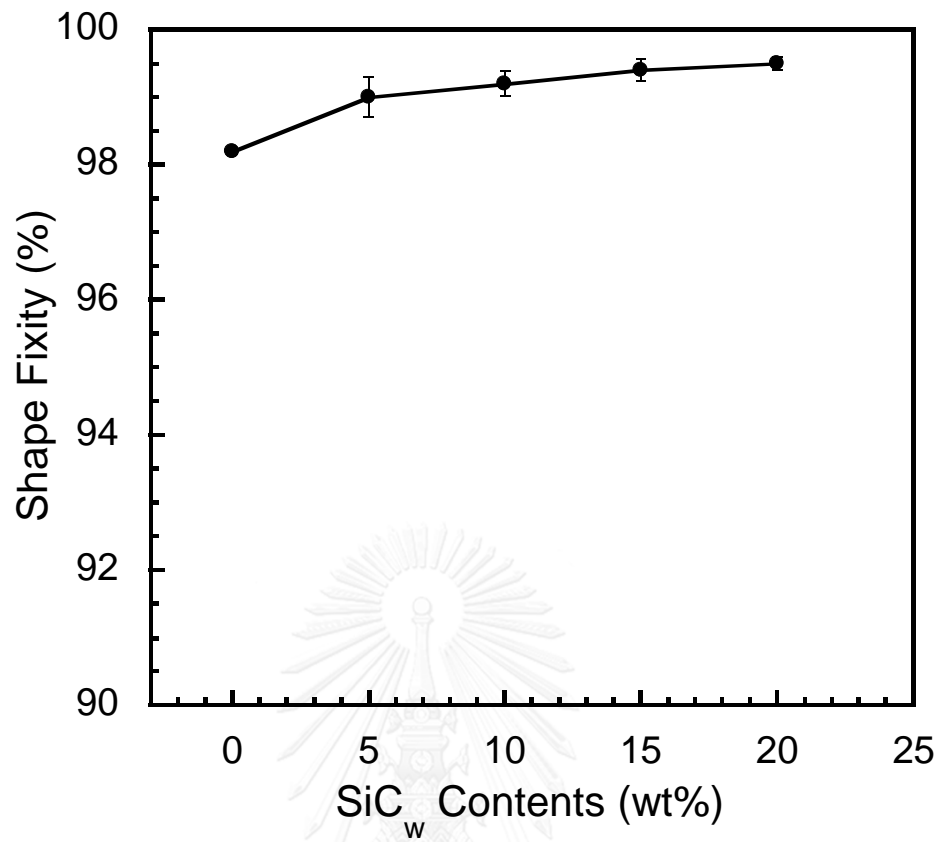


Figure 5.12 Effect of silicon carbide whisker contents on shape fixity of silicon carbide whisker-filled benzoxazine-epoxy SMPs.

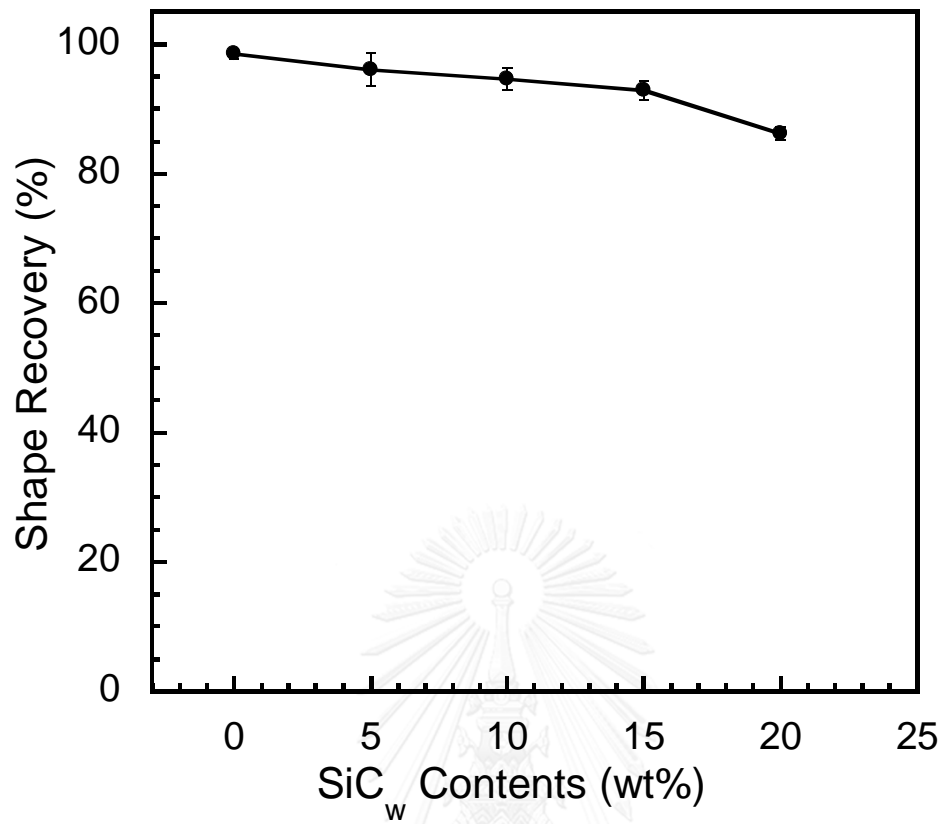


Figure 5.13 Effect of silicon carbide whisker contents on shape recovery of silicon carbide whisker-filled benzoxazine-epoxy SMPs.

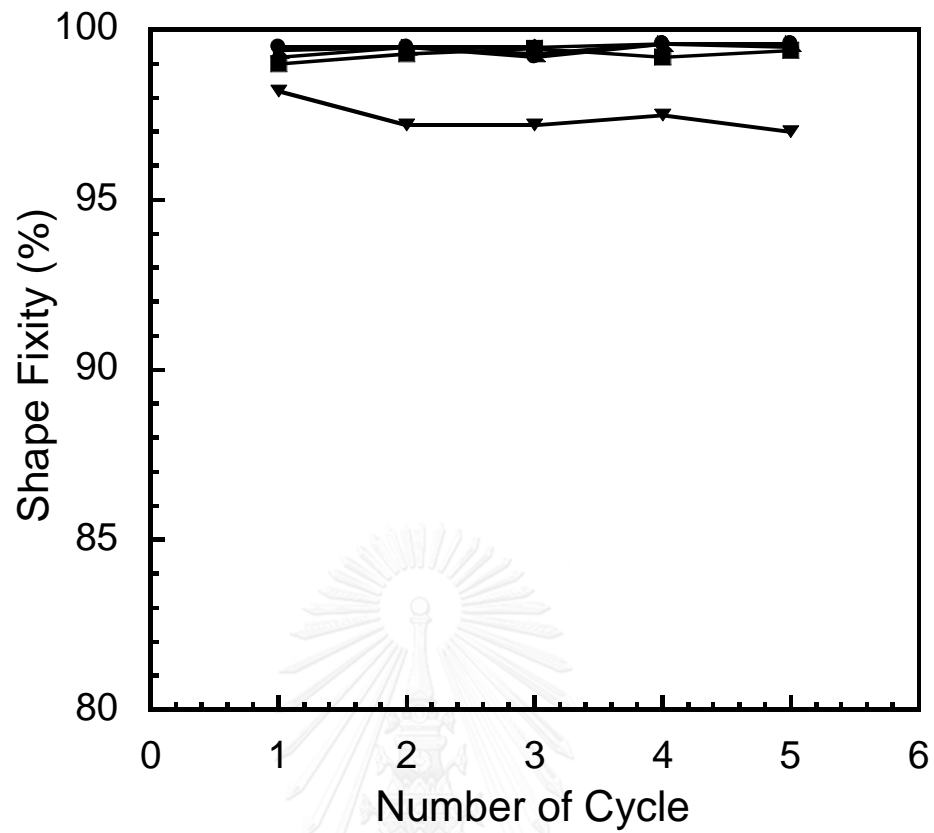


Figure 5.14 Shape fixity versus number of cycle of silicon carbide whisker-filled benzoxazine-epoxy SMPs at various silicon carbide whisker contents: (\blacktriangledown) 0wt%, (\blacksquare) 5wt%, (\blacklozenge) 10wt%, (\blacktriangle) 15wt%, (\bullet) 20wt%.

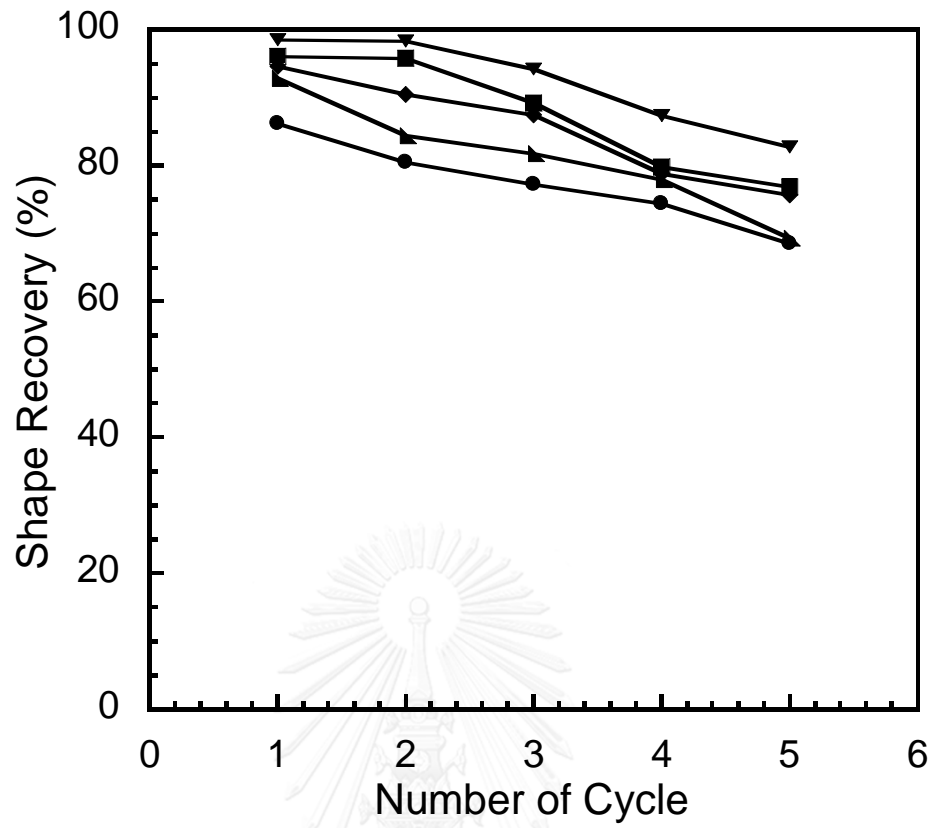


Figure 5.15 Shape recovery versus number of cycle of silicon carbide whisker-filled benzoxazine-epoxy SMPs at various silicon carbide whisker contents: (▼) 0wt%, (■) 5wt%, (◆) 10wt%, (▲) 15wt%, (●) 20wt%.

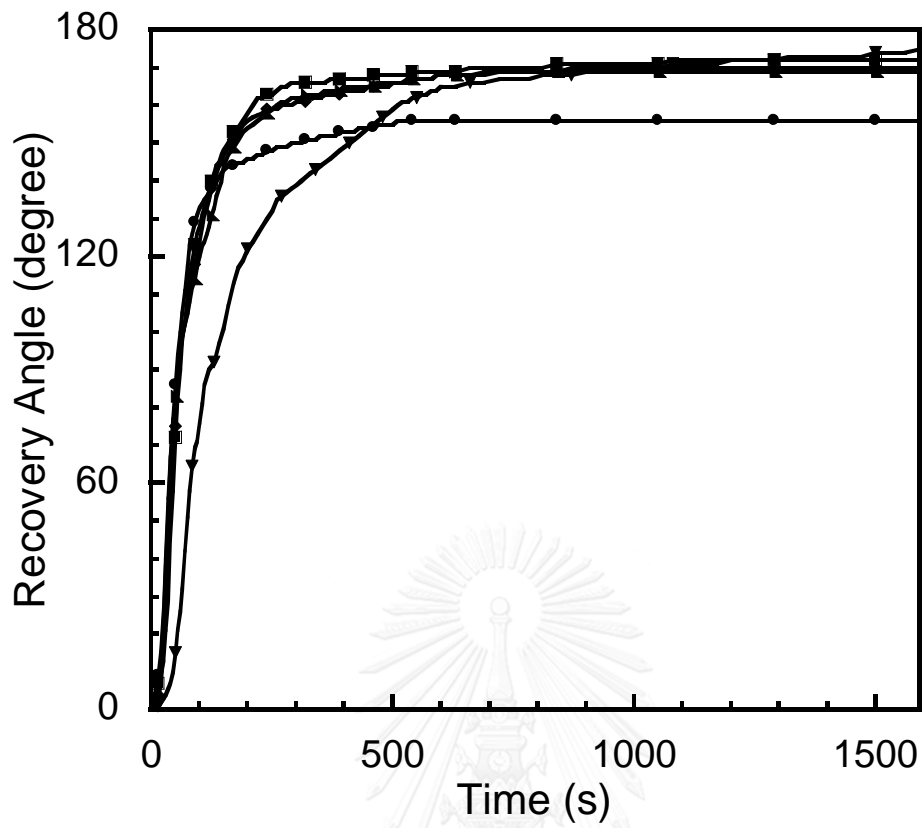


Figure 5.16 Recovery angle as a function of recovery time during the shape recovery process of silicon carbide whisker-filled benzoxazine-epoxy SMPs at various silicon carbide whisker contents: (▼) 0wt%, (■) 5wt%, (◆) 10wt%, (▲) 15wt%, (●) 20wt%.

Table 5.1 Reported recovery angle and recovery time in fold-deploy test as various silicon carbide contents.

SiC _w Contents (wt %)	Recovery Angle (degree)	Recovery Time (min:sec)
Matrix	175	26:30
5	172	18:00
10	170	14:30
15	169	11:30
20	156	8:30

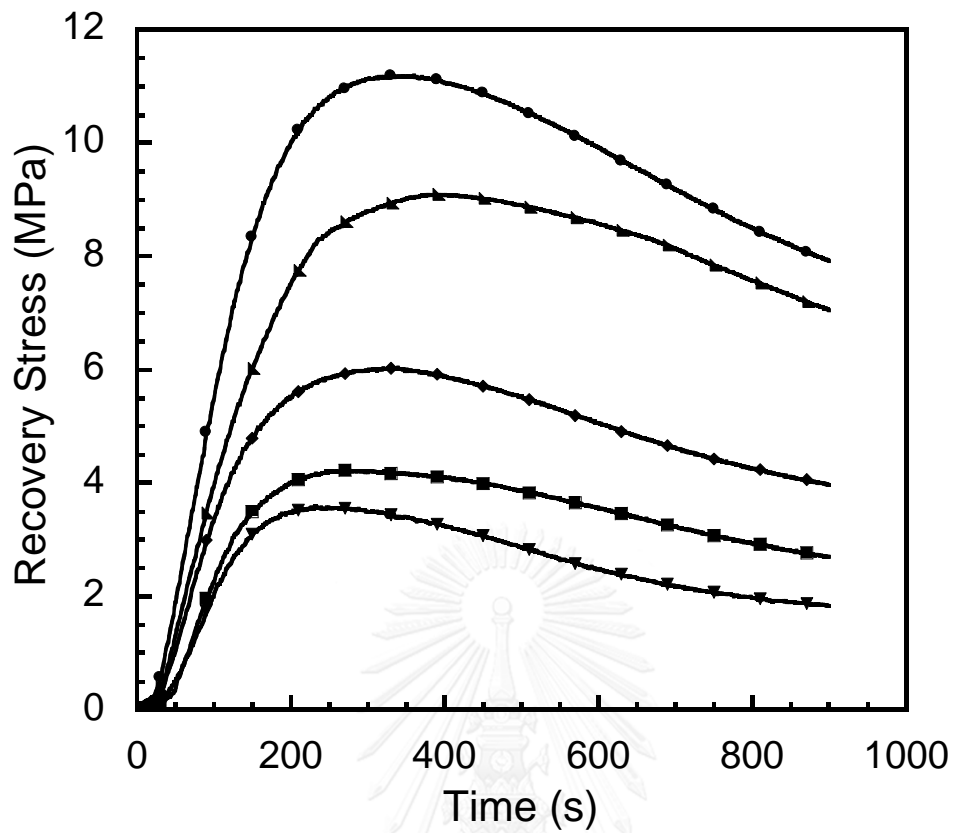


Figure 5.17 Recovery stress versus time of silicon carbide whisker-filled benzoxazine-epoxy SMPs at various silicon carbide whisker contents: (▼) 0wt%, (■) 5wt%, (◆) 10wt%, (▲) 15wt%, (●) 20wt%.

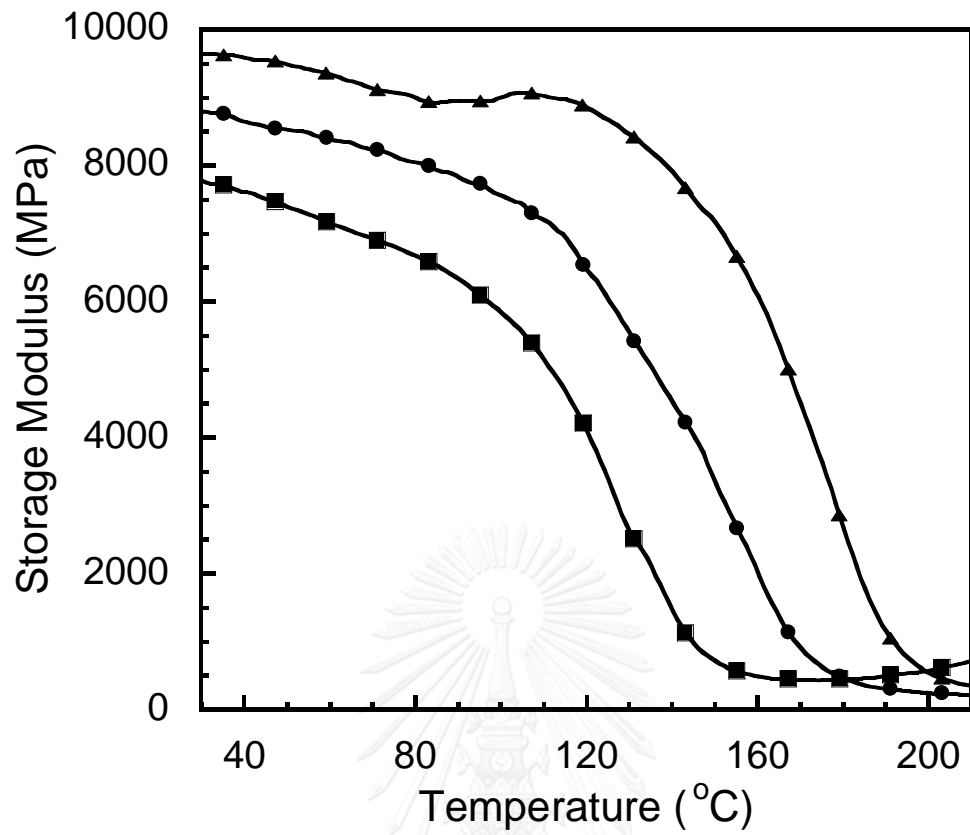


Figure 5.18 Storage modulus of silicon carbide whisker-filled benzoxazine-epoxy SMPs at various mole percent of the benzoxazine: (■) 40mol%, (●) 50mol%, (▲) 60mol%.

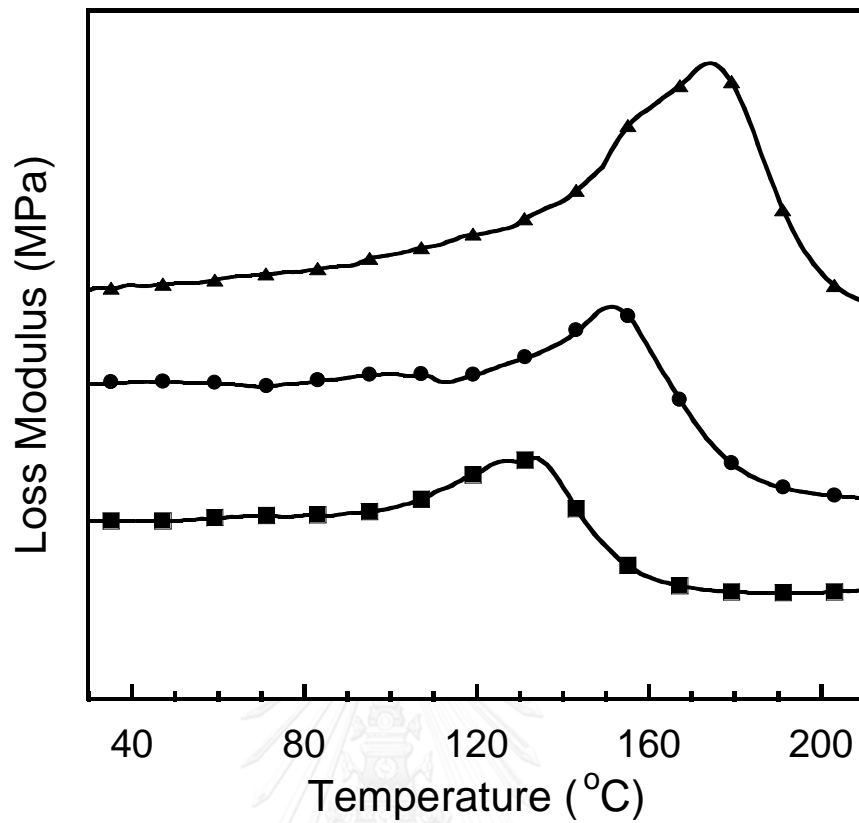


Figure 5.19 Loss modulus of silicon carbide whisker-filled benzoxazine-epoxy SMPs at various mole percent of the benzoxazine: (■) 40mol%, (●) 50mol%, (▲) 60mol%.

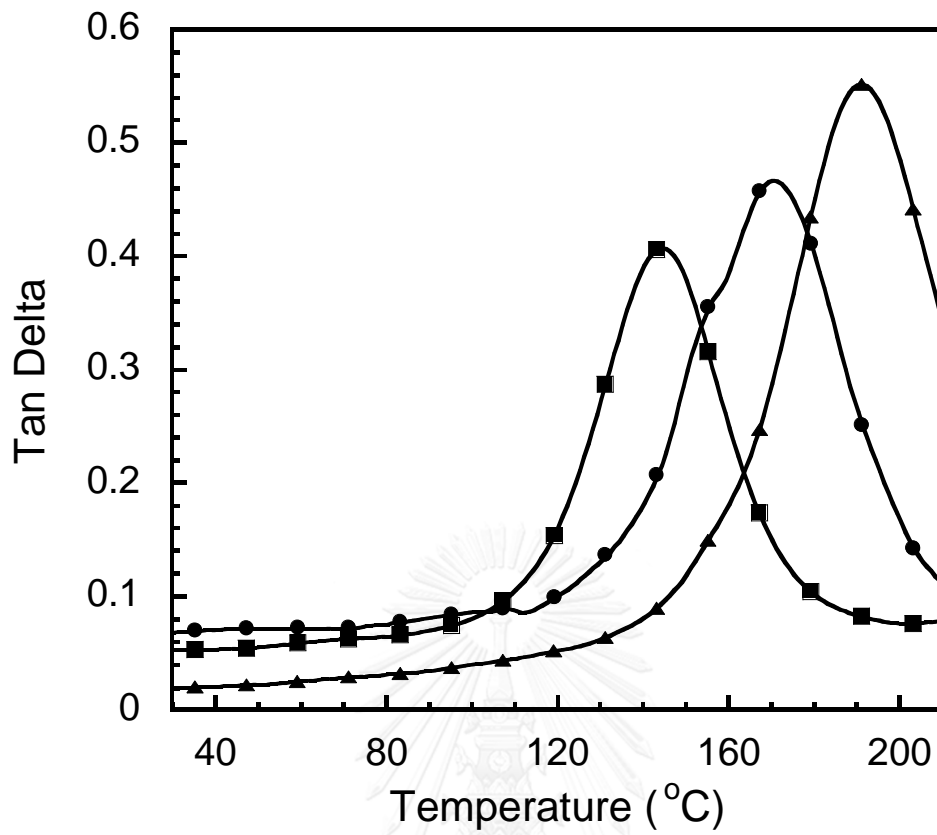


Figure 5.20 Loss tangent of silicon carbide whisker-filled benzoxazine-epoxy SMPs at various mole percent of the benzoxazine: (■) 40mol%, (●) 50mol%, (▲) 60mol%.

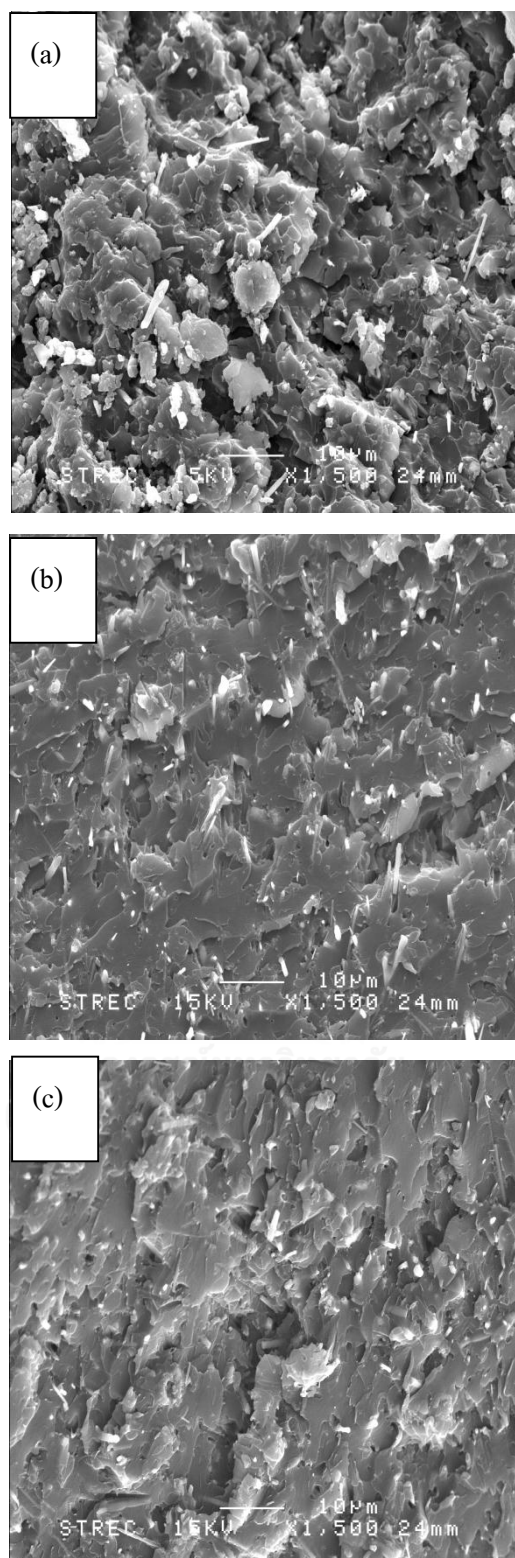


Figure 5.21 SEM micrographs of fracture surface of silicon carbide whisker-filled benzoxazine-epoxy SMPs: (a) BA-a 40 mole% (PBZ), (b) BA-a 50 mole%, (c) BA-a 60 mole%.

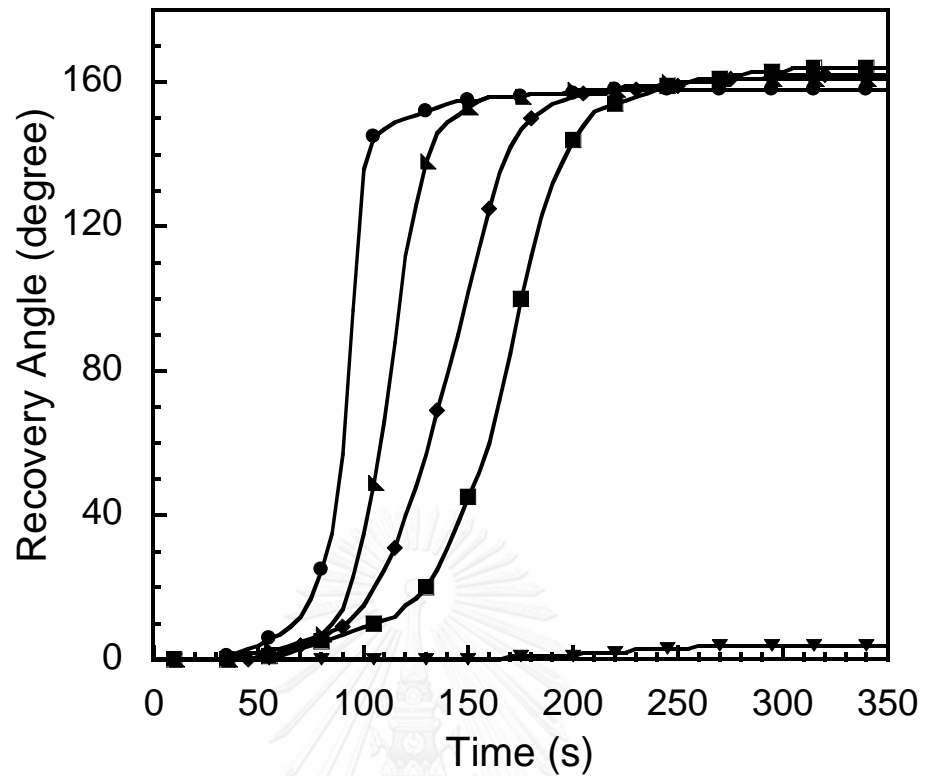


Figure 5.22 Recovery angle as a function of recovery time during microwave-induced shape recovery test of silicon carbide whisker-filled benzoxazine-epoxy SMPs at various silicon carbide whisker contents: (▼) 0wt%, (■) 5wt%, (◆) 10wt%, (▲) 15wt%, (●) 20wt%.

Table 5.2 Reported recovery angle and recovery time in microwave-induced shape recovery test as various silicon carbide contents.

SiC _w Contents (wt %)	Recovery Angle (degree)	Recovery Time (min:sec)
Matrix	4	-
5	164	5:05
10	162	4:55
15	161	4:20
20	158	3:25

CHAPTER VI

CONCLUSIONS

Benzoxazine-epoxy shape memory polymer (SMP) was developed by adding silicon carbide whisker. The silicon carbide whisker-filled benzoxazine-epoxy SMP exhibits development in thermal and mechanical properties.

An addition of silicon carbide whisker in benzoxazine-epoxy SMP resulted in an increase of storage modulus with increasing silicon carbide whisker contents. Additionally, glass transition temperature and thermal stabilities of silicon carbide whisker-filled benzoxazine-epoxy SMP were found to increase with the increasing amount of silicon carbide whisker in the SMPs. The same trend was also observed in their flexural strength and flexural modulus

In shape memory properties, the obtained SMPs provided an outstanding shape fixity value up to 99%. The recovery time are various in range 8 to 27 minutes in conventional heat. Then, the silicon carbide whisker-filled benzoxazine-epoxy SMP can recover their shape in microwave induced with more speed recovery compare to heat. Furthermore, the incorporation of silicon carbide whisker in benzoxazine-epoxy SMPs provided a further recovery stress 3.5 of the matrix to 11.2MPa of benzoxazine-epoxy composites. The obtained SMPs are interested as a good candidate for shape memory materials to be used in high recovery stress and modulus such as hinge or deployable structure.

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APPENDIX

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APPENDIX A

Characterization of SiC_w-Filled Benzoxazine-epoxy SMP Composites.

Table A. 1 Glass transition temperature of benzoxazine-epoxy SMP and SiC_w-filled benzoxazine-epoxy SMP at various compositions from DMA analysis.

SiC _w contents (wt%)	Storage Modulus (GPa)	T _g from Loss Modulus (°C)	T _g from Loss Tangent (°C)
0	5.1	136	154
5	5.9	142	165
10	6.8	143	165
15	7.2	146	168
20	8.8	151	170

Table A. 2 Density of benzoxazine-epoxy SMP and SiC_w-filled benzoxazine-epoxy SMP.

SiC _w contents (wt%)	Density (g/cm ³)
0	1.1821±0.0001
5	1.2254±0.0050
10	1.2576±0.0070
15	1.3025±0.0067
20	1.3522±0.0056

Table A. 3 Thermal stability of benzoxazine-epoxy SMP and SiC_w-filled benzoxazine-epoxy SMP.

SiC _w contents (wt%)	T _{d5} (°C)	T _{d10} (°C)	Solid residue (%)
0	293	313	28.1
5	295	315	31.6
10	297	316	34.8
15	300	320	38.5
20	303	324	43.0

Table A. 4 Flexural strength and flexural modulus of benzoxazine-epoxy SMP and SiC_w-filled benzoxazine-epoxy SMP at various SiC_w compositions at room temperature and T_g+20°C.

SiC _w contents (wt%)	At glassy state (room temperature)		At rubbery state (T _g +20°C)	
	Flexural strength (MPa)	Flexural modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)
0	134.8±7.0	4768.0±113.0	3.4±0.1	58.8±5.6
5	141.5±11.1	5902.4±205.7	4.5±1.1	75.5±16.0
10	155.4±9.0	6603.5±140.5	6.2±0.8	90.5±14.1
15	172.4±4.8	7255.4±143.5	9.5±0.5	130.7±9.9
20	178.0±4.3	8088.7±119.9	10.9±0.5	174.1±8.4

Table A. 5 Recovery time of SiC_w-filled benzoxazine-epoxy SMP samples at various compositions.

SiC _w contents (wt%)	Recovery time (min:sec)	
	Conventional heat	Microwave induce
0	26:30	-
5	18:00	5:05
10	14:30	4:55
15	11:30	4:20
20	8:30	3:25

APPENDIX B

Comparison of Shape memory Properties of Shape Memory Polymer.

Table B. 1 Overview on selected examples of SMP.

Matrix	Filler	R_s	R_r (%)	R_f (%)	Modulus at room temp.	Test method	Ref.
BA-a, NGDE	SiC _w	11.2 MPa	87	99.0	8.8 GPa	Flexural	-
BA-a, Aromatic epoxy, NGDE	-	38.2 kPa	~100	98.9	4.7 GPa	Flexural	[9]
BA-a, NGDE	-	1.59 MPa	~100	98.1	4.5 GPa	Flexural	[20]
PLLCA	CaCO ₃ (w)	-	87	99.5	28 MPa	Tensile	[47]
Epoxy SMP	SiC	500 mN	-	-	~2 GPa	Bending(micro beam)	[46]
Epoxy SMP	SiC	1.5 MPa	-	-	2.2 GPa	Flexural	[15]
PU SMP	CNT	4.5 MPa	90	95.0	600MPa	Tensile	[32]
PS SMP	CB, Short CF	-	72-94	-	1.5GPa	Flexural	[33]
SMP	Chop stand GF	9 MPa	40-60	-	2.5GPa	Tensile	[34]

VITA

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