จุฬาลงกรณ์มหาวิทยาลัย

รายงานผลการวิจัย

การเปรียบเทียบพฤติกรรมทางกลของพอลิเบนซอกซาซีนที่เติมด้วยซิลิกอนคาร์ไบด์วิสเกอร์จากการบ่มด้วยไมโครเวฟและความร้อน

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ซิลิกอนคาร์ไบด์วิสเกอร์จากการบ่มด้วยไมโครเวฟและด้วยความร้อน
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บทคัดย่อ

งานวิจัยนี้มีจุดมุ่งหมายศึกษาผลของการบ่มด้วยคลื่นไมโครเวฟและการบ่มด้วยความร้อนของซิลิกอนคาร์ไบด์วิสเกอร์ (SiC$_w$) ที่ถูกเติมลงในพอลิเบนซอกซาซีน (PBZ) คอมพอสิทที่มีต่อคุณสมบัติทางความร้อนและทางกล ซิลิกอนคาร์ไบด์วิสเกอร์ถูกใช้เป็นสารเติมสำหรับเบนซอกซาซีนเรซินเพื่อเพิ่มความสามารถในการดูดซับคลื่นไมโครเวฟของสารผสมและเพื่อทำให้คอมพอสิทแข็งแรงขึ้นด้วย จากผลการทดลองพบว่าเบนซอกซาซีนเรซินถูกบ่มได้ยากแม้ที่กำลังไฟสูง 1 กิโลวัตต์เป็นเวลา 15 นาที อย่างไรก็ตาม ที่ปริมาณของสารเติมน้อยๆที่ 4 เปอร์เซ็นต์โดยน้ำหนักของซิลิกอนคาร์ไบด์วิสเกอร์ เบนซอกซาซีนเรซินจะถูกบ่มได้ง่ายขึ้นมา ดังนั้น การเกิดปฏิกิริยาที่โดดเด่นของคลื่นไมโครเวฟกับสารผสมระหว่างเบนซอกซาซีนเรซินกับซิลิกอนคาร์ไบด์วิสเกอร์จึงสามารถลดเวลาในการบ่มได้อย่างมากจาก 2 ชั่วโมงที่อุณหภูมิ 200 องศาเซลเซียสเป็นเวลาน้อยกว่า 30 นาทีที่อัตราส่วน 4 เปอร์เซ็นต์โดยน้ำหนักของซิลิกอนคาร์ไบด์วิสเกอร์โดยใช้กำลังของคลื่นไมโครเวฟเพียงประมาณ 300 วัตต์ ที่ภาวะการบ่มอย่างสมบูรณ์สำหรับระบบพอลิเบนซอกซาซีนกับซิลิกอนคาร์ไบด์วิสเกอร์คอมพอสิทพบว่าการบ่มด้วยเตาไมโครเวฟจะประหยัดพลังงานกว่าระบบการบ่มด้วยความร้อนประมาณ 20-30 เท่า นอกจากนี้ที่อัตราส่วน 4 เปอร์เซ็นต์โดยน้ำหนักของซิลิกอนคาร์ไบด์วิสเกอร์ในพอลิเบนซอกซาซีนคอมพอสิทจะให้ค่าคุณสมบัติทางกลและทางความร้อนที่ไม่แตกต่างกันมากนัก ค่ามอดูลัสของการดัดโค้งและค่าความแข็งแรงของการดัดโค้งของคอมพอสิทที่อัตราส่วน 4 เปอร์เซ็นต์โดยน้ำหนักของซิลิกอนคาร์ไบด์วิสเกอร์ของคอมพอสิทที่บ่มด้วยความร้อนจะค่าอยู่ในช่วง 5.3 ± 0.48 จิกะปาสคาลและ 119 ± 28 เมกะปาสคาล ในขณะที่ชิ้นงานที่บ่มด้วยคลื่นไมโครเวฟมีค่าอยู่ในช่วง 5.7 ± 0.2 จิกะปาสคาลและ 118 ± 7 เมกะปาสคาลตามลำดับที่อัตราส่วนสารเติมเดียวกัน พอลิเบนซอกซาซีนและพอลิเบนซอกซาซีนที่ถูกเติมด้วยซิลิกอนคาร์ไบด์วิสเกอร์มีอุณหภูมิเปลี่ยนสถานะคล้ายแก้วที่ทดสอบด้วยเครื่อง DSC อยู่ในช่วงอุณหภูมิ 155 ถึง 160 องศาเซลเซียสทั้งจากการบ่มด้วยความร้อนและการบ่มด้วยคลื่นไมโครเวฟ นอกจากนี้ คุณสมบัติทางความร้อนและทางกลยังเพิ่มขึ้นตามอัตราส่วนของซิลิกอนคาร์ไบด์วิสเกอร์ที่เพิ่มขึ้นอีกด้วย ผลจากพื้นผิวการแตกหักที่พิจารณาด้วยวิธี SEM แสดงให้เห็นการยึดเกาะที่ดีระหว่างเฟสทั้งสอง พื้นผิวการแตกหักของคอมพอสิทจะหยาบกว่าของเมทริกซ์อย่างเดียว การใช้คลื่นไมโครเวฟในการบ่มพอลิเบนซอกซาซีนที่ถูกเติมด้วยซิลิกอนคาร์ไบด์วิสเกอร์สามารถลดเวลาในการบ่มและลดการใช้พลังงาน ในขณะที่คุณสมบัติทั้งทางกลและทางความร้อนของคอมพอสิทที่บ่มด้วยคลื่นไมโครเวฟมีค่าใกล้เคียงเดิม

Project Title   Comparison of mechanical behaviors of microwave and thermal cured on SiC whisker-filled polybenzoxazine

Name of the Investigator Dr. Sirijutaratana Cavavisaruch

Year   2004

Abstract

This research aims to investigate the effect of microwave cure and thermal cure in silicon carbide whisker (SiC_w) filled in polybenzoxazine (PBZ) composite on its corresponding thermal and mechanical behaviors. SiC whisker is thus, used as a filler of the polybenzoxazine to enhance the microwave absorption capability of the molding compound and to reinforce the material. The experimental results reveal that the benzoxazine resin (BA-a) was hardly cured at a high power of 1 kW for 15 min. However, with a relatively low content at 4% by weight SiC_w, the benzoxazine resin was found to be cured relatively well. Therefore, the strong microwave interaction of the benzoxazine molding compound, due to the presence of SiC_w, significantly helps reduce the processing time of the molding compound from few hours at 200°C to be less than thirty minutes at 4% by weight of SiC_w using the irradiation power of merely around 300 Watts. To achieve the maximum cure, polybenzoxazine/SiC_w composite cured by microwave oven consumed less energy than that required by the traditional thermal cure by approximately 20 to 30 times. At 4 wt% of SiC_w content, the mechanical and thermal properties of the polybenzoxazine composites cured by thermal and microwave heating showed no significant change. The flexural modulus and strength of the thermal cured composites at 4 wt% SiC_w were determined to be 5.3 ± 0.48 GPa and 119 ± 28 MPa while those of the microwave cured specimens were about 5.7 ± 0.2 GPa and 118 ± 7 MPa respectively at the same filler content. The neat polybenzoxazine and the SiC_w-filled polybenzoxazine composites possess a glass transition temperature, determined by DSC, ranging from 155 to 160°C for both thermal and microwave cured. Moreover, the thermal and mechanical properties were increased with increasing the SiC_w content. Their fracture surface morphology could be observed by SEM studies, which revealed substantial bonding between the two phases. The fracture surface of the composites was significantly rougher than that of the pure matrix. The microwave cure for SiC_w-filled polybenzoxazine composite could drastically reduce the curing time and energy-consumption while the microwave-cured specimens still maintained the good thermal and mechanical properties.

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CHAPTER I

INTRODUCTION

1.1 General Introduction

Conventional thermal cure of thermosets is widely practiced. The technique has also been applied in the processing of thermosetting composites with various shapes without the need of large-scale devices. However, the technology cannot meet the increasing requirements of economic development due to its disadvantages of high energy-consumption and long production period (Thostenson and Chou, 1999; Zhou et al., 2003). Moreover, the processing of very thick cross-section parts requires complex cure schedules with very slow thermal ramp rates and isothermal holds to control overheating which arise from cure reaction exotherms and poor thermal conductivity. Consequently, an efficient and energy-saving cure technology is urgently required. The curing of thermoset systems is known to be the bottleneck of the whole production process. Alternative accelerated curing, such as Ultra Violet light, Gamma rays or electron beams is possible but each still has many disadvantages. UV light offers limited applications due to its poor penetration ability and limited dose rate (Li et al., 2003). Gamma rays, from naturally radiating sources such as Cobolt-60, generate enormous radiation hazards and environmental problems (Nho, Kang and Park, 2004). Although, electron beam curing has proven to be an accelerated and efficient curing method, it often requires unacceptably high capital outlay (Zhang et al., 2002).

1.2 Microwave Processing

The application of microwave was found to be an alternative method for curing thermosets with a significant increase in the rate of reaction (Boey, Yap and Chia, 1999). In addition, the microwave heated thermosetting composite was also shown to

possess slightly higher mechanical properties than those cured by conventional thermal process. This was believed to be due to the homogeneity heating that can reduce the thermal stress in the composites (Bai et al. 1995). Microwave-cured composites were also found to exhibit stronger interfacial bonding than the thermal-cured epoxy composites (Bai and Djafari, 1995). However, the microwave heating ability of any materials depends on their dielectric constant and dielectric loss factor (Thostenson and Chou, 1999). Since most polymers are materials with low dielectric constant (Wypych, 2000); therefore, microwave heating of neat polymer is not favorable. Epoxy resin can be used in microwave heating due to the presence of the polar group in its molecular structure. A significant increase in the rate of reaction was reported and an improvement in some mechanical properties was observed in earlier study (Zhou et al., 2003). However, microwave curing of epoxy composites sometimes led to more void content within the composite than those from conventional thermal curing. This is owing to the volatile by-produce released during curing reaction and lower external applied pressure. Therefore epoxy is hardly used for microwave curing of thick composites (Bai and Djafari, 1995).

1.3 Polybenzoxazine

Polybenzoxazine is a novel class of phenolic resins that has been developed and studied to overcome the shortcomings of traditional phenolic resins (Ishida, 1996). Polybenzoxazine has the advantages of neither using any strong acids as catalysis nor producing any volatile by-product during polymerization. Its crosslinking reaction is achieved by a thermally activated ring-opening reaction (Takeichi, 2002). Therefore, polybenzoxazine is highly attractive for microwave-processed composites or even conventional heat-treated composite products.

Polybenzoxazine can be synthesized using the patented solventless technology to yield a relatively clean precursor without the need of solvent elimination or monomer purification (Ishida, 1996). The polymerization reaction of benzoxazine monomers is initiated by heat, without using a curing agent, through the ring-opening reaction to yield polybenzoxazine. Benzoxazine resin based on bisphenol-A and aniline can be

synthesized according to the reaction shown in Figure 1.1 (Ning and Ishida, 1994). As a consequence, there are no volatile by-products in the curing process. The fact that polybenzoxazine has low viscosity enables the manufacture of complicated products. It possesses good dimensional stability owing to the ring-opening curing process (Jang and Shin, 1995; Ishida and Allen, 1996).

Bisphenol-A   Formaldehyde   Aniline

Benzoxazine monomer
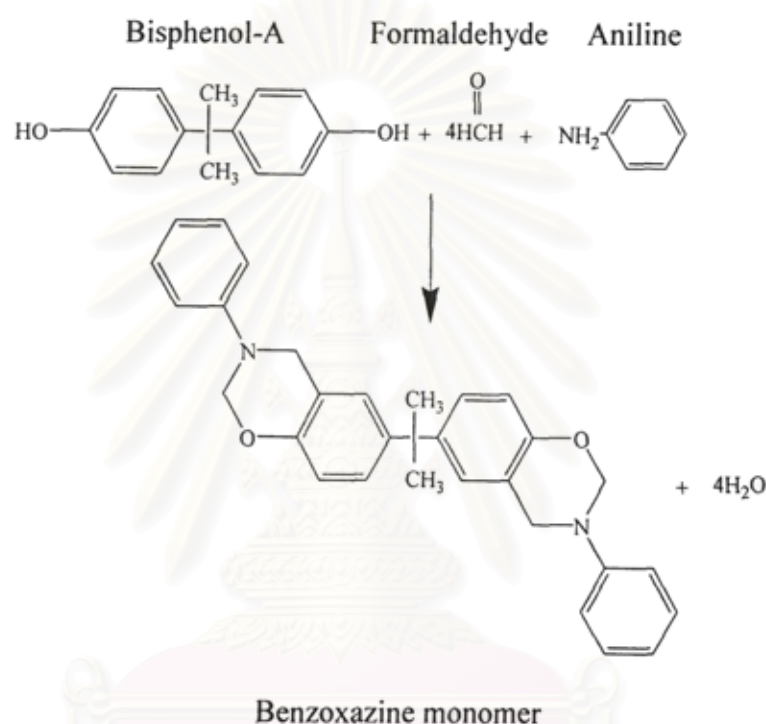
Figure 1.1: Synthesis of bifunctional benzoxazine monomer.

Polybenzoxazine has a wide range of mechanical and physical properties that can be tailored to various needs. Many attractive properties such as excellent mechanical properties, high char yield, near zero shrinkage, highly tailor-made molecular structure, low water absorption, excellent electrical properties, high mechanical integrity, low melt viscosity and self-polymerized upon heating have been reported on polybenzoxazine (Nair, 2004). Like most polymeric materials, the low dielectric constant of polybenzoxazine means that it can not be cured conveniently by microwave radiation. Fortunately, the problem of low dielectric constant of polymers can be improved by adding therein a high dielectric constant filler (Xu, Chung and Mroz, 2001).

1.4 Silicon Carbide Whisker (SiC_w)

SiC_w is one kind of reinforcing material that is widely used in ceramic, metal, and polymer matrix composites in an effort to achieve increased toughness of brittle matrix composites (Deng and Ai, 1998; Bengisu and Inal, 1994). Physically, SiC_w is discontinuous, monocrystalline hair or ribbon-shaped fibers in the size range of 0.3-2 μm in diameter and 5-50 μm in length. Their aspect ratio (length/diameter) ranges from 20 to several hundreds. SiC_w is all grown from gas phase on solid or liquid substrates under conditions that lead to very small defects of about 0.1-0.4 μm in the whisker, leaving the SiC_w strength still very high around 9-17 GPa. Whiskers grown at temperature below 1800 °C are composed mostly of β-SiC, whereas those grown above 2000°C are of α-SiC (Harries, 1995). In this research, β-SiC was used throughout the study.

Silicon carbide whisker (SiC_w) is used in the present study for its high dielectric constant as well as high strength-to-density ratio. It is anticipated that the incorporation of SiC_w into the polybenzoxazine matrix should render at least twofold benefits to the benzoxzine resin, i.e. the inherent rigidity of polybenzoxazine may be reduced by the toughening mechanisms occurred in the filled systems while the high electric constant of the SiC_w should help improve the microwave cure of the filled polybenzoxazine. The curing process of the SiC_w-filled polybenzoxazine is, thus, expected to be accomplishable by using microwave irradiation. Mechanical properties of the SiC_w-filled polybenzoxazine cured thermally by conventional method and those cured with microwave will be compared in this study.

1.5 Toughening Brittle Matrix

In general, brittle matrix can be toughened by several means including copolymerization, alloying, blending and compositing. Previous investigations include the utilizations of a) fiber-reinforced materials (e.g. SiC_w and carbon fiber) (Xu et al., 2002; Deng and Ai, 1998), b) tough matrix materials (e.g. rubber-modified

thermosets and thermoplastics) (Jang and Yang, 2000), c) fiber hybridization (e.g. mixtures of E-glass, and graphite fibers) (Khatri and Koczakb, 1996), d) fiber coatings with appropriate polymers either fully or intermittently distributed along the fiber length, and e) duplex-structure fibers consisting of a sheath and core fiber, etc. (Kim, Baillie and Mai, 1992; Kim and Mai, 1991). Fiber-reinforced polymer composites have found widespread applications. Given the critical and demanding applications in which they are employed, an understanding of the fracture behaviors of composites is essential and can lead to a better insight on the toughening characteristics. Much effort have been emphasized through earlier studies on fracture behavior of polymer composites because they have been used in a variety of applications in which catastrophic fracture can lead to disastrously loss of life, for example in the construction and repair applications such as bridges, pipelines, helicopter blades, yacht hulls, aircraft fuselages, aerospace applications and other types of constructions (Avci, Arikan and Akdemir, 2004).

1.6 Objectives

The primary objectives of the present study are the followings:

(i)   To study the effect of SiCw on benzoxazine resin cured by microwave radiation and by conventional thermal cure.

(ii)   To compare the mechanical properties of composites cured by microwave radiation and conventional thermal cure.

1.7 Scope of Research

(i)   Search information and literature reviews.

(ii)   Prepare chemicals and equipments to be used in this research.

(iii)   Synthesize benzoxazine monomer (BA-a type).

(iv)   Prepare benzoxazine/SiCw molding compounds at 100/0, 98/2, 96/4, 94/6 by weight.

(v)   Study the effect of microwave power ranging from 150 to 600 W and cure duration of microwave radiation on benzoxazine resin molding compounds.

(vi)   Examine proper thermal curing conditions of the molding compounds using Differential Scanning Calorimeter (DSC).

(vii) Evaluate thermal properties of the composites from (v) and (vi) by comparing at identical SiCw content.

(viii) Study the crosslink density of composite using Dynamic Mechanical Analysis (DMA).

(ix)   Determine flexural properties and fracture toughness of the composites from (v) and (vi).

(x)   Investigate the fracture surface of the composites from (viii).

(xi)   Compare the energy cost of processing by microwave radiation and thermal curing.

(xii) Discuss and conclude the results.

CHAPTER II

THEORY

2.1 Microwave Processing

2.1.1 Microwave Fundamentals

Microwave is electromagnetic waves in frequency band from 300 MHz (3×10^8 cycles/second) to 300 GHz (3×10^{11} cycles/second). Microwave energy is produced by a microwave generator, propagated down the wave guide, and injected directly into the microwave cavity where the mode stirrer distributes the incoming energy in various directions. The percentage of the incoming energy that is absorbed depends upon a sample size and a material dissipation factor. Industrial microwave processing is usually accomplished at the frequencies set aside for industrial use namely, 915 MHz, 2.45 GHz, 5.8 GHz, and 24.124 GHz, as shown in Figure 2.1. It was first controlled and used during the Second World War in radar systems. The usefulness of microwaves in the heating of materials was first recognized in 1946. Up to present, the microwave oven has become a well-know technology. Despite its long history and widespread use, there still remains a great deal that is not fully understood about microwave and their use.

2.1.2 Microwave Applications in Polymer and Polymer Matrix Composites

Typical, thermoset curing process consists of three basic steps namely preheating of the component, reaction producing the corresponding exotherm and cooling of the cured materials (Van and Gourdene, 1987). Prior to curing, thermosetting resins are low-viscosity liquids that can flow into a mold or around fibers. During processing, polymerization took place, resulting in an increase of both the molecular weight and the viscosity. As the cure reaction progresses, it may be difficult to control the temperature due to the additional heat input caused by the exothermic polymerization

reaction. Eventually highly cross-linked, insoluble, infusible materials are obtained. Most polymers tend to be efficient absorbers of microwave radiation initially, with dielectric loss (ε'') increasing as the resin is heated.
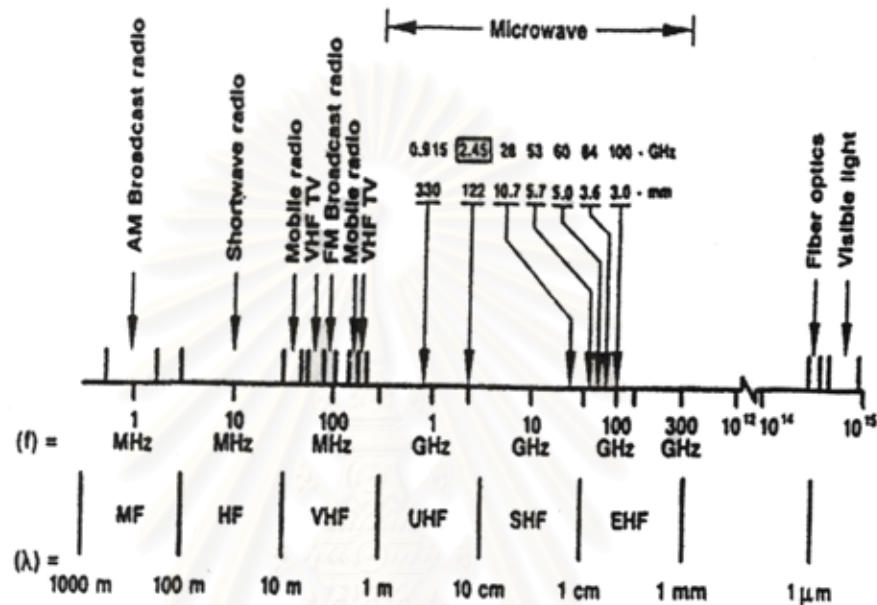
Figure 2.1: Electromagnetic spectrum and frequencies used in microwave processing (Sutton, 1993).

If the resins to be cured by microwave processing are typically not conductive, particles and fibers that are conductive, or have dielectric properties significantly different from the matrix resin, may be included to aid microwave processing. The presence of these inclusions can strongly influence the way in which the composite material interacts with the microwave radiation. Conductors also modify the electric-field pattern in and around the composite, potentially resulting in very different heating profiles than with the neat resin. Some examples of these conductive additives include carbon black, which is used extensively in rubber formulation; carbon or metal fibers; and metal flakes, spheres, or needles with sizes ranging from 0.1 to 100 μm. The surface of the conducting inclusion interacts strongly with the microwave radiation. The effect of conductive additives on microwave heating and skin depth of the composite depends on the size, shape, concentration and electrical

resistivity of the inclusions and their distribution within the matrix (Lagarkov et al., 1992). The dielectric properties determine energy that is transferred to materials by interaction with the applied electromagnetic field at the molecular level. The interaction of microwaves with molecular dipole results in rotation of dipoles, and energy is dissipated as heat from molecularly frictional resistance to the molecular rotation. Table 2.1 shows dielectric constant of some interesting materials.

Table 2.1 Dielectric constant of some interesting materials (Wypych, 2000).

Chemical name	Dielectric constant	Chemical name	Dielectric constant
Air (dry)	1.0	Bakelite	3.5-5.0
Water (stream)	1.0	Epoxy resin	3.6
Polypropylene	1.5	Glass (silica)	3.8
Carbon dioxide	1.6	Silicon dioxide	4.5
Alumina powder	1.6-1.8	Diamond	5.5-10.0
Teflon	2.0	Wood (wet)	10.0-30.0
Wood (dry)	2.0-6.0	Silicon	11.0-12.0
Polyimide	2.2-3.2	Aluminum oxide	30.0
Carbon black	2.5-3.0	Silicon carbide whisker	40
Rubber	3.0	Water ($20^{o}C$)	80.4
Polybenzoxazine	3.0-4.0	Titanium dioxide	90-110

Microwave processing provides material processors with a new, powerful, and significantly different tool to process materials that may not be amenable to conventional means of processing. The technique was found to improve the performance characteristics of epoxy (Zhou et al., 2003). However, due to the complexity of microwave interactions with materials, simply placing a sample in a microwave oven and expecting it to heat efficiently will seldom lead to success.

There are increasing demands across broad product line for new polymeric materials and process that are cost-effective and environmentally safe. Over the past

few decades, research in the area of microwave processing has shown some potential advantages in the ability not only to process polymers at lower cost but also to fabricate new materials and composites that may not be possible using conventional thermal treatments.

Microwave processing can be used for a broad range of polymers and products, including thermoplastic and thermosetting resins, and composites. Nevertheless, not all polymers are suitable for microwave processing. However, many polymers contain groups that form strong dipoles (e.g. epoxy, hydroxyl, amino, cyanate, etc.) which make it easy to be heated by microwave radiation. Permittivity and dielectric loss factor of thermosets generally increase with temperature and decrease with the extent of cure (Jow et al., 1988).

An example of microwave processing of polymeric materials was first found the vulcanization of rubber in the tire industry during the 1960s. Commercial application began later in that decade (Chabinsky, 1983, Schwartz et al., 1975). The principal of using the microwave radiation to the rubber occurred by filling carbon black in various types of rubber formulations. Since various grades of carbon black tend to have different coupling characteristics (Ippen, 1971), the rubber compound was controlled via the heating patterns throughout the layered product through variation of carbon black grade and concentration. Application of this processing technique was limited due to the non-uniformity of microwave curing induced by the thermal loss at the edge of specimen to its surrounding atmosphere (Ku et al., 2001).

2.2 Theoretical Density Determination

The theoretical density of composite is an important factor to check the amount of filler and the void content in polymer composites, especially when the significant density between filler and matrix are involved. The theoretical density by mass which compared to actual density can be calculated as follow (Piyawan, 1998):

$$\rho_c = \cfrac{1}{\cfrac{W_f}{\rho_f} + \cfrac{(1-W_f)}{\rho_m}} \qquad (2.1)$$

where
W_f = filler weight fraction

$(1-W_f)$ = matrix weight fraction

ρ_f = filler density, g/cm^3

ρ_c = matrix density, g/cm^3.

2.3 Mechanical Analysis

2.3.1 Dynamic Mechanical Properties

In studies of the response of a material to vibrational forces, stress, strain, and frequency are the key variables. The stress applied to a viscoelastic body results in a linear or nonlinear dynamic response. For example, if the stress varies sinusoidally with time at a given frequency, the strain varies cyclically at the same frequency. If the amplitude of the stress is small enough, the strain is also sinusoidal with time, and the amplitude of the strain is proportional to the amplitude of the stress at a given temperature and frequency, i.e. the behavior is linear. However, if the amplitude of the stress is large enough, the strain varies with the same frequency but is nonsinusoidal; it can have high harmonics, showing nonlinear viscoelastic behavior.

The crosslinking density can be estimated related to the glass transition temperature of the polymer network according to Fox and Loshaek Equation as shown in Equation (2.2).

$$T_g = T_g(\infty) \frac{-k}{M_n} + k_n\, \rho \qquad (2.2)$$

where
T_g = glass transition temperature, ^{o}C

$T_g(\infty)$ = T_g of infinite molecular weight linear polymer, ^{o}C

k, k_n = numerical constants

M_n = averaged molecular weight

ρ = crosslinking density.

2.4 Theories of Adhesion (Hull, 1990)

Adhesion can be attributed to five main mechanisms, which can occur at the interface either in isolation or in combination to produce the bond.

2.4.1 Adsorption and Wetting

When two electrically neutral surfaces are brought sufficiently close together there is a physical attraction which is best understood by considering the wetting of solid surfaces by liquids as illustrated in Fig. 2.2. The physical situation of a liquid drops on a solid surface are calculated by using the Young's Equation as showed in following equation.

$$W_{SL} = \gamma_{LV}(1+\cos\theta) = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \qquad (2.3)$$

Where W_{SL} = work of adhesion of solid-liquid phase

θ = contact angle

γ_{LV} = the surface tensions of liquid-vapor phase

γ_{SV} = the surface tensions of solid-vapor phase

γ_{SL} = the surface tension of solid-liquid phase.

Where θ is the contact angle and γ is the surface tensions of solid-vapor (SV), solid-liquid (SL), and liquid-vapor (LV) interfaces, respectively.

(a)   (b)
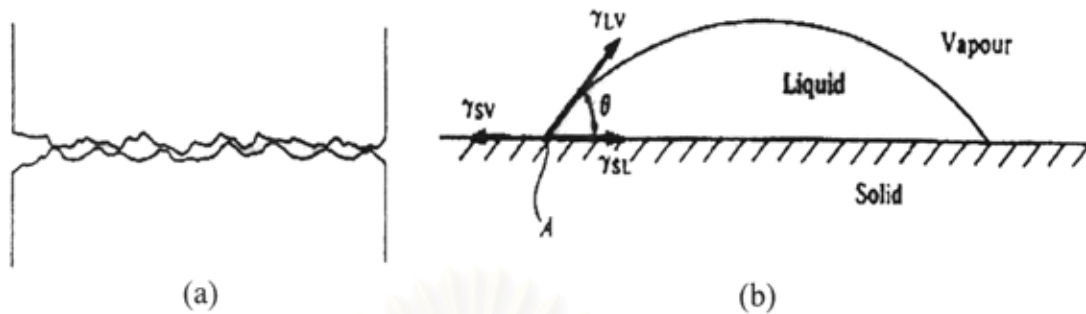
Figure 2.2: The wetting of solid surface by liquid: (a) isolated contact points leading to weak adhesion between two rigid rough surfaces, (b) surface tensions (γ) for a liquid drop on a solid surface.

2.4.2 Mechanical Adhesion

Some bonding may occur purely by the mechanical interlocking of two surfaces as illustrated in Figure 2.3(a). The strength in shear may be very significant and depends on the degree of roughness.

2.4.3 Electrostatic Attraction

Forces of attraction occur between two surfaces when one surface carries a net positive charge and the other surface a net negative charge as tin the case of acid-base interactions and ionic bonding and coupling agents laid down on the surface of the filler, as shown in Figure 2.3(b).

2.4.4 Chemical Bonding

A chemical bond is formed between a chemical grouping on the fiber surface and a compatible chemical group in the matrix as seen in Fig. 2.3(c) and (d) respectively. The strength of the bond depends on the number and type of bonds and interface failure must involve bond breakage.

2.4.5 Interdiffusion

It is possible to form a bond between two polymer surfaces by the diffusion of polymer molecules on one surface into the molecular network of the other surface, as shown in Fig. 2.3(e) and (f) respectively. The bond strength will depend on the amount of molecular entanglement and the number of molecules involved.
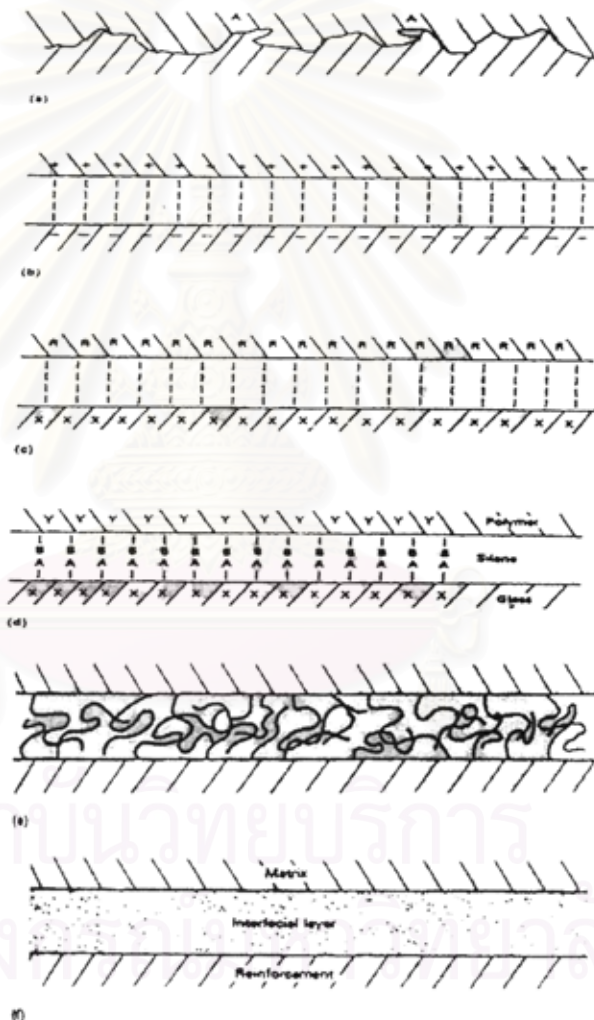
Figure 2.3: Mechanism of interfacial adhesion. Mechanical bond (a), Bond formed by electrostatic attraction (b), Chemical bond (c) and (d), Bond formed by molecular entanglement following interdiffusion (e) and Bond formed by interfacial layer by interdiffusion (f) (Matthew, 1994).

CHAPTER III

LITERATURE REVIEWS

3.1 Comparison of Microwave and Thermal Curing

Bai et al. (1995) studied the epoxy resin cured by microwave and conventional oven. They investigated the effects of the two cure techniques via the glass transition temperature and tensile properties. Their results showed that the microwave curing improved the strength of the cured epoxy better than those cured by conventional heating. Moreover, the glass transition temperature of the microwave-cured epoxy was 136 ^{o}C, this was indifferent from the conventional-cured ones. The tensile strength and the tensile modulus of the microwave cured epoxy were greater than those of the thermal cured ones. Another study by Bai and Djafari (1995) compared the mechanical behavior of E-glass/epoxy composite cured by microwave and by thermal heating. The microwave polymerization improved slightly the mechanical properties as compared with the thermal cured composites. This improvement is considered to be due to a better homogeneity induced by microwave curing. It was found that more voids exist in the microwave-cured composites than in the thermal-cured ones due to the lower external applied pressure. Microwave processing was also faster than the traditional thermal one as shown in Table 3.1. The fully cured composites achieved from both cure techniques exhibited the glass transition temperature at 144 ^{o}C. From SEM micrographs, they also reported that fiber-matrix interfacial bonding of the microwave cured composites seemed stronger than that the thermal cured ones.

Jacob et al. (1995) studied the curing of methyl methacrylate (MMA) by microwave radiation and thermal heating. MMA was cured by microwave radiation at three different powers of 200, 300 and 500 Watt. Under comparable experimental conditions, the rate of cure by microwave radiation did not show a significant rate enhancement. In the thermal cure at 69, 78 and 88 ^{o}C, the polymerization proceeded

until about 90% conversion while in the microwave cure, it progressively decreased from 88% at 200 Watt to 84% at 300 Watt and to 78% at 500 Watt. This was because the glass transition temperature of the system exceeded the reaction temperature, so the percentage conversions of the reaction become limited.

Table 3.1 The curing conditions for microwave and thermal heating of E-glass-reinforced epoxy composites (Bai and Djafari, 1995).

Curing	Mould	Specimen dimensions (mm)	Process	Pressure (bar)	$T_g(^{o}C)$
Microwave heating	Teflon	250×36×(1,3)	1 kW., 20 min.	10	144
Thermal heating	Metallic	250×180×(1,3)	140°C, 1.5h	14	144

Boey et al. (1999) showed the effect of curing agent on the rate enhancement between thermal cured and microwave cured epoxy/amine systems. Curing was done at microwave power between 200 Watt and 600 Watt. They found unreacted epoxy, implying that only a limiting conversion was achieved at the low power of 200 Watt. At a higher microwave power of 600 Watt, the radiation was sufficient to initiate a reaction fast enough to reduce the amount of unreacted functional groups.

Nightingal and Day (2002) studied carbon fiber prepregs using epoxy resin as a matrix. They compared the mechanical properties of the carbon fiber/epoxy composites cured by microwave and conventional thermal methods. The thermal-cured composites showed higher flexural properties than the microwave-cured ones. Composites that were partially autoclave-cured and then post-cured with microwaves had the worst flexural properties. The void content of the microwave-cured composites was high, compared with the autoclave-cured ones. They noted that this was the direct result of the low pressure applied during cure compared to the autoclave technique. Nightingal and Day suggested that microwave curing, under the correct conditions of pressure and vacuum, could produce composites with comparable mechanical properties to the autoclave-cured composites but in a much shorter time.

Zhou et al. (2003) studied the advantages of microwave heating compared with thermal heating of epoxy resin cured with maleic anhydride. Cure time by microwave was found to decrease by about two-thirds of the conventional thermal curing. The curing temperature also decreased by about 15–20 °C. In addition, the microwave processing also increased slightly the compressive strength and the bending strength of the epoxy resin as shown in Table 3.2 and Table 3.3 respectively.

Table 3.2 The compressive strength of epoxy resin cured by microwave and thermal heating (Zhou et al., 2003).

Curing process	phr (%)	Curing time (h)	Curing temperature (°C)	Compressive strength (MPa)
Microwave	30	1	135±5	105.07
Microwave	35	1	135±5	92.29
Microwave	40	1	135±5	93.97
Thermal	30	3	150±5	88.68
Thermal	35	3	150±5	90.38
Thermal	40	3	150±5	88.54

Table 3.3 The bending strength of epoxy resin cured by microwave and thermal heating (Zhou et al., 2003).

Curing process	phr (%)	Curing time (h)	Curing temperature (°C)	Bending strength (MPa)
Microwave	30	1	135±5	56.68
Microwave	35	1	135±5	44.84
Microwave	40	1	135±5	36.81
Thermal	30	3	150±5	-
Thermal	35	3	150±5	34.76
Thermal	40	3	150±5	-

Yarlagadda and Hsu (2004) compared the glass transition temperature and the mechanical properties of microwave and conventional thermal cured epoxy resins. The glass transition temperature was noted as 92.48 and 89.16 °C respectively for microwave-cured and conventionally-cured epoxy. The results obtained from flexural and tensile tests indicated that microwave curing improved the mechanical properties of the epoxy resin better than those cured by conventional heating.

3.2 Polybenzoxazine

Ning and Ishida (1994) investigated the synthesis of bifunctional benzoxazine precursors. These bifunctional benzoxazine were found to exhibit excellent mechanical and thermal properties with good handling capability for resin processing and composite manufacturing. The glass transition temperature was found to be as high as 190 °C. The tensile modulus was 3.2 GPa while the tensile strength was 58 MPa. In addition, the bifunctional benzoxazine resins offered greater flexibility than conventional phenolic resins in terms of molecular design. They did not release any by-products during curing reactions and no solvent was needed in the resin production.

Ishida and Rodriguez (1995) studied the curing reactions of benzoxazine precursors based on bisphenol A and aniline to determine the feasibility of processing polybenzoxazine. They found that polybenzoxazine could be cured via a ring-opening mechanism that did not produce any condensate or other reaction by-products.

Ishida and Allen (1996) studied the properties of polybenzoxazine thermosetting resin (BA-a). It was synthesized from inexpensive raw materials and could be cured without the aid of the strong acid catalysts normally required by phenolic materials. Dynamic mechanical analysis revealed high moduli and high glass transition temperature with low crosslink densities. The flexural modulus was 4.5 GPa while the flexural strength was 126 MPa. Polybenzoxazines had significantly higher tensile moduli than both phenolics and epoxies yet they still maintained adequate tensile

strength and impact resistance. In addition, low water absorption and good dielectric properties allowed these materials to perform well in electronic applications.

Polybenzoxazine has been used as a matrix for various reinforcements. Ishida and Rimdusit (1998) investigated the thermal properties of the boron nitride-filled polybenzoxazine. The thermal conductivity of the composite was found to increase with increasing boron nitride content. A maximum boron nitride content of 78.5 % by volume was found to correspond with the thermal conductivity of 32.5 W/mK. The high thermal conductivity of the composite was accomplished by using highly thermal conductive filler with a matrix resin which has low melt viscosity with good filler wetting and good adhesion to the filler. Boron nitride-filled polybenzoxazine has many outstanding properties which makes it suitable for an application as a molding compound for the electronic packaging industry and other applications with high thermal conductivity. The water absorption at room temperature of this composite was also very low, i.e. for an 85 % by weight of boron nitride; the absorption was only 0.02 % for duration of 24 hr. This work revealed the ease of processing and good interfacial bonding of the matrix resin used in composite fabrication.

Wang and Ishida (1999) studied the cationic ring-opening polymerization of benzoxazine resin. With certain initiators, rings could be opened and polymerized at room temperature. Fourier transform infrared spectroscopy, ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy, size exclusion chromatography, differential scanning calorimetry, and thermogravimetric analysis had been used to study the polymerization process and to characterize the obtained polymers. High performance bisphenol-A/aniline based polybenzoxazine with a glass transition temperature (T_g) of 220 °C was obtained. Its char yield was approximately 60 % at 800 °C under nitrogen.

Kim and Ishida (2003) investigated the effect of amine functional groups on the hydrogen bonding network structure by using FT-IR and NMR technique. They found that polybenzoxazines can be synthesized from a wide selection of raw materials consisting of phenolic derivatives and primary amines. They offered greater

flexibility than phenolic resins in terms of molecular design. Since the wide variety of benzoxazine monomers could be easily obtained by changing the primary amine component. Thus there were many forms of polybenzoxazine types, which should be of great interest for commercial applications.

3.3 Silicon Carbide Whisker in Composite

SiC_w have been added to a wide variety of ceramics as reinforcement. Ray et al. (1995) studied the fractography of 25 wt% of SiC_w reinforced alumina composite. The addition of SiC_w in the alumina ceramic composite was found to improve the fracture toughness and the fracture strength of the ceramic composites tested by four points bending. Their SEM micrographs showed the whisker pullout mechanism during crack growth. They also found that the mechanical properties could be increased by improving the whisker distribution.

Lin et al. (1996) studied the microstructure and the mechanical properties of hot-pressed SiC_w-reinforced ZrO_2 (2 mol% Y_2O_3). The presence of 30 vol% SiC_w in ZrO_2 matrix increased the elastic modulus from 220 GPa for the neat ZrO_2 to 308 GPa. An addition of 10 vol% SiC_w increased the flexural strength from 888 MPa for the neat ZrO_2 to a maximum value of 1404 MPa. Further increment of SiC_w to 20 vol% and 30 vol% decreased the flexural strength to 1354 MPa and 1337 MPa respectively. SiC_w was found uniformly distributed within the matrix. Inhibition of crack propagation was found due to the presence of SiC_w. However, the addition of SiC_w also adversely effected the flexural strength of the composites. The residual stress caused by the thermal incompatibility between the SiC_w and the $ZrO2$ matrix was believed to be high.

In polymer matrix composites, Xu et al. (2002) applied silicon-fused SiC_w to reinforced dental composites based on urethane and triethylene glycol dimethacrylate. They varied the whisker/silica mass ratio at the filler mass percentage of 60%. The elastic modulus of the composite, which was measured with a nano-indentation technique, was found to increase with increasing whisker ratio. The elastic modulus

increased from 12.3 GPa to 17.7 GPa when the filler was changed from silica to silicon carbide whisker. From the SEM micrographs, the whiskers appeared to be well-bonded with the matrix. Whisker entanglement and agglomeration at high whisker content were also observed microscopically.

CHAPTER IV

EXPERIMENTAL

4.1 Materials and Monomer Preparation

The materials in this research were benzoxazine resin and silicon carbide whisker. Benzoxazine resin is based on bisphenol-A, aniline, and formaldehyde. Bisphenol-A (Commercial grade) was kindly supplied by Thai Polycarbonate Co., Ltd. (TPCC). Para-formaldehyde (AR grade) was purchased from Merck Company and aniline (AR grade) was purchased from APS Finechem Company. Silicon carbide whisker, from Tokay Carbon Co., was contributed by Prof. Takeshi Kitano (retired) of AIST, Tsukuba, Japan. All chemicals were used without further purification.

4.1.1 Benzoxazine Monomer Preparation

The benzoxazine resin used is based on bisphenol-A, aniline and formaldehyde in the molar ratio of 1:4:2. This resin was synthesized by using a patented solventless method in the U.S. Patent 5,543,516 (Ishida, 1996). The obtained benzoxazine monomer is clear-yellowish powder at room temperature and can be molten to yield a low viscosity resin at about 70-80 $^\circ$C. The product is then ground to fine powder and can be kept in a refrigerator for future-use. The density is 1.2 g/cm^3 and it has a reported dielectric constant of about 3-3.5 (Nair, 2004).

4.1.2 Silicon Carbide Whisker Characteristics

Silicon carbide whisker (SiC$_w$) used was TWS-200. It is nearly perfect single crystal with diameters ranging from 0.3 to 2 μm and lengths ranging from 5 to 50 μm. The density is 3.2 g/cm^3 and it has a reported dielectric constant of about 40 (Harper, 2004).

4.2 Specimen Preparation

Silicon carbide whisker was thoroughly mixed by hand with benzoxazine resin in an aluminium container at 85 °C for at least 10 min to ensure particles wet out by the resin. The filler to matrix ratio were 0:100, 2:98, 4:96, and 6:94 by weight to yield molding compounds. For thermal-cured specimen, the compound was compression-molded by hot pressing; the thickness was controlled by using a metal spacer. The hot-pressed temperature of 200 °C was applied for 2 hr simultaneously with a hydraulic pressure of 35 MPa. In the case of microwave curing, an opened Teflon mold was used. The molding compounds were cured in the open mold at 165 Watt for 60 min and further cured at 270 Watt for 30 min in the Microwave Digestion Oven (MARS5) model 907045. All samples were left to air cooled to room temperature in the open mold.

4.3 Characterization Methods

4.3.1 Differential Scanning Calorimetry (DSC)

The curing characteristic of the benzoxazine-silicon carbide composites were examined by using a differential scanning calorimeter (DSC) model 2910 from TA Instrument. For each test, a small amount of the sample ranging from 5-10 mg was placed on the aluminum pan and sealed hermetically with aluminum lids. The experiment was done using a heating rate of 10 °C/min to heat the sealed sample from 30 °C to 300 °C under N_2 purging. The processing temperature, time and glass transition temperature were obtained from the thermograms while the percentage of resin conversion was calculated from the DSC thermograms.

4.3.2 Actual Density Determination

The density of each specimen was determined by water displacement method according to ASTM D 792-91 (Method A). All specimens were prepared in a

rectangular shape (50 mm x 25 mm x 2 mm). Each specimen was weighed in air and in water at 27 ± 2 °C. The density was calculated as shown in Equation (4.1). An average value from at least five specimens was calculated.

$$\rho = \left(\frac{A}{A-B}\right) \times \rho_o \qquad (4.1)$$

where

ρ = density of the specimen (g/cm^3)

A = weight of the specimen in air (g)

B = weight of the specimen in liquid (water) at 27 ± 2 °C (g)

ρ_o = density of the liquid (water) at the given temperature (g/cm^3)

(This value depends on the temperature, see in appendix A-1)

4.3.3 Thermogravimetric Analysis

The thermogravimetric analyzer model TGA/SDTA 851^e from Mettler-Toledo (Thailand) was used to study thermal stability, degradation of SiC$_w$ composites and residual amount of SiC$_w$. The initial mass of the composite to be tested was about 10 mg. It was then heated from room temperature to 800 °C with a heating rate of 20°C/min under dried air purge. The degradation temperature at 5% weight loss and the residual amount of filler at 800 °C were recorded for each specimen.

4.3.4 Flexural Properties Measurement

Flexural modulus and flexural strength of composite specimens were determined utilizing a Universal Testing Machine (model 5567) from Instron Instrument. The dimension of the specimens was 50 mm x 25 mm x 2 mm. The test method used was a three-point bending mode with a support span of 32 mm, bending was performed at the crosshead speed of 1.2 mm/min. The flexural modulus and the flexural strength were determined according to the procedure set out in ASTM D 790M-93, they were calculated by using Equations (4.2) and (4.3):

$$E_B = \frac{L^3 m}{4bd^3} \qquad (4.2)$$

$$S = \frac{3PL}{2bd^2} \qquad (4.3)$$

where E_B = flexural modulus, MPa)

               S = flexural strength, MPa

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

               L = support span, mm

               b = width of beam tested, mm

               d = depth of beam tested, mm

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

4.3.5 Fracture Energy under Compressive Mode

A Universal Testing Mechine (model 5567) from Instron Instrument was used to determined compressive properties under compression mode. The dimension of the specimen was 10 mm x 10 mm x 3 mm. The test was calculated by using a 1 kN load cell, compression was performed at a crosshead speed of 1 mm/min according to the procedure outlined in ASTM 695-02. The fracture energy was calculated from the work done under the load-displacement curve per unit area. The specific energy absorption for the compression tests was then calculated by integrating the area under the load–displacement curve and then divided by the volume of specimen crushed times the material density as shown in Equation (4.4). The energy during crush (E) was calculated by integrating under the crush load vs. crush distance curve as shown in Equation (4.5).

$$S_s = \frac{W_d}{V \times \rho} = \frac{\int_{S_b}^{S_i} P\,(S_i - S_b)}{AL_c\rho} \qquad (4.4)$$

where S_s = specific energy absorption, kJ/kg

               W_d = total work done, J

V = specific volume, m^3

ρ = density, g/cm^3

A = cross-section area, m^2

L = crushed length of specimen, m.

$$E = \int_0^{S_f} F \cdot ds \qquad (4.5)$$

where   E = energy absorption during crush load, J/m^2

F = crush load, J

s = crush distance, m.

4.3.6 Dynamic Mechanical Analysis (DMA)

A dynamic mechanical analyzer (DMA) model DMA242 from NETZSCH Instrument was used to investigate dynamic mechanical properties. The specimen dimension was 40 mm × 10 mm × 2.5 mm. The test was performed under bending mode. A strain in the range of 0 to 30 μm was applied sinusoidally at a frequency of 1 Hz. The specimen was heated at the rate of 2°C/min from room temperature to 260 °C. The glass transition temperature was taken as the maximum point on the loss modulus curve in the temperature sweep tests. The storage modulus (G'), loss modulus (G''), and damping curve (tanδ) were obtained.

4.3.7 Interfacial Characterization

Observation of the interfacial bonding within the composites was investigated using a scanning electron microscope (JEOL JSM-6400) at an acceleration voltage of 15 kV. Samples were coated with a thin film of gold using a JEOL ion sputtering device (model JFC-1100E) for 4 min to obtain a thickness of approximately 300Å before micrographs of the magnified fracture surfaces of the composite were taken. The obtained micrographs were used to evaluate qualitatively the interfacial interaction between the polybenzoxazine matrix and the silicon carbide whisker.

Energy dispersive X-ray spectroscopy (EDX) was used to determine the concentration of SiC_w distributed in the composite using Link Isis 300 software.

4.3.8 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectra of SiCw-filled polybenzoxazine composites under thermal and microwave curing methods were acquired by using Spectrum GX FT-IR spectometer from Perkin Elmer Instrument equipped with a KBr beam splitter. A small amount of the solid composites, preferably 0.5-1.0 mg, were grinded and mixed with potassium bromide (KBr) disks at room temperature. All of the polybenzoxazine composites with SiC_w used in this study were sufficiently thin with optical thickness of a fraction of a millimeter in compliance with the thickness specified under the Beer-Lambert's law. The composites were then mounted on a sample holder. All spectra were taken as a function of time with 32 scans at a resolution of 4 cm^{-1} and spectra range of 4000-400 cm^{-1}. The polymerization reactions of the samples were examined at room temperature.

CHAPTER V

RESULTS AND DISCUSSION

5.1 Processing Conditions of the Molding Compound

5.1.1 Influence of Silicon Carbide Whisker Content on Curing Temperature

Fig. 5.1 demonstrates the DSC thermograms of benzoxazine resin filled with different SiC_w contents at temperature elevating from 30 to 300 $^{\circ}$C. The heating rate was 10 $^{\circ}$C/min. The step changes observed in all of the thermograms with different SiC_w contents at about 45 $^{\circ}$C was related to the glass transition temperature of the benzoxazine monomer, Tg_o. Polymerization of benzoxazine was known to occur by a simple ring-opening addition reaction and does not yield any reaction by-products (Ishida, 1998).

The curing exotherm of the benzoxazine molding compound at different SiC_w contents showed the onset of cure at 150 $^{\circ}$C. A maximum exotherm peak was observed at 225 $^{\circ}$C, which is the characteristics of this resin (Rimdusit and Ishida, 2000); such exothermic peak reflects the cure characteristic and appropriate thermal curing scheme of the benzoxazine resin. The silicon carbide whisker has no direct effect on chemical reaction during the curing process of the benzoxazine monomers. This is because there is no peak shift and the reaction temperature of SiC is about 1000 $^{\circ}$C (Ryu et al., 2001; Satapathy et al., 2005). However, the area under the curing peak was found to decrease with increasing SiC_w content while the weight of the composite was kept constant. This means that the exothermic heat generated during curing decreases with the amount of benzoxazine resin. The exothermic heat during polymerization was minutely absorbed by SiC_w; hence the lower content of SiC_w would lead to a lesser amount of heat lost to absorption by SiC_w.

5.1.2 Determination of Thermal Cure Condition

Fig. 5.2 exhibits the DSC thermograms of the composite consisting of benzoxazine resin and 4% by weight of SiC_w, cured by conventional thermal method. All composites were cured isothermally at 200 ^{o}C for various durations. The extent of cure suggested by Fig. 5.2 can be utilized to device the thermal cure scheme. A cure temperature of 200 ^{o}C was used because, at this temperature, polymerization by ring-opening addition reaction had definitely occurred, as suggested by Fig. 5.1. It is not too high as temperature for processing while the economical advantage is maintained. The disappearance of the exothermic peak between 180 ^{o}C and 290 ^{o}C suggested that suitable duration for complete cure of benzoxazine molding compounds at 200 ^{o}C was 120 min.

5.1.3 Determination of Microwave Cure Condition

Fig. 5.3 demonstrates the effect of microwave heating on benzoxazine resin. The DSC thermogram of benzoxazine resin heated by a microwave at a high power of 1 kW for 30 min shows that under such condition it was hardly cured; the degree of conversion was almost negligible. This is due to the intrinsic nonpolar nature of the benzoxazine monomer (Nair, 2004). However, with a relatively low content of SiC_w of only 4% by weight, the benzoxazine resin was found to be cured relatively well. This is evident in the DSC thermograms shown in Fig. 5.4 when SiC_w of 4% by weight was applied. Moreover, the input power needed to heat the SiC_w-filled benzoxazine to its fully cured condition can be reduced substantially from over 1 kW to only 270-330 W. Earlier studies on microwave curing of E-glass fiber/epoxy composite reported the microwave power required to be as high as 1000 W for 20 min under pressure of 10 bars to achieve fully cured E-glass fiber-filled epoxy composite due to the intrinsic polar nature of epoxy (Bai and Djafari, 1995). Hence, it is apparent that the presence of SiC_w has a dramatic effect on the curing of the benzoxazine molding compound. It was also found that a higher microwave input power was needed as the SiC_w content reduced. With SiC_w loading of 4% by weight, the microwave radiation power of 270 W for 20 min was found to be most suitable for

processing of the benzoxazine molding compound. Coupled with curing time of 20 min, such microwave cure condition was found to have yielded a conversion of nearly 100%. In another study on microwave curing of the epoxy/4,4'-Diamino-di-phenyl-sulfone (DDS) systems (Boey et al, 1999), curing was done between 200 W and 600 W for over 20 min, but the maximum conversion was found to be limited and not approaching 100%. It was suggested that rapid cross-linking created a molecular network which was rigid enough to trap unreacted functional groups, thus causing a lower degree of cure.

5.1.4 Comparison between the Conventional Thermal Cure and the Microwave Cure Techniques

The conversion-time diagram of the microwave-cured benzoxazine resin filled with 4% by weight of SiC_w at 270 W is compared with that of the regular thermal cure in an oven heating at 200 °C as shown in Fig. 5.5. The benefit of using the microwave technique is evidently depicted in the rapid rise of conversion in the microwave-cured compound. As shown in the diagram, curing time of only 20 minutes was required to convert the benzoxazine resin to its maximum cure by microwave processing at 2.45 GHz and 270 W, while the traditional oven cure at 200°C required at least 120 minutes. This is in good agreement with previous study by Boey et al. (1999) who showed a decrease of curing time required in microwave curing as compared with that for thermal curing of the epoxy/amine system. The energy consumptions to the fully cured conversion by microwave and the traditional oven are compared in Table 5.1. The maximum curing of the polybenzoxazine/SiC_w composite by microwave oven consumed less energy than that required by the traditional thermal curing by a approximately 20 to 30 times depending on the power used. So, for polybenzoxazine/SiC_w composite, microwave processing can save greater cost per unit mass of composite than that of the traditional thermal processing.

5.2 Properties of Silicon Carbide Whisker-filled Polybenzoxazine

5.2.1 Density Measurement

Fig. 5.6 shows the density of polybenzoxazine filled with 0, 2, 4, and 6% by weight of SiC$_w$. The actual density was measured by a procedure described in Section 4.3.2. The theoretical density of the composites at room temperature was calculated by using Equation (2.1) based on the earlier report that the density of the SiC$_w$ and of the polybenzoxazine are 3.17 g/cm^3 (Nair, 2004) and 1.20 g/cm^3 (Harper, 2004) respectively. The actual density was calculated following Equation (4.1). The addition of SiC$_w$ raised the density of the composite. The results in Fig. 5.6 reveal that the theoretical and actual density increases with the SiC$_w$ content following the rule of mixture. The curing methods do not exert any influence on the actual density of the composite. It shows the benefit of using polybenzoxazine as a matrix for microwave cured system when compare with thermal cured system. In another study that was reported by Nightingale and Day (2002). It used carbon fiber/epoxy composites cured by thermal heating and microwave heating. The result showed the increasing of void content in the carbon fiver/epoxy composite that is a result of the decreasing in the actual density because of the low applied pressure during cure compare to the thermal cured composite.

5.2.2 FT-IR Spectroscopic Investigation

The FT-IR spectra of as-synthesized BA-a is shown in Fig. 5.7. The C-H stretching of benzene ring can be detected at 3029 cm^{-1}. The symmetric methylene wagging and twisting bands are shown by weak band at 1370-1250 cm^{-1}. The region from 1490-1460 cm^{-1} is assigned to the methylene antisymmetric deformation. The C-H out-of-plane deformation of the 1,2,4-tri-substituted benzene ring can be found in the band centered near 949 cm^{-1}. The band around 1495-1497 cm^{-1} attributed to the tri-substituted benzene ring mode in the oxazine ring structure. The antisymmetric and symmetric C-N-C stretching modes could be found at 1159 cm^{-1} and in the region from 830 cm^{-1} to 740 cm^{-1}, respectively. The region of 1240-1210 cm^{-1} was due to the aromatic ether C-O-C antisymmetric stretching, while the symmetric stretching mode appeared around 1040-1020 cm^{-1}. For BA-a monomer,

the methyl group vibration occurred at 2968 cm^{-1} and 2872 cm^{-1} whereas that of hydroxyl group of the phenolic structure appeared at 3421 cm^{-1} (Agag and Takeiche, 2001).

The polymerized structure of benzoxazine resin can also be analyzed more thoroughly by FT-IR to determine the nature of the polymerization reactions. Fig. 5.7 shows the region from 940-920 cm^{-1} associated with the oxazine ring which almost completely disappeared, indicating a nearly complete loss of the oxazine ring in the benzoxazine monomers. This band agrees well with the frequency predicted for the out-of-plane, out-of-phase hydrogen-wagging mode for 1,2,3,5-tatrasubstituted aromatic ring. This ring substitution is expected if the reaction takes place ortho to the phenolic moiety. The regions associated with the aromatic C-O and aromatic ether C-O-C stretches were nearly absent as well. A new characteristic band of a phenolic C-O species arose at 1285 cm^{-1} (Ishida and Sanders, 2000).

5.2.3 Effect of Silicon Carbide Whisker Content on Glass-transition Temperature

Fig. 5.8 shows the DSC thermograms depicting the glass-transition temperature (T_g) of the neat benzoxazine resin and of the SiC$_w$-filled polybenzoxazine. At heating rate of 10 ^{o}C/min, the T_g of the polybenzoxazine was found to be 156 ^{o}C. The T_g's of all the SiC$_w$-filled polybenzoxazine composites are slightly higher than that of the neat polybenzoxazine ranging from 157 to 160 ^{o}C. The SiC$_w$ filler was found to elevate the T_g's of the composites. The maximum T_g of microwave cured epoxy-amine system was lower than those achieved by thermal curing because the sluggish reaction with microwave-cured of the epoxy-amine system could entrap the functional group in the crosslink network (Boey and Yap, 2001). The different heating mechanisms, i.e. by conduction of heat throughout the whole compound in the oven-cured technique and by sporadic heating from the surface of tiny silicon carbide whisker as well as the inside-out heating mechanism of the microwave during the processing may be one reason for the observed discrepancy. However, at 4 wt% SiC$_w$ content, the microwave cured SiC$_w$-filled polybenzoxazine composites possess T_g of

approximately 160 °C, this is close to that of the oven-cured ones. This result is supported by Bai and Djafari (1995) who studied E-glass fibre/epoxy composite that cured by traditional thermal treatment and by microwave, their corresponding glass transition temperatures were observed to be almost equivalent.

5.2.4 Degradation Temperature

Fig. 5.9 exhibits the TGA thermograms of the neat polybenzoxazine and SiC_w-filled polybenzoxazine composites at various SiC_w contents. They were all heated at the heating rate of 20 °C/min under air purging. From the thermograms, the degradation temperature was found to slightly increase when SiC_w was present. This was due to the barrier effect of the inert ceramic SiC_w filler. The degradation temperature as a function of the SiC_w content is shown in Fig. 5.9. The TGA curves showed the decomposition temperature of the neat polybenzoxazine at 5 wt% loss to be 341 °C. The degradation temperatures of SiC_w-filled polybenzoxazine composite at 0, 2, 4, and 6 wt% of SiC_w content was increased by about 10 °C from the value of 341 °C of the neat polybenzoxazine as shown in inset picture. This graph also showed the degradation temperatures at 5 wt% loss of the thermal cured and the microwave cured composites at 4 wt% of SiC_w to be close to 349 °C. Another important feature in the thermograms is the amount of residue at 800 °C, or the residual weight of the SiC_w-filled polybenzoxazine composite which is precisely the amount of SiC_w in composite. The results of the TGA test confirmed the amount of SiC_w present in the composites.

5.2.5 Edge Effect in Microwave Heating of SiC_w-filled Polybenzoxazine Composite

Microwave radiation is believed to heat the whole composite simultaneously. Since polymerization took place only within the resin and the reaction is exothermic, the temperature of the surrounding and of the mold was always lower than that within the microwave heated resin. Therefore, a temperature gradient may have existed due

to heat conduction from the hot benzoxazine molding compound to the surrounding. For this reason, the percent conversion at the different locations of the microwave cured composite was investigated, the results are shown in Table 5.2. It is evident from this Table that a relatively uniform curing of over 97 percents conversion was achieved at all locations in the fully cured composite. The maximum cure conversion of nearly 100% was found at the center of the composite plate. This verified the uniformity of cure achieved in the microwave-cured polybenzoxazine/SiC$_w$ composites prepared for further investigation in our study. Different heating mechanisms, i.e. heating by conduction of heat throughout the whole compound in the oven-cured technique and by heating sporadically from the surface of tiny silicon carbide whisker as well as the inside-out heating mechanism of the microwave during the processing may be one reason for the observed some discrepancy. Ku et al. (2001) showed the non-uniform microwave heating for 33% by weight of carbon fiber-reinforced polystyrene at different positions. The areas with higher heat created hot spots which could lead to thermal runaway or the degradation of the composites.

5.2.6 Flexural Properties Evaluation

The mechanical properties of the SiC$_w$-filled polybenzoxazine obtained from flexural tests as a function of the amount of SiC$_w$ content are shown in Figure 5.10-5.11. The flexural strength and the flexural modulus increased when SiC$_w$ was presented. The enhancement in the flexural modulus was induced by the exceedingly high flexural modulus of SiC$_w$, ranging from 400 to 500 GPa (Harries, 1995), whereas that of polybenzoxazine was only about 4.4 GPa (Rimdusit et al., 2006). As the SiC$_w$ content increased, the flexural modulus of the polybenzoxazine composites became greater. The flexural strength also showed significant changes when the polybenzoxazine was filled with SiC$_w$. For unfilled polybenzoxazine, the flexural strength ranged from 69 to 135 MPa. Polybenzoxazine composites with 2-6 wt% SiC$_w$ tended to possess greater flexural strength than the neat polybenzoxazine with a noticeable maximum at 4 wt% SiC$_w$, beyond which a slight decrease was observed at 6 wt% SiC$_w$. The flexural modulus and the strength of the thermal cured composites at 4 wt% SiC$_w$ ranged from 4.8 to 5.8 GPa and 91 to 147 MPa while those of the

microwave cured composites ranged from 5.5 to 5.9 GPa and 111 to 125 MPa respectively. It is evident that the flexural modulus of SiC_w-filled polybenzoxazine composite cured by microwave is slightly superior to those of the thermally cured systems. This is in good agreement with previous study by Bai et al. (1995) who reported the tensile modulus of microwave-cured epoxy resin to possess a little higher tensile modulus than the thermal-cured ones.

5.2.7 Fracture Energy Investigation

Fig. 5.12 shows the stress-strain relation under axial compression. It was apparent from all compression tests that the load increases with the displacement until it reached the intrinsic yield point, then it dropped gradually despite increasing displacement until the composite failed. Strain softening, which was lacking in neat polybenzoxazine, was observed in all SiC_w-filled polybenzoxazine composites. The specific energy absorption (SEA) for the axial compression can be calculated by integrating the area under the load-displacement curves and then divided by the volume of SiC_w-filled polybenzoxazine composite crush times the material density. From Fig. 5.13-5.14, the fracture energy and SEA were found to increase with increasing the SiC_w content. A previous study on the effect of resin properties and resin processing parameter on crush and the behavior of thermoset composite revealed that the processing conditions played a significant effect on the compressive properties and energy absorption (Warrior et al., 2003). The SEA of polyester resin, for example, changed considerably in the range of 20 to 60 kJ/kg upon variation of the processing conditions. However, both of the fracture energy and the specific energy absorption of the composites cured by both curing methods are closely comparable, since the thickness of the all composites by both cure methods was only 3 mm. Therefore, there is a little thermal stress for thermal-cured composite as the same with microwave-cured ones.

5.2.8 Dynamic Mechanical Analysis (DMA)

The dynamic mechanical properties of SiC_w-filled polybenzoxazine composites are shown in Fig. 5.15-5.17. Fig. 5.15 exhibits the dynamic flexural moduli of the SiC_w-filled polybenzoxazine composites cured by traditional thermal heating with SiC_w contents ranging from 0 to 6 % by weight and microwave heating with 4 wt% SiC_w content with the temperature ranging from 30 to 260 °C based on a heating rate of 2 °C/min. The storage modulus of SiC_w-filled polybenzoxazine at its glassy state tends to slightly increase with increasing the SiC_w fraction in the composites as a result of the more rigid characteristics of the composites. At room temperature, the modulus of SiC_w-filled polybenzoxazine composite increased from 5.5 GPa of a neat polybenzoxazine to 6.2 GPa of the 6 % by weight of SiC_w composite. The modulus of the SiCw-filled polybenzoxazine in the rubbery plateau was increased with increasing SiC_w content because the load transfer in the composite occurred mainly through the SiC_w, when the two phases contact. Therefore, the mobility and the deformability of the rubber matrix were reduced by the presence of the hard SiC_w. Since there was only a small amount of SiC_w content in the composite, the dynamic mechanical properties showed slightly increase. In this figure also compares the storage modulus of 4 wt% SiC_w-filled polybenzoxazine composites cured by thermal heating and microwave irradiation. The storage modulus of the microwave-cured composites slightly increased from 6.8 GPa to 6.1 GPa of the thermal-cured ones because of the different nature of heating. Microwave heated the outer and the inner parts of the SiC_w-filled polybenzoxazine composite simultaneously. Therefore, there was no overheating at the surface of the microwave-cured composite.

Fig. 5.16 compares the glass transition temperature, T_g, of the conventional thermal cured and microwave cured SiC_w-filled polybenzoxazine composites. T_g was obtained from the peaks of the loss modulus plotted as a function of temperature. The glass-transition temperature of the neat resin and the composites were in the range of 150 to 160 °C, there was a minor change after adding a small amount of SiC_w in polybenzoxazine composite. The high modulus of SiC_w and the good adhesion between the polybenzoxazine and the SiC_w were probably responsible for the observed enhancement of the T_g of the composites. The added amount; however, is

not sufficient to cause the obvious enhancement in the T_g as seen in the loss modulus peaks in Fig. 5.16. Moreover, the T_g's obtained by DMA thermograms are the same trend with obtained by DSC thermograms.

Fig. 5.17 is the plot of loss tangent versus temperature of SiC_w-filled polybenzoxazine composites. It shows an increase in the peak maxima of tan δ from 0.56 of 2 wt% SiC_w-filled polybenzoxazine composites to 0.62 of 6 wt% SiC_w-filled polybenzoxazine composite. Tan δ curves obtained from the ratio of energy loss (G") to storage energy (G') in sinusoidal deformation. The magnitude of tan δ peak reflects the large scale mobility associated with α relaxation, while the width of tan δ relates to the network homogeneity. The peak height of tan δ was found to increase with increasing mass fraction of SiC_w. This confirmed the reduction in segmental mobility chain with the presence of the hard SiC_w. These curves become flatter when the SiC_w content was increased due to the introduction of a rigid segment into the polybenzoxazine matrix as mentioned earlier.

5.2.9 Morphological Observations

Figure 5.18 shows the EDX mapping along the thickness of the 6% by weight SiC_w-filled polybenzoxazine composite in order to study the SiC_w distribution within the composite. SiC_w is shown as light granules in all micrographs. The white patches in the EDX mapping picture expressed the entities rich of SiC_w in polybenzoxazine composite. They are signs of whisker agglomeration at high whisker content. However, it can be seen that SiC_w was relatively well dispersed all over the composites and had no obvious SiC_w sedimentation at the bottom side of picture. A previous study on the SiC_w distribution in SiC_w-filled TiB_2 composites showed the homogeneity of SiC_w distribution along the fracture surface with a small volume fraction, less than 10 wt%, of SiC_w was better than that in the composite with a large volume fraction, 30 wt%, of SiC_w.

Fig. 5.19 (a) to (e) shows the interfacial characteristics along the fracture surface at 500 times magnification of the silicon carbide whisker-filled polybenzoxazine cured by hot-pressed and microwave radiation. The fracture surface of the neat polybenzoxazine is much smoother when compared to that of the SiC_w-filled polybenzoxazine composite because the adding of SiC_w are help to increase the loading area that enhance the polybenzoxazine matrix deformation. Fig. 5.20 (a) to (b) show the interfaces at 20,000 times magnification between the silicon carbide whisker and the polybenzoxazine matrix that was cured by hot-pressed and by microwave oven; the micrographs depict substantial interfacial adhesion between the silicon carbide whisker and the polybenzoxazine matrix. Protruding whiskers and holes where the whiskers were initially lodged before fracture was also observed. They are evidences of whisker pullout and bridging. This implies that polybenzoxazine cured by hot-pressed and by microwave oven is at least partly toughened by the SiC_w while the results on the elastic modulus of the SiC_w-filled polybenzoxazine was also enhanced, as shown in Section 5.2.6. Interfacial adhesion between SiC_w and polybenzoxazine is postulated due to the existence of crack deflection around the whiskers. This implies that thermal-cured and microwave-cured SiC_w-filled polybenzoxazine composites show increasing in interfacial behavior. Moreover, the interfaces between the matrix and the SiC_w filler in the composite cured by microwave radiation show the same toughening mechanisms compared with thermal cured. This is in good agreement with previous study by Deng and Ai (1998) that showed the fracture surface of SiC_w-filled TiB_2 composites which presented the toughening mechanisms of crack deflection around whisker and whisker bridging due to whisker pullout.
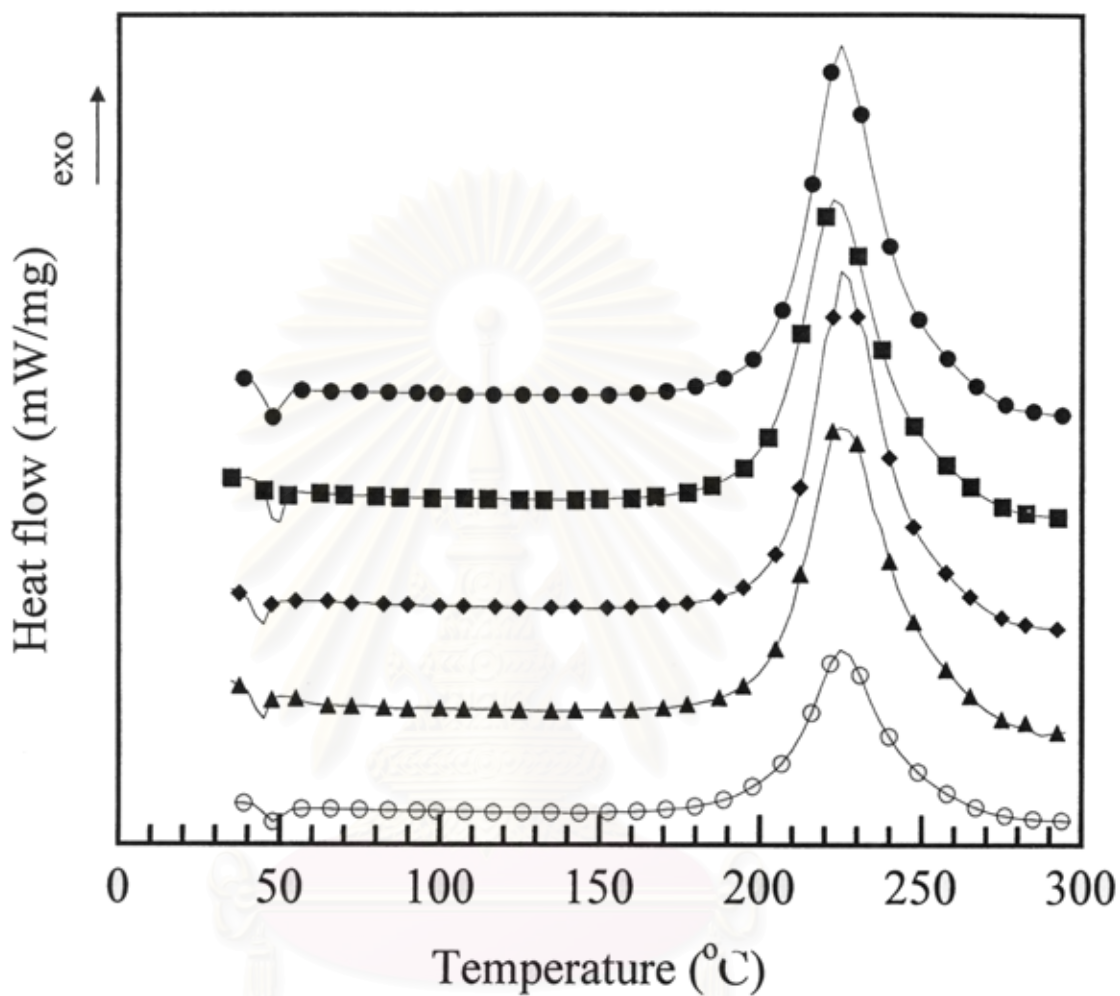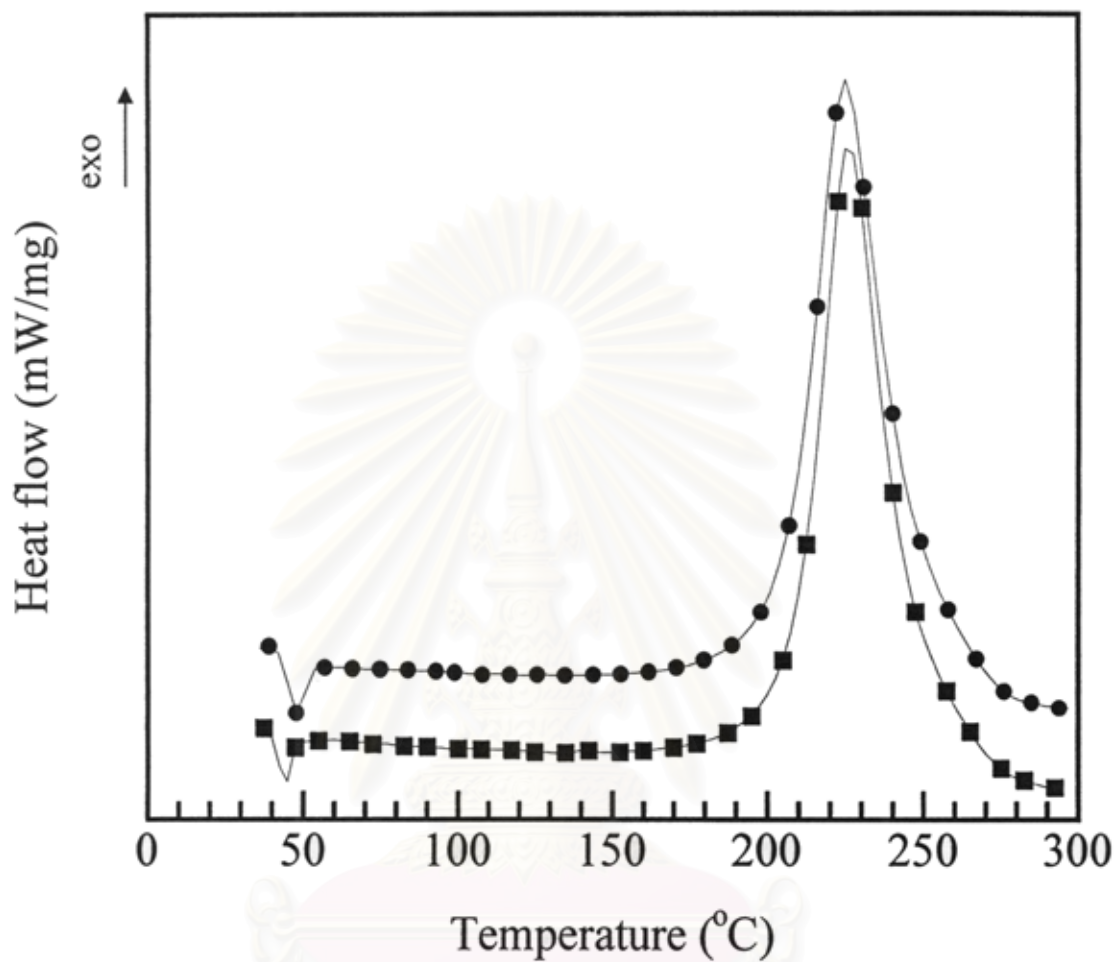
Figure 5.1: DSC thermograms of benzoxazine molding compound at different SiC whisker contents: (●) BA-a monomer, (■) 2wt%, (♦) 4wt%, (▲) 6wt%, (○) 20wt%.
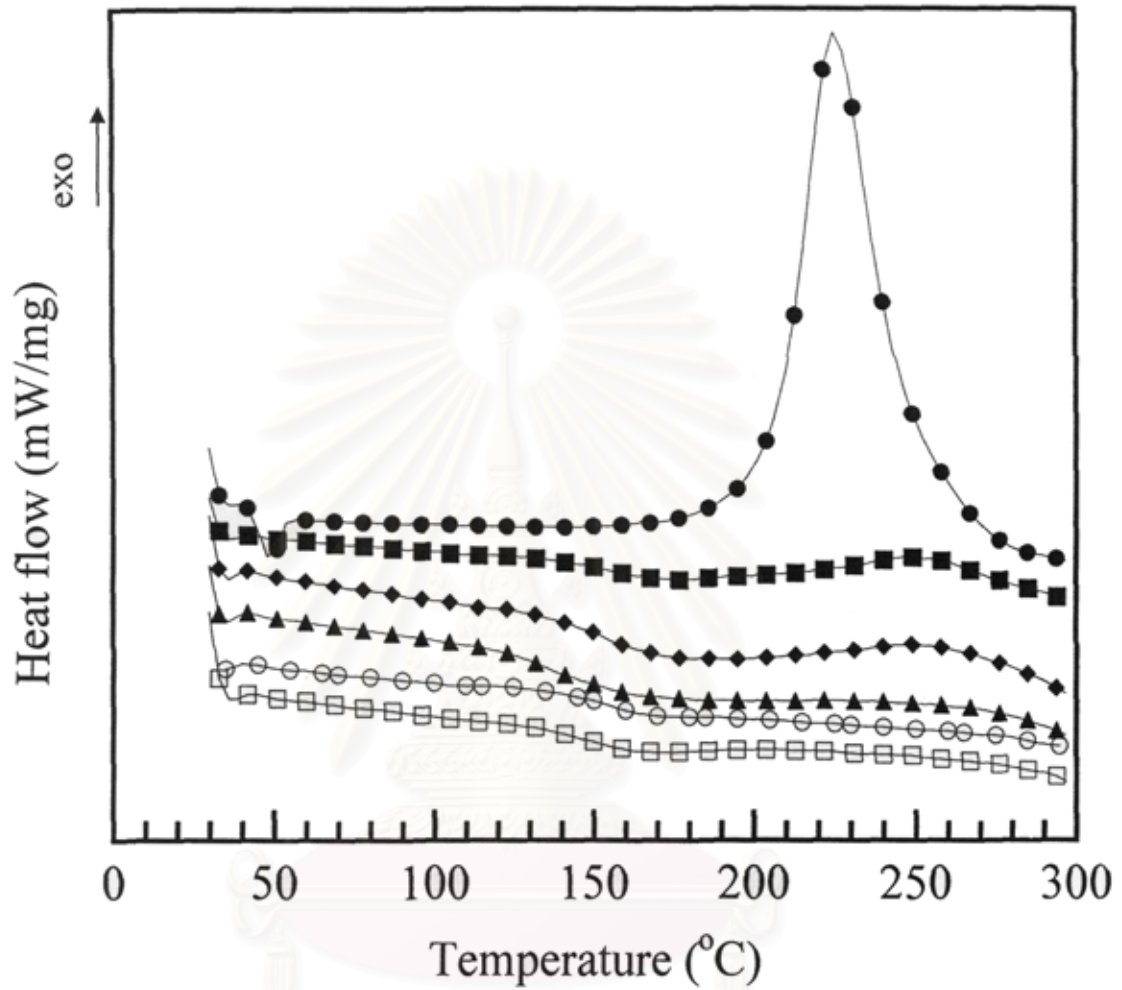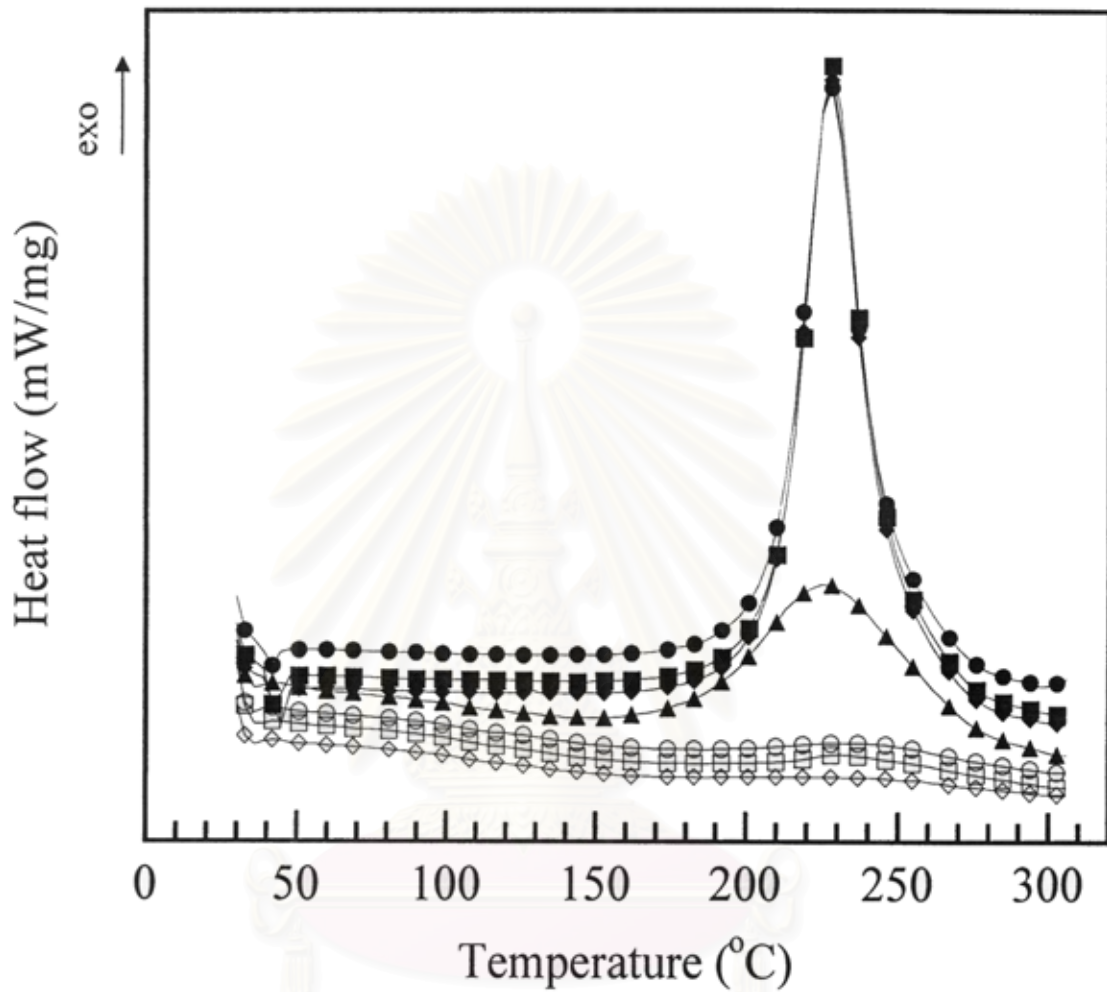
Figure 5.2: Effect of curing time with thermal heating at 200°C on composites of 4wt% SiC$_w$ content. (●) 0 min, (■) 30 min, (♦) 60 min, (▲) 90 min, (○) 120 min, (□) 150 min.

Figure 5.3: Effect of microwave heating on benzoxazine resin: (●) BA-a monomer, (■) BA-a monomer after cured with high microwave power at 1000 W for 15 min.

Figure 5.4: DSC thermograms of microwave treated 4 wt% SiC_w-filled polybenzoxazine molding compound at irradiation time of 15 min: (●) 150 W, (■) 180 W, (♦) 210 W, (▲) 240 W, (○) 270 W, (□) 300 W, (◊) 330.
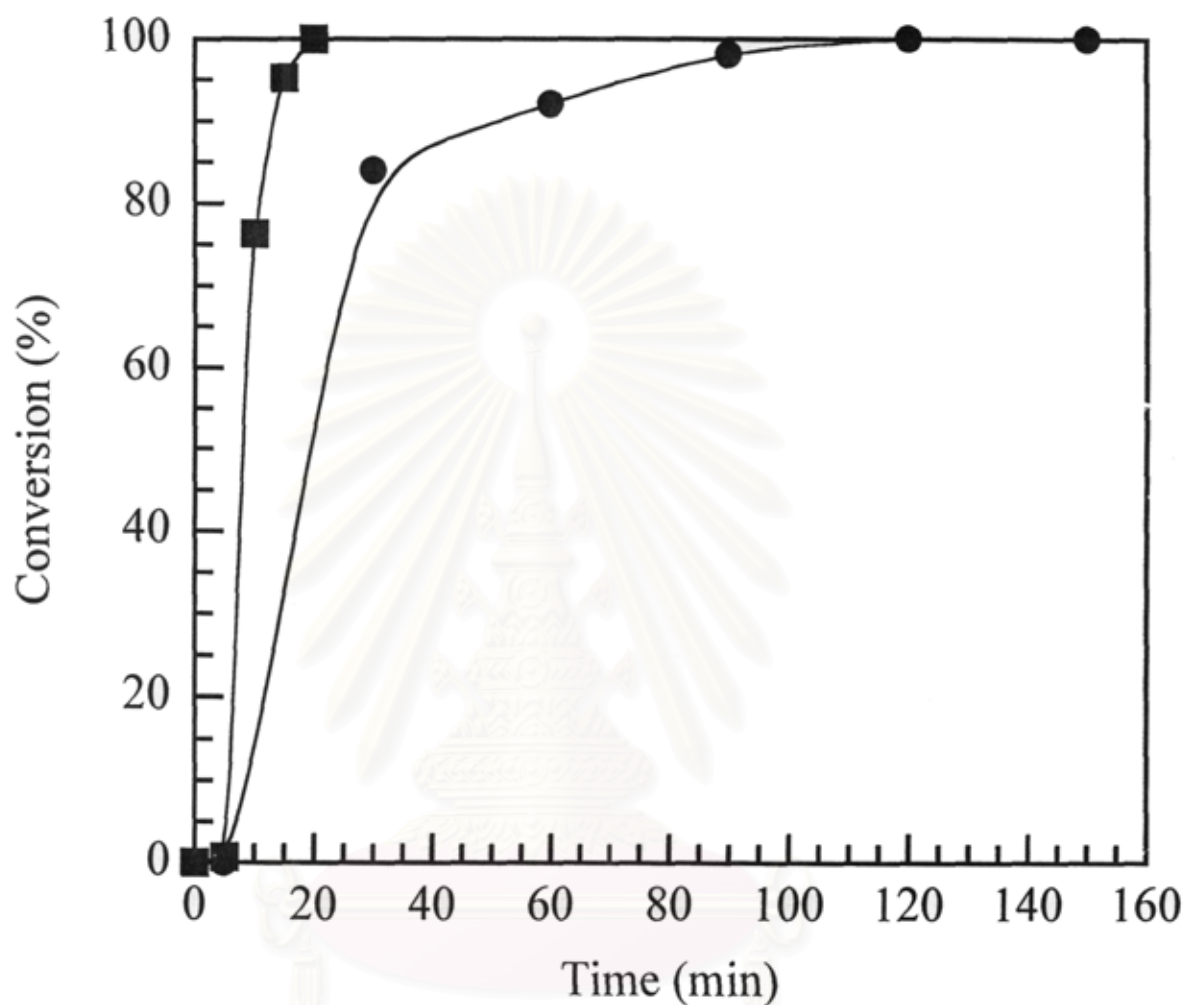
Figure 5.5: The conversion-time curve of 4 wt% SiC$_w$-filled polybenzoxazine composite: (■) microwave-cured at 2.45 GHz and 270 W, (●) thermal-cured at 200°C.

Table 5.1: Comparative energy consumption for curing 4 wt% SiC$_w$/PBZ composite to over 97% conversion by conventional thermal cure and by microwave processing.

Equipment for Cure	Power (W)	Time (min)	Energy Consumption (J/g)	Cost* (Baht/10 g)
Hot-pressed (200°C)	1,000-1,500	120	7.2-10.8 × 10^6	7.25-10.9
Microwave Oven	270	20	0.32 × 10^6	0.36

* based on small business at working day between 9.00 am. to 10.00 pm. (www.pea.co.th).
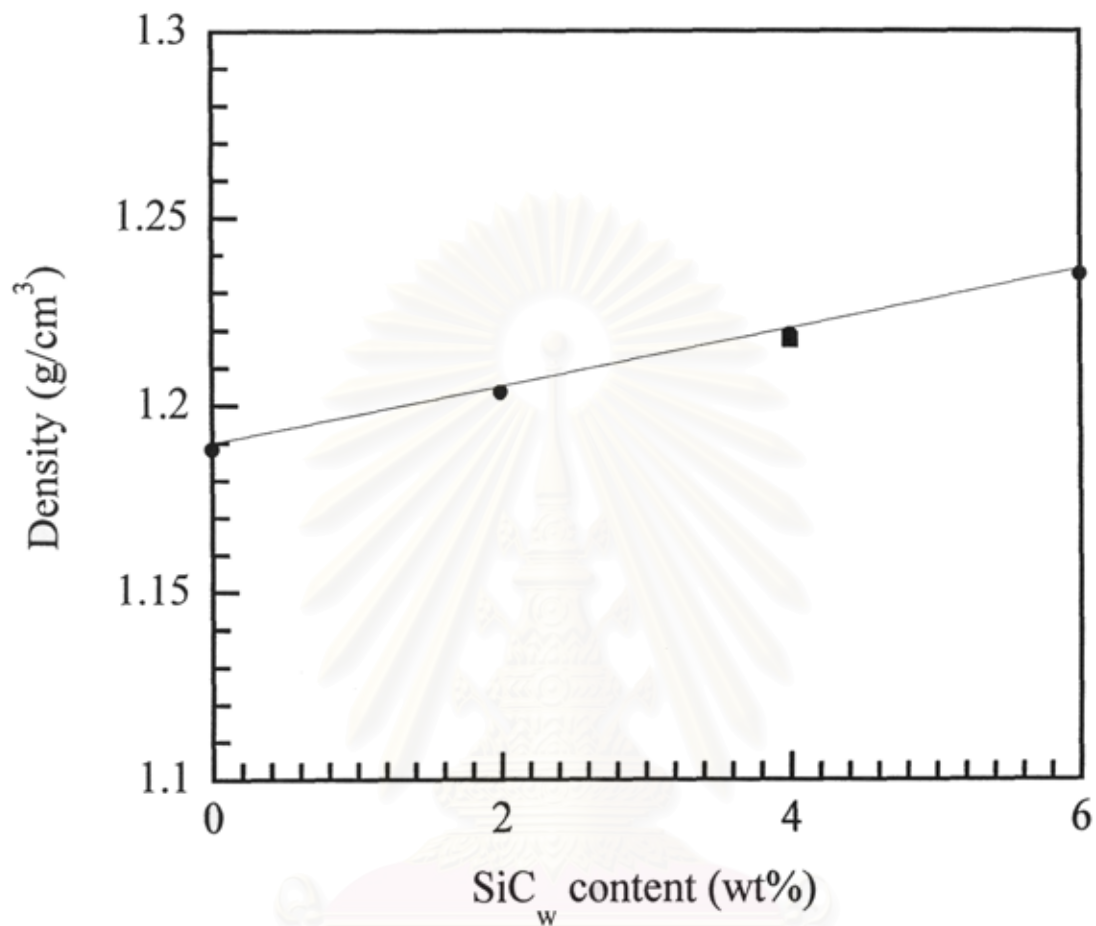
Figure 5.6: The theoretical and actual density of SiC$_w$-filled polybenzoxazine composites at different content of SiC$_w$: (−) theoretical density, (●) actual density of thermal-cured composite, (■) actual density of microwave-cured composite.
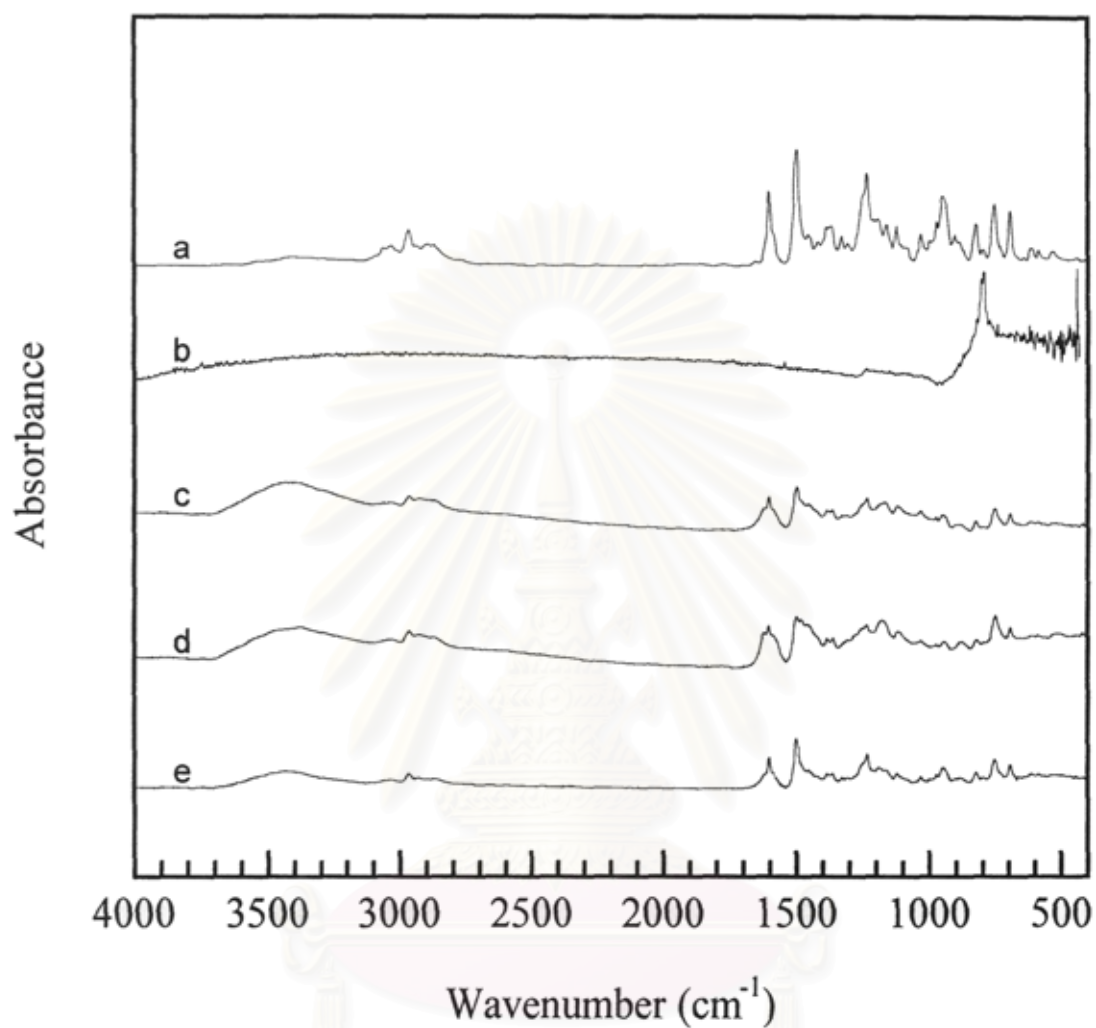
Figure 5.7: FT-IR Spectra of compounds: (a) benzoxazine monomer, (b) silicon carbide whisker (SiC$_w$), (c) polybenzoxazine (PBZ), (d) SiC$_w$-filled PBZ composite at 4 wt% of SiC$_w$ cured by thermal heating, and (e) SiC$_w$-filled PBZ composite at 4 wt% of SiC$_w$ cured by microwave heating.
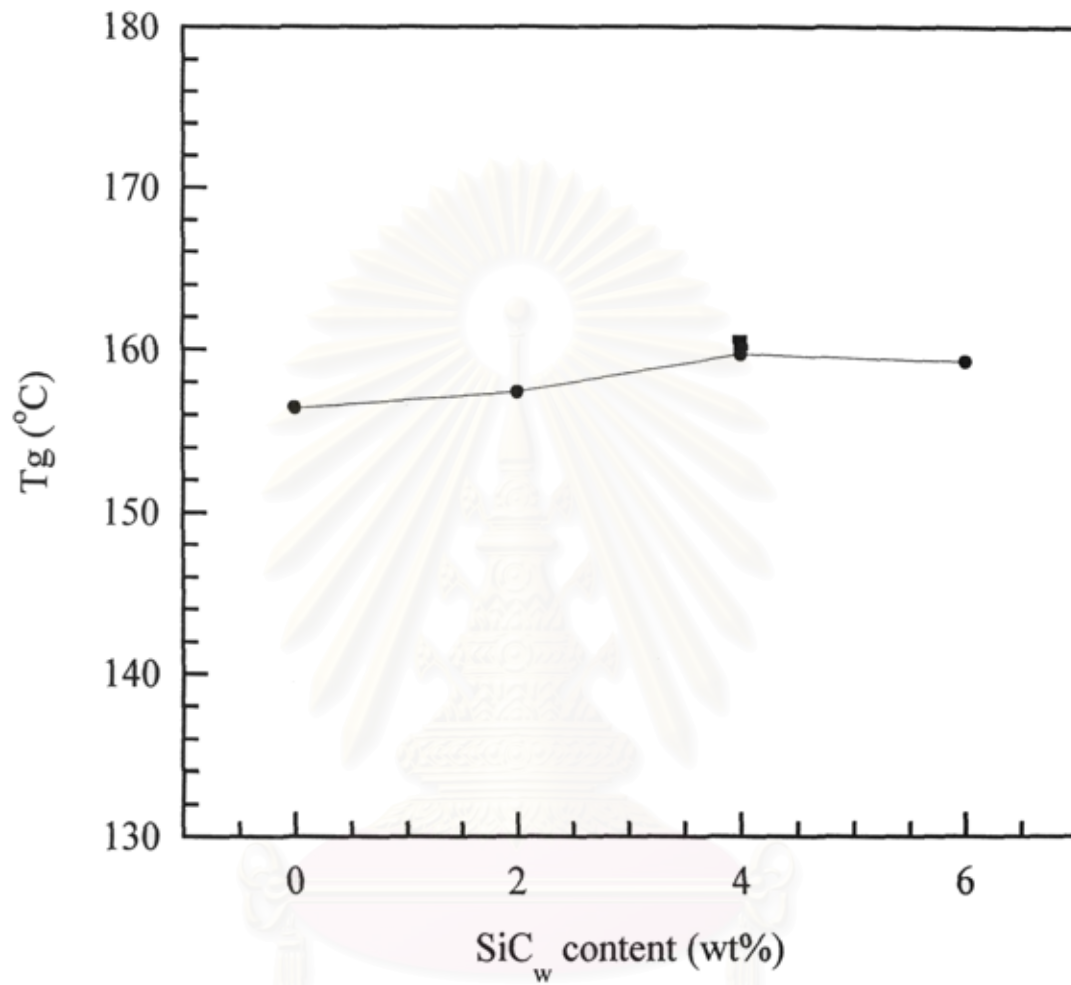
Figure 5.8: Relation between SiC whisker content and glass transition temperature of polybenzoxazine composite: (●) thermal-cured, (■) microwave-cured.
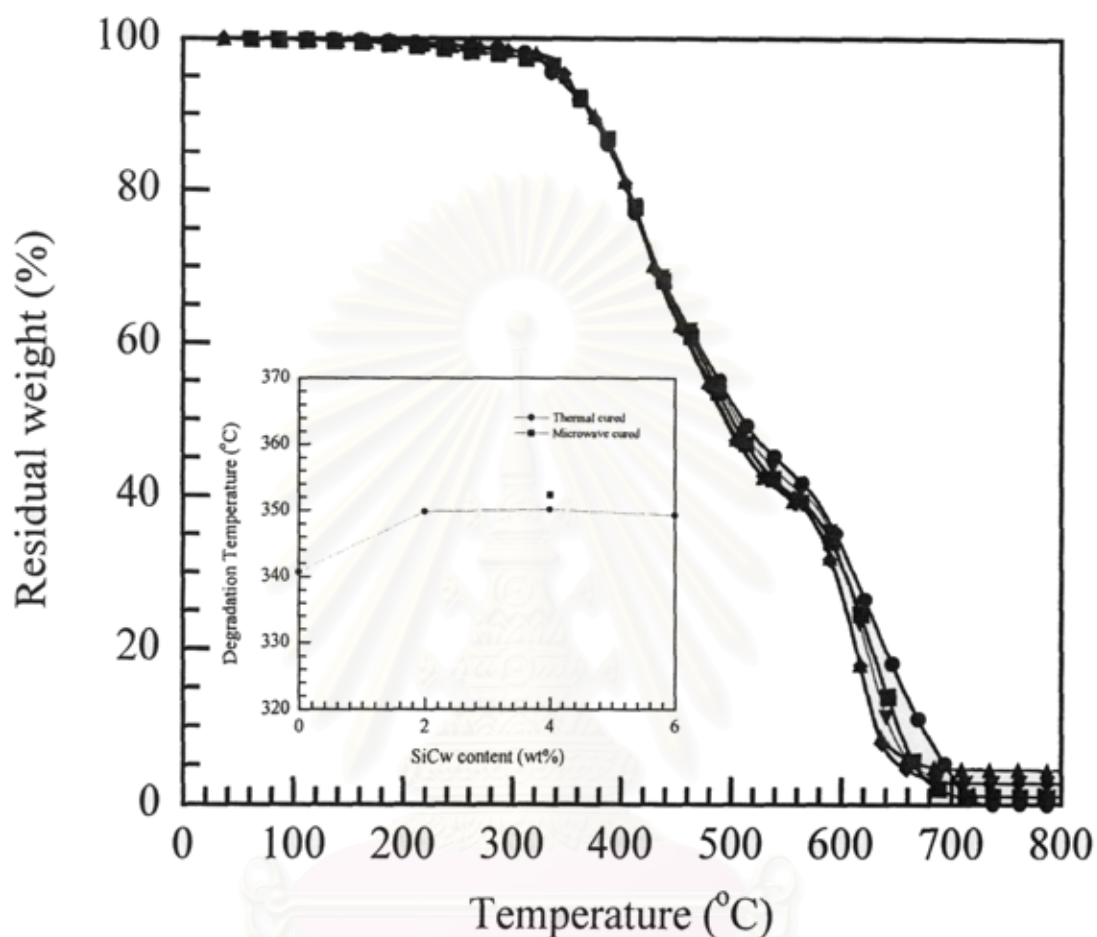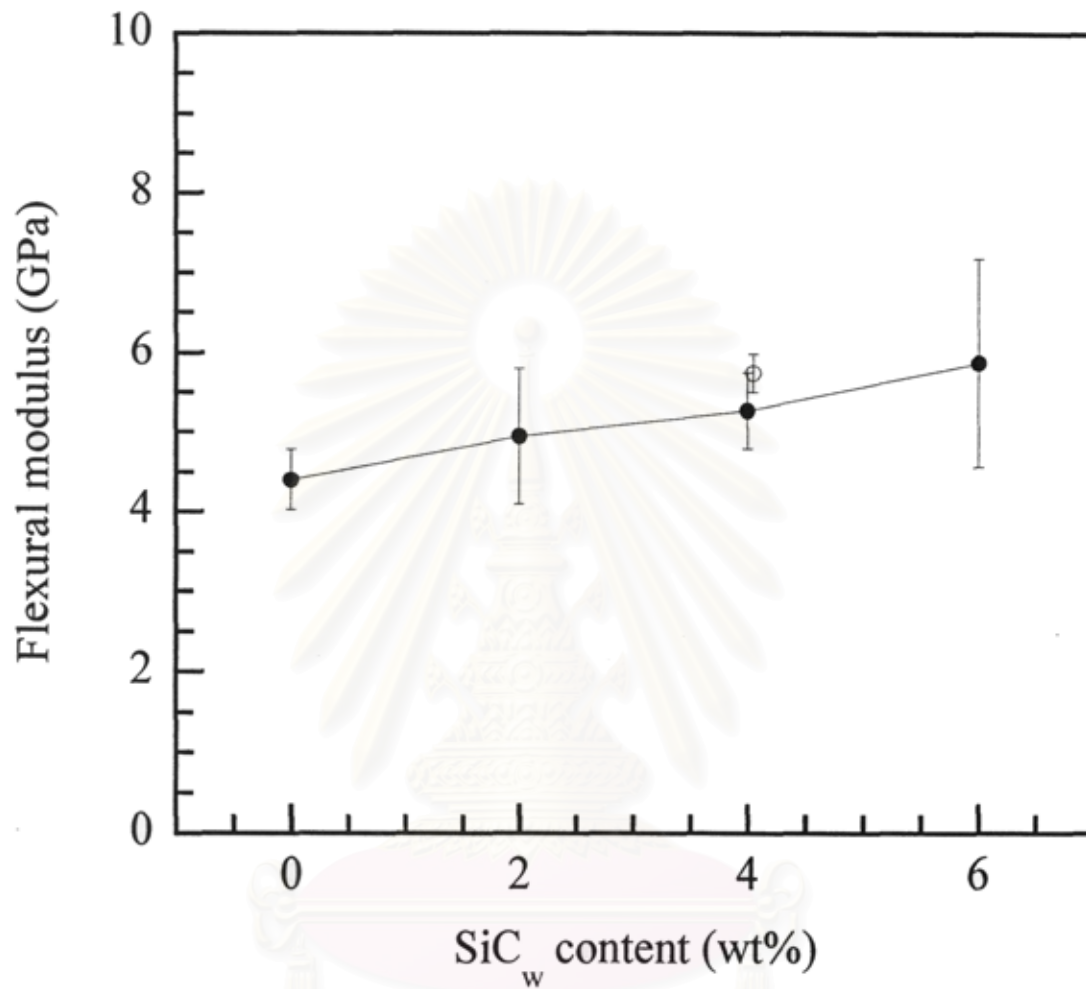
Figure 5.9: The TGA thermograms of composites: (●) polybenzoxazine cured by heat, (■) 2 wt% SiC_w cured by heat, (♦) 4 wt% SiC_w cured by heat, (▲) 6 wt% SiC_w cured by heat, (▼) 4 wt% SiC_w cured by microwave radiation.

Table 5.2: The conversion at different position of SiC$_w$-filled polybenzoxazine composite with microwave-cured.

Distance from Center (cm)	Conversion (%)
-2	98.78
-1	98.25
0	100.00
1	98.50
2	97.74

Figure 5.10: Relation between SiC whisker content and the flexural modulus of polybenzoxazine composites: (●) thermal-cured, (○) microwave-cured.
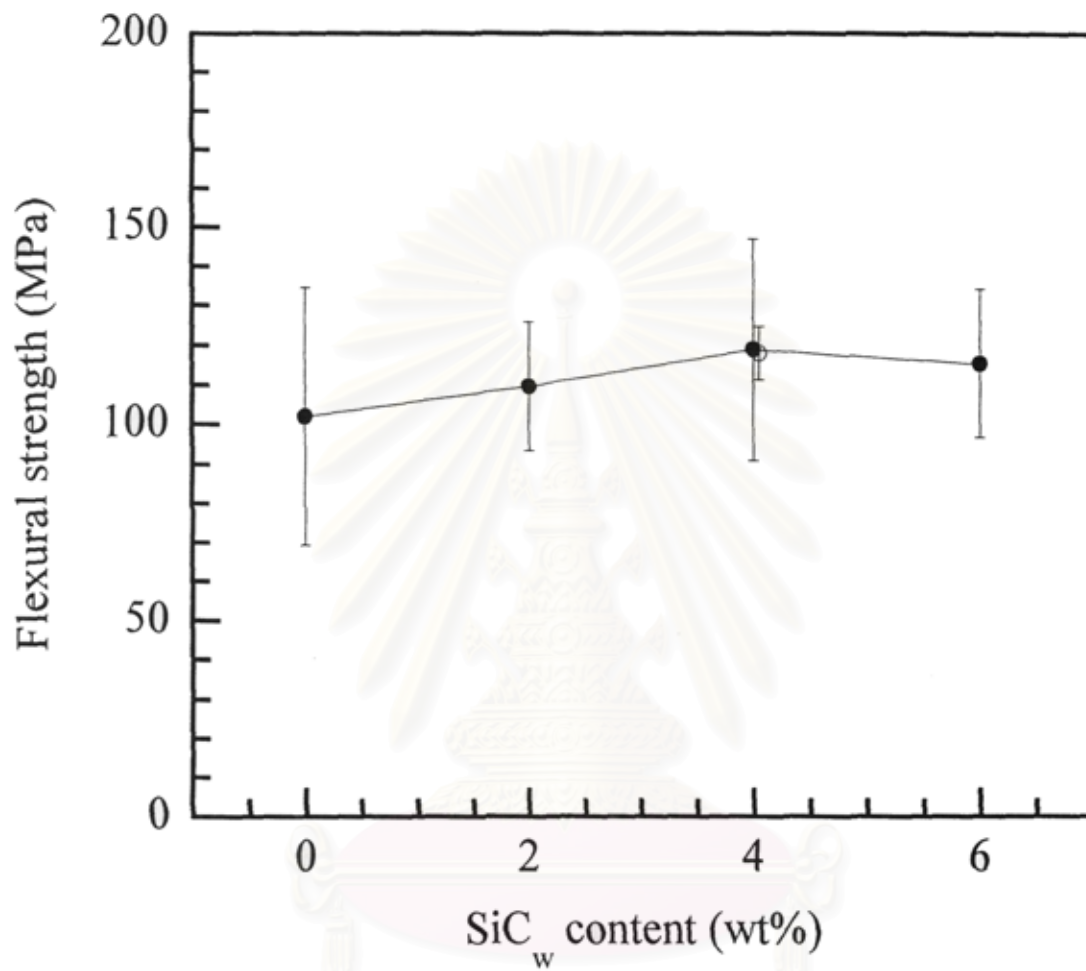
Figure 5.11: Relation between SiC whisker content and the flexural strength of polybenzoxazine composites: (●) thermal-cured, (○) microwave-cured.

Figure 5.12: The stress-strain curve under axial compression: (●) neat polybenzoxazine, (■) 2% SiC_w-filled PBZ cured by thermal, (♦) 4% SiC_w-filled PBZ cured by thermal, (▲) 6% SiC_w-filled PBZ cured by thermal, (○) 4% SiC_w-filled PBZ cured by microwave.
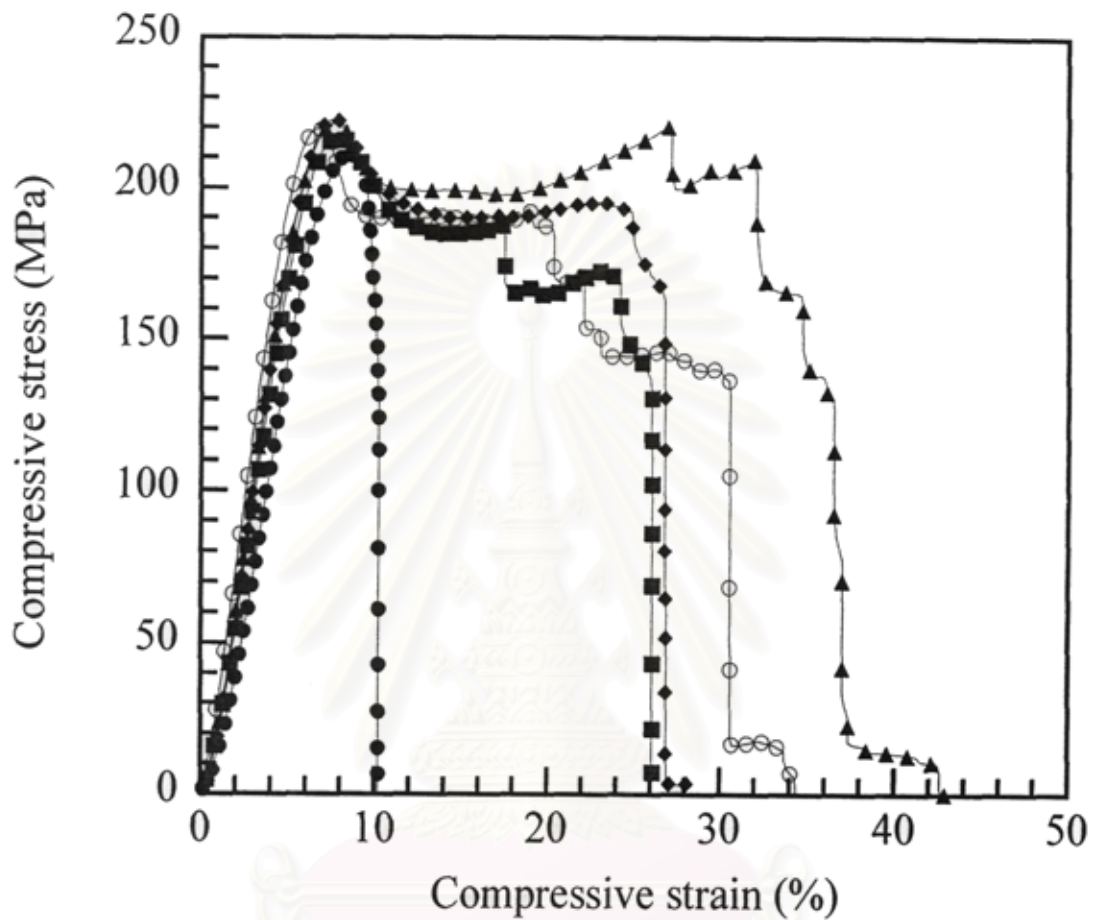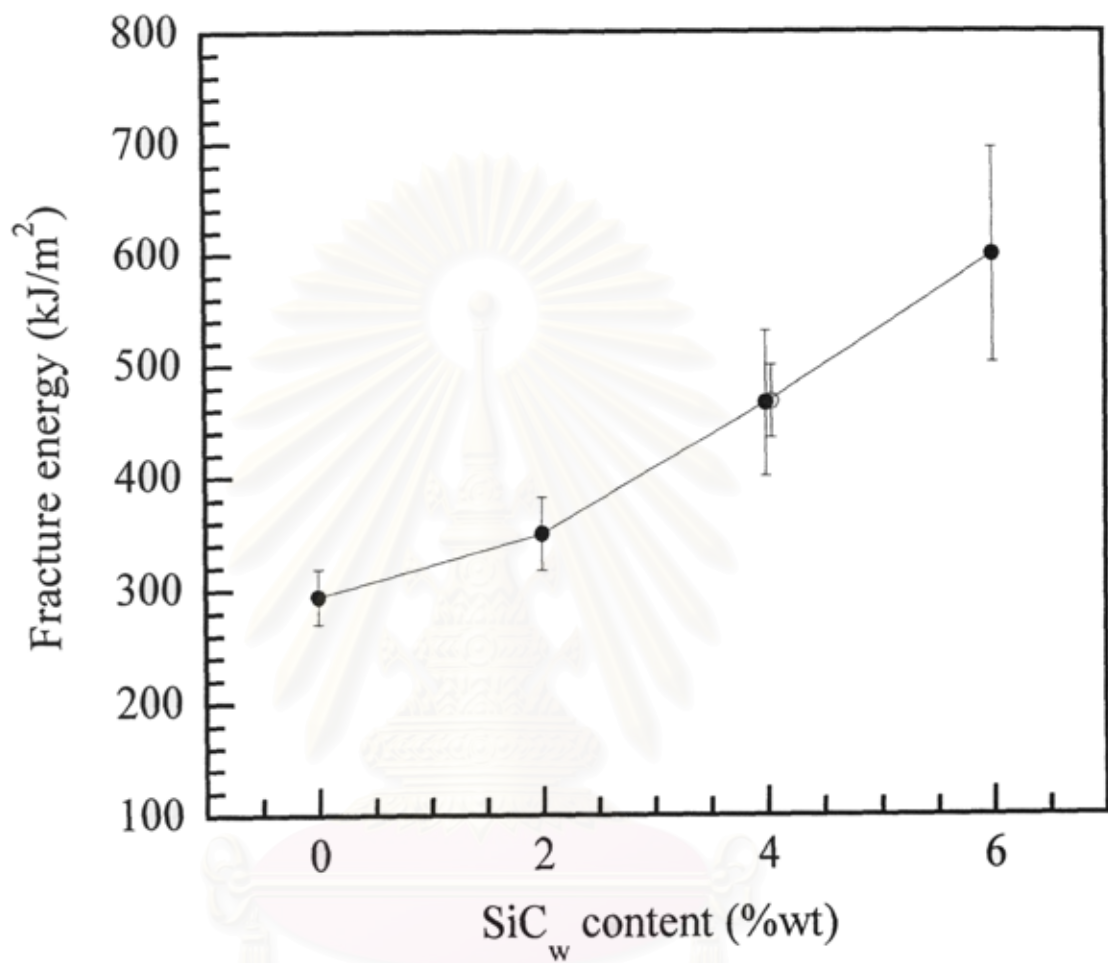
53

Figure 5.13: Relation between SiC whisker content and fracture energy of polybenzoxazine composites: (●) thermal-cured, (○) microwave-cured.
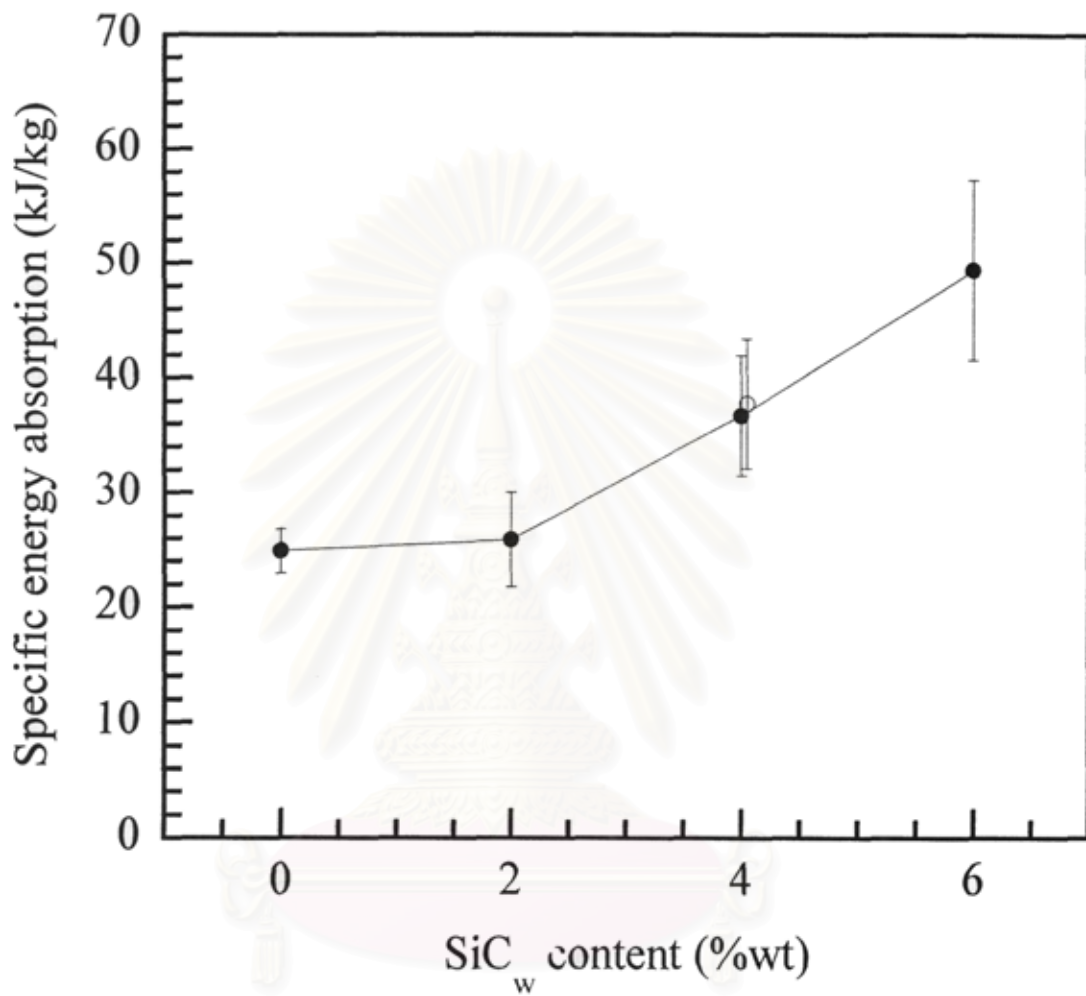
Figure 5.14: Relation between SiC whisker content and specific energy
absorption of polybenzoxazine composites:
(●) thermal-cured, (○) microwave-cured.
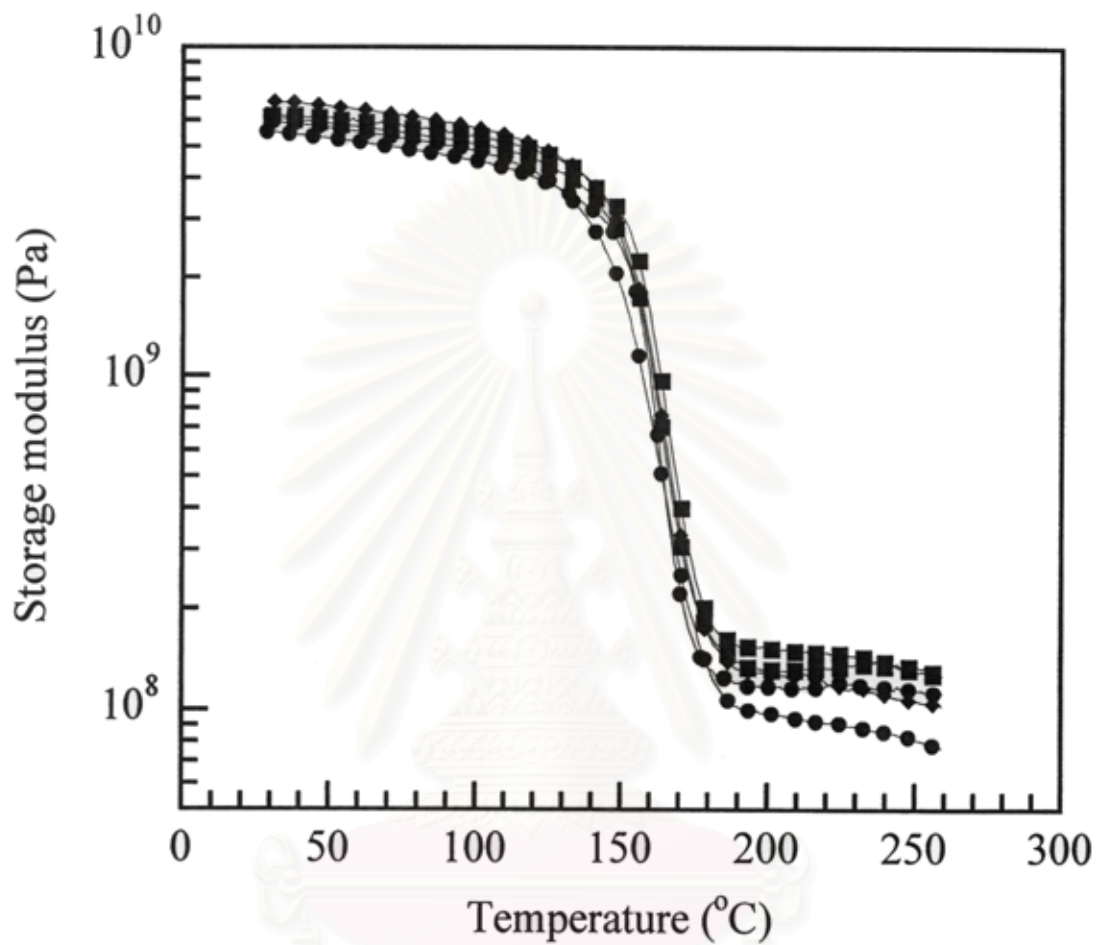
Figure 5.15: The DMA thermograms of storage modulus: (•) neat polybenzoxazine (PBZ) cured by thermal, (■) 2% SiC$_w$-filled PBZ cured by thermal, (♦) 4% SiC$_w$-filled PBZ cured by thermal, (▲) 6% SiC$_w$-filled PBZ cured by thermal, (▼) 4% SiC$_w$-filled PBZ cured by microwave.
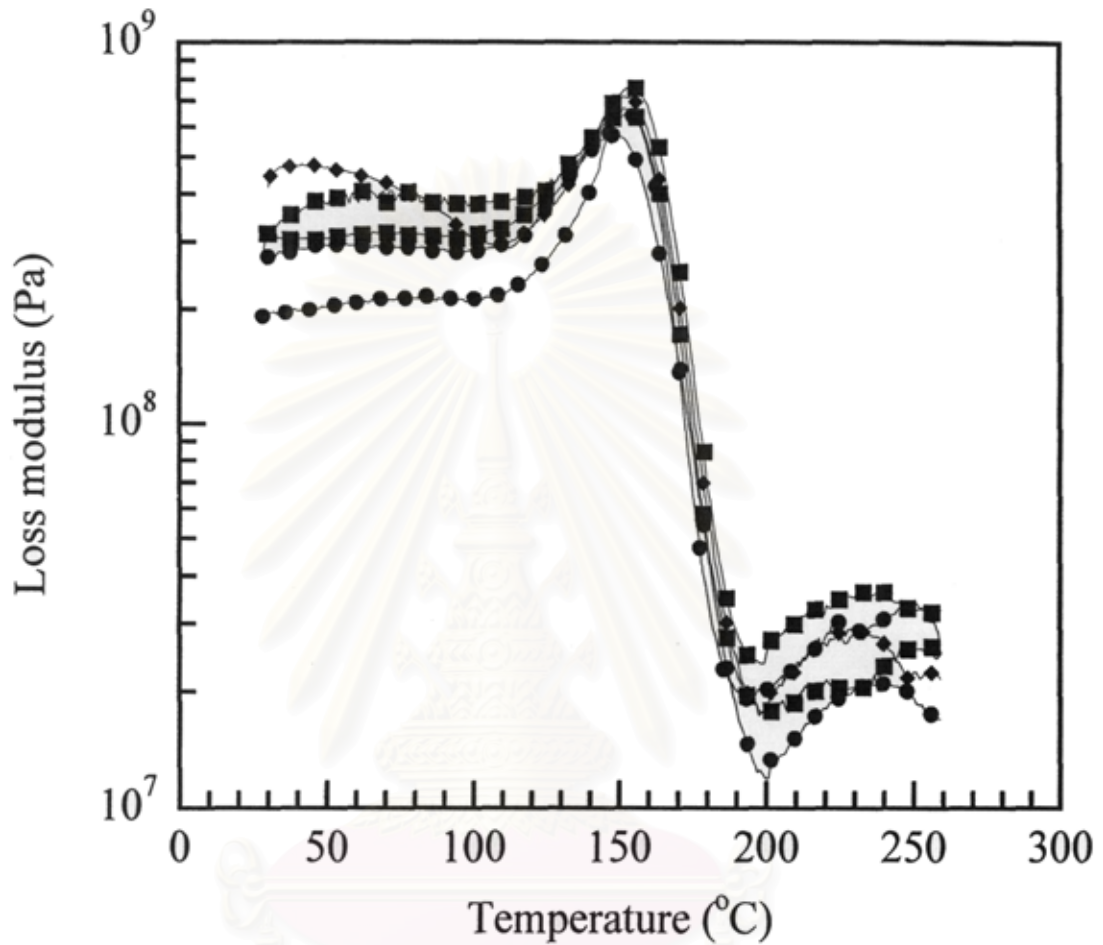
Figure 5.16: The DMA thermograms of loss modulus: (●) neat polybenzoxazine (PBZ) cured by thermal, (■) 2% SiC$_w$-filled PBZ cured by thermal, (♦) 4% SiC$_w$-filled PBZ cured by thermal, (▲) 6% SiC$_w$-filled PBZ cured by thermal, (▼) 4% SiC$_w$-filled PBZ cured by microwave.
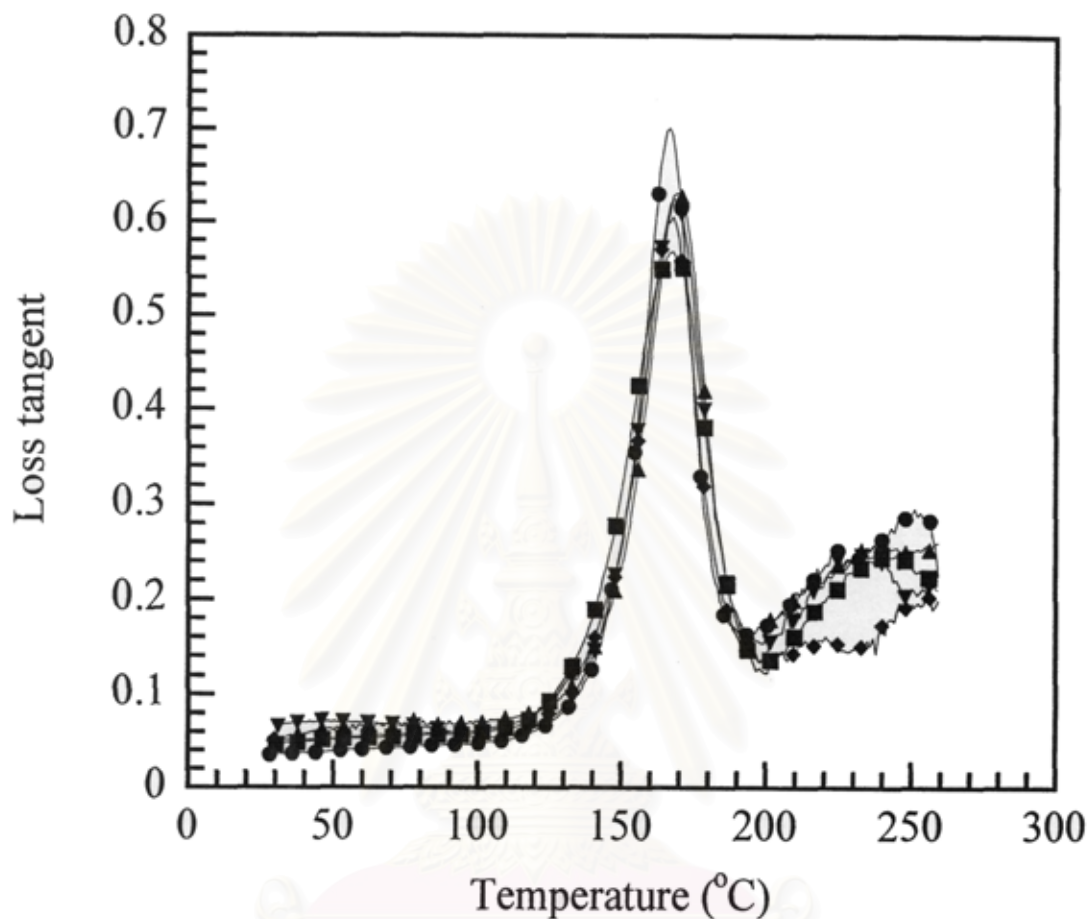
Figure 5.17: The DMA thermograms of loss tangent: (•) neat polybenzoxazine (PBZ) cured by thermal, (■) 2% SiC_w-filled PBZ cured by thermal, (♦) 4% SiC_w-filled PBZ cured by thermal, (▲) 6% SiC_w-filled PBZ cured by thermal, (▼) 4% SiC_w-filled PBZ cured by microwave.

Top side
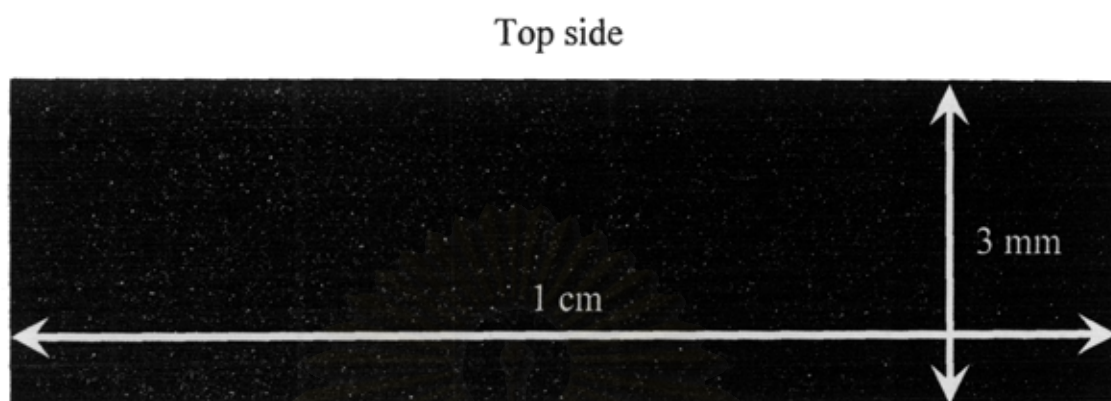
Bottom side

Figure 5.18: EDX mapping along fracture surface with the thickness of 3 mm at 50 times magnification of 6 wt% SiC_w-filled polybenzoxazine composite.
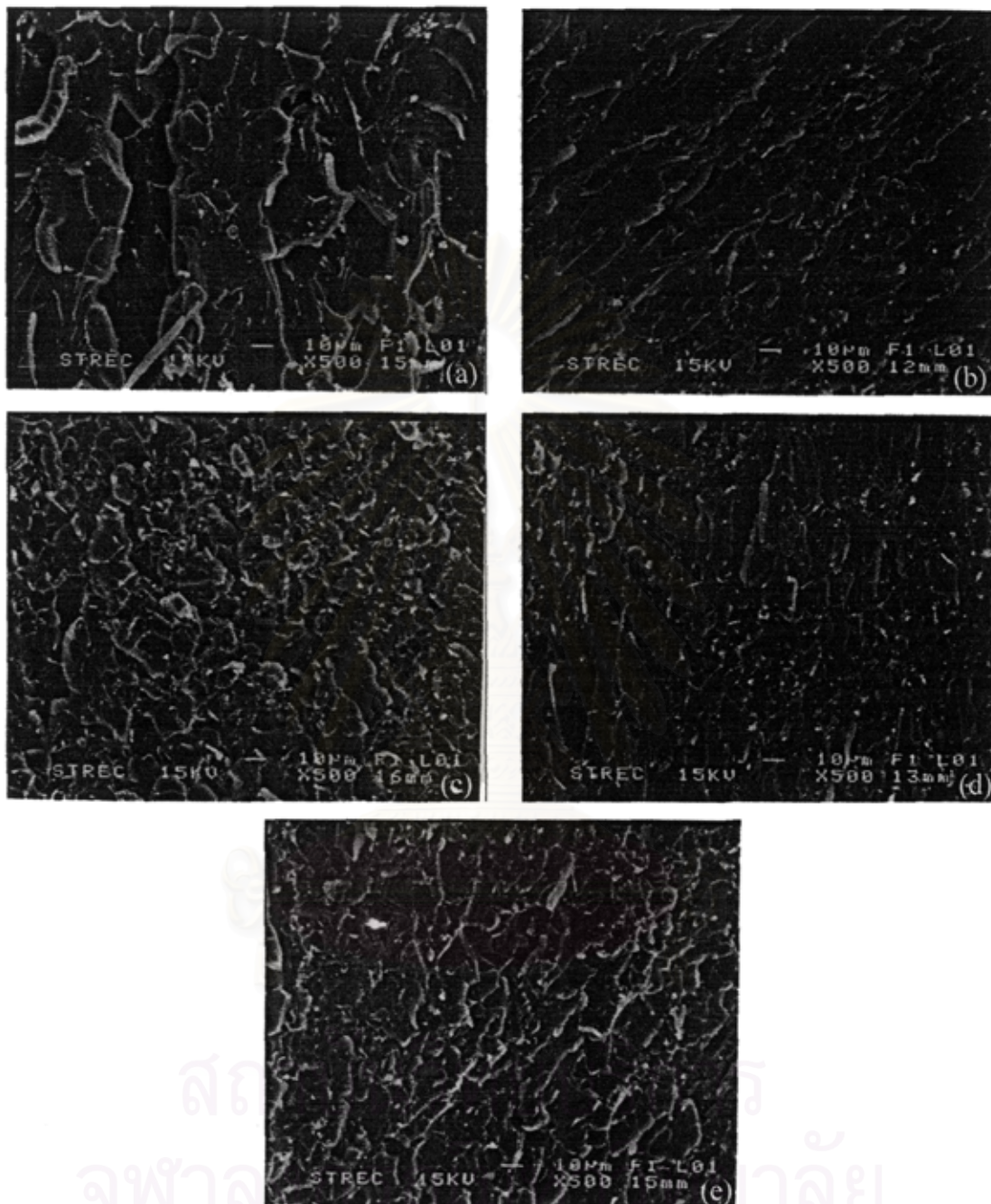
Figure 5.19: SEM micrographs of fracture surface of SiC_w-filled polybenzoxazine composites cured by thermal heating: (a) neat polybenzoxazine (PBZ), (b) 2 wt% SiC_w-filled PBZ, (c) 4 wt% SiC_w-filled PBZ, (d) 6 wt% SiC_w-filled PBZ.
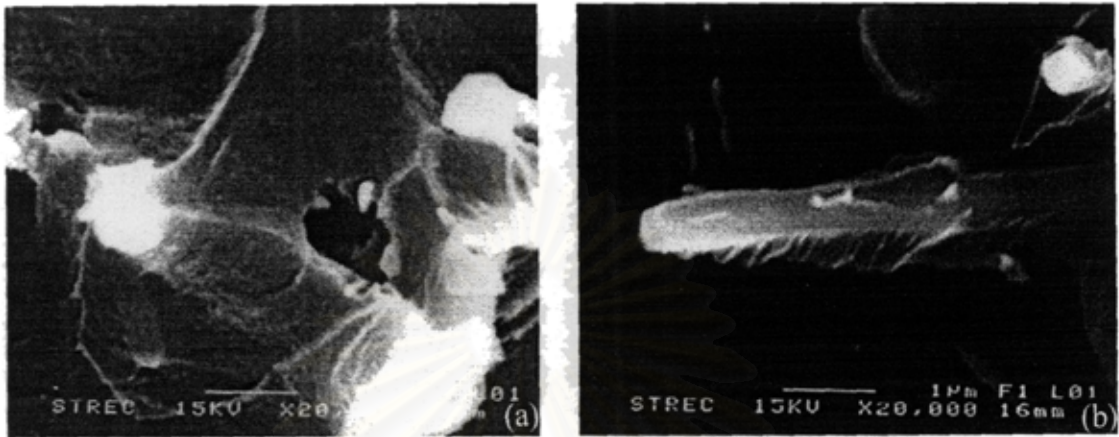
Figure 5.20: SEM micrographs of SiC$_w$-filled polybenzoxazine composites: (a) hole, (b) protruding SiC$_w$.

CHAPTER VI

CONCLUSIONS

The effect of microwave cure and conventional thermal cure on thermal and mechanical properties of SiCw-filled polybenzoxazine was investigated. The optimal SiC_w content to effectively couple with microwave to yield a fully cured polybenzoxazine was found to be about 4% by weight. The optimum processing condition of SiC_w-filled polybenzoxazine composites for thermal curing was 200^oC for 2 hours and for microwave curing was 270 W for 20 minutes. The glass transition temperature and flexural modulus of the composites increased slightly within the evaluated SiC_w content up to 6% by weight and was not significantly affected by the two processing methods. The specific energy absorption upon uniaxial compression was found to increase with the SiC_w content. The SEM micrographs of the composite fracture surface revealed substantial adhesion between the SiC_w and the polybenzoxazine matrix.

6.1 Recommendation for Further Study

1. The mechanical properties of microwave-cured composite can be higher than thermal-cured composite by increasing the thickness of the composite.
2. The microwave absorption can be increased by using high dielectric constant material.
3. The microwave processing for SiC_w-filled polybenzoxazine can be used in complicate structure.

REFERENCES

Agag, T. and Takeichi, T. Novel Benzoxazine Monomers Containing ρ-Phenyl Propargyl Ether: Polymerization of Monomers and Properties of Polybenzoxazine. Macromolecules. 34 (2001) : 7257-7263.

Agag, T. and Takeichi, T. Polybenzoxazine - montmorillonite hybrid nanocomposites: synthesis and characterization. Polymer. 41 (2000) : 7083-7090.

Avci, A.; Arikan, H. and Akdemir, A. Cement. Concrete. Res. 34 (2004) : 429-434.

Bai, S.L. and Djafari, V. Interfacial properties of microwave cured composites. Composites. 26 (1995) : 645-651.

Bai, S.L.; Djafari, V.; Andreani, M. and Francois, D. A comparative study of the mechanical behavior of an epoxy resin cured by microwaves with one cured thermally. Eur. Polym. J. 31(9) (1995) : 875-884.

Beldjoudi, N. and Gourdenne, A. Microwave curing of epoxy resins with diaminodiphenylmethane – III. Pulse frequency dependence in pulsed irradiations. Eur. Polym. J. 24(1) (1988) : 53-59.

Bengisu, M. and Inal, O.T. Whisker toughening of ceramics: toughening mechanisms, fabrication, and composite properties. Annu. Rev. Mater. Sci. 24 (1994) : 83-124.

Bershtein, V. A. and Egorov, V. M. Differential Scanning Calorimetry of Polymers: Physics, Chemistry, Analysis, Technology. New York: Ellis Horwood Limited., 1994.

Boey, F.Y.C. and Yap, B.H. Microwave curing of an epoxy-amine system: effect of curing agent on the glass-transition. Polym. Test. 20 (2001) : 837-845.

Boey, F.Y.C.; Yap, B.H.; and Chia, L. Microwave curing of epoxy-amine system – effect of curing agent on the rate enhancement. Polym. Test. 18 (1999) : 93-109.

Callister W.D. Materials Science and Engineering an Introduction, 6th edition. United States of America: John Wiley & Sons, 2003.

Chabinsky I.J. The practice of microwave preheating rubber prep stocks in compression and transfer molding operations. Rubber World. 188(1) (1983): 34-36.

Charrier J.M. Polymeric Materials and Processing: Plastics, Elastomers and Composites. New York: Hanser Publishers, 1990.

Deng, J. and Ai, X. Microstructure and mechanical properties of hot-pressed TiB$_2$-SiCw composites. Mater. Res. Bull. 33(4) (1998) : 575-582.

Fadini A. and Schnepel, F. –M. Vibrational Spectroscopy: Methods and Applications. New York: John Wiley & Sons, 1989.

Feit E. D. and Wilkins C.W. Jr "Polymer Materials for Electronic Applications". ACS symposium series, Washington. D.C. 184, 1982.

Harper C.A. Electronic Packaging and Interconnection Handbook, 4th edition. New York: McGraw-Hill, 2004.

Harries G.L. Properties of Silicon Carbide. London: INSPEC, the Institutions of Electrical Engineers. 1995.

Hatakeyama T. and Quinn, F. X. Thermal Analysis: Fundamentals and Applications to Polymer Science. New York: John Wiley & Sons, 1994.

Hull, D. An Introduction to Composite Materials. Cambridge: Great Britain at the University Press, 1990.

Ippen, J. Formulation for continuous vulcanization in microwave heating systems. Rubber. Chem. Technol. 44(1) (1971) : 294-306.

Ishida, H. Process of benzoxazine compounds in solventless systems. U.S. Patent 5,543,516 (1996).

Ishida, H. and Allen, D.J. Physical and mechanical characterization of near-zero shrinkage polybenzoxazines. J. Polym Sci. 34(1996) : 1019-1030.

Ishida, H. and Chaisuwan, T. Mechanical property improvement of Carbon fiber reinforce polybenzoxazine by rubber interlayer. Polym. Compos. 24 (2003) : 597-607.

Ishida, H. and Rimdusit, S. Very high thermal conductivity obtained by boron nitride-filled polybenzoxazine. Thermochim. Acta. 320(1998) : 177-186.

Ishida, H. and Rodriquez, Y. Curing Kinetics of a New Benzoxazine based Phenolic Resin by Differential Scanning Calorimetry. Polymer, 36(1995) : 3151-3158.

Jacob, J.; Chia, L.H.L.; and Boey, F.Y.C. Comparative study of methyl methacrylate cure by microwave radiation versus thermal energy. Polym. Test. 14(1995) : 343-354.

Jang, J.; Kim, J.; and Bae, J.Y. Synergistic effect of ferric chloride and silicon mixtures on the thermal stabilization enhancement of ABS. Polym. Degrad. Stabil. 90(2005) : 508-514.

Jang, J. and Seo, D. Performance improve of rubber-modified polybenzoxazine. J. Appl. Polym. Sci. 67(1998) : 1-10.

Jang, J. and Shin, S. Cure studies of a benzoxazine based phenolic resin by isothermal experiment. Polym. J. 27 (1995) : 601.

Jang, J. and Yang, H. Toughness improvement of carbon-fibre/polybenzoxazine composites by rubber modification. Compos. Sci. Technol. 60 (2000) : 457-463.

Kim, J.; Baillie, C.; and Mai, Y.W. Interfacial debonding and fibre pull-out stresses: Part. A critical comparison of existing theories with experiments. J. Mater. Sci. 27(1992) : 3143-3154.

Kim, H. and Char, K. Dielectric changes during the curing of epoxy resin based on the diglycidyl ether of bisphenol A (DGEBA) with diamine. Bull. Korean. Chem. Soc. 20(11) (1999) : 1329-1334.

Kim, H.D. and Ishida, H. Model compounds study on the network structure of polybenzoxazines. Macromolecules. 36 (2003) : 8320-8329.

Kim, J. and Mai, Y.W. High strength, high fracture toughness fibre composites with interface control-a review. Compos. Sci. Technol. 41 (1991) : 333-378.

Kim, J. and Mai, Y.W. Engineered interfaces in fibre-reinforced composites. UK: Elsevier Publisher, 1998.

Khatri, S.C. and Koczakb, M.J. Thick-section AS4-Graphite/E-glass/PPS hybrid composites:Part 1. tensile behavior. Compos. Sci. Technol. 56 (1996) : 181-192.

Koenig J.L. Spectroscopy of Polymer, 2nd edition. Amsterdam: Elsevier, 1999.

Ku, H.S.; Siu, F.; Siores, E.; Ball, J.A.R.; and Blicblau, A.S. Applications of fixed and variable frequency microwave (VFM) facilities in polymeric materials processing and joining. J. Mater. Process. Tech. 113 (2001) : 184-188.

Largarov, A.N.; Matitsin, S.M.; and Sarychev, A.K. Microwave properties of polymer materials containing conducting inclusions. Proceedings of the American Chemical Society. 66(1992) : 426-427.

Li, G.; Pourmohamadian, N.; Cygan, A.; Peck, J.; Helms, J.E.; and Pang, S.S. Fast repair of laminated beam using UV curing composites. Compos. Struct. 60 (2003) : 73-81.

Lin, G.Y.; Lei, T.C.; Wang, S.X.; and Zhou, Y. Microstructure and mechanical properties of SiC whisker reinforced ZrO_2 (2 mol% Y_2O_3) based composites. Ceram. Int. 22 (1996) : 199-205.

Mark, H. F., Gaylord, N. G. and Bikales, N. M. Encyclopidia of polymer science and engineer. Volume 5. New York: John Wiley & Sons, 1966.

Mark, H. F., Gaylord, N. G. and Bikales, N. M. Encyclopidia of polymer science and engineer. Supplement Volume 1. New York: John Wiley & Sons, 1976.

Matthews, F.L., Rawlings, R.D. Composite Materials: Engineering and Science, 1st edition, London: Chapman & Hill, 1994.

Nair, C.P.R. Advances in addition-cure phenolic resins. Prog. Polym. Sci. 29 (2004) : 401-498.

Nightingale, C. and Day, R.J. Flexural and interlaminar shear strength properties of carbon fiber/epoxy composites cured thermally and with microwave radiation. Compos. Part A. 33 (2002) : 1021-1030.

Ning, X. and Ishida, H. Phenolic Materials via ring-opening polymerization of benzoxazines: effect of molecular structure on mechanical and dynamic mechanical properties. J. Polym. Sci. 32 (1994) : 921-927.

Nho, Y.C.; Kang, P.H.; and Park, J.S. The characteristics of epoxy resin cured by γ-ray and E-beam. Radiat. Phys. Chem. 71 (2004) : 241-244.

Otoishi, S. and Tange, Y. Effect of a catalyst on the formation of SiC whiskers from polysilane. Bull. Chem. Soc. Jpn. 72 (1999) : 1607-1613.

Piyawan, T. Studies of Natural Fiber/Polymer Composites from Bamboo(*Bambusa blumeana* Schult). Master Dissertation, Graduate School, Chulalongkorn University, 1998.

Ray, A.K.; Fuller, E.R. and Banerjee, S. Fatigue crack growth rate and fracture toughness of 25 wt% Silicon carbide whisker reinforced alumina composite with residual porosity. J. Eur. Ceram. Soc. 16 (1996) : 503-513.

Rimdusit, S. and Ishida, H. Development of new class of electronic packaging materials based on ternary systems of benzoxazine, epoxy, and phenolic resins. Polymer. 41 (2000) : 7941-7949.

Rimdusit, S. and Ishida, H. Synergism and multiple mechanical relaxation observed in ternary systems based on benzoxazine, epoxy, and phenolic resins. J. Polym. Sci. Pol. Phy. 38 (2000) : 1687-1698.

Rimdusit, S.; Tanthapanichakoon, W. and Jubsilp, C. High performance wood composites from highly filled polybenzoxazine. J. Appl. Polym. Sci. 99 (2006): 1240-1253.

Ryu, Z.; Zheng, J.; Wang, M.; and Zhang, B. Synthesis and characterization of silicon carbide whisker. Carbon. 39 (2001) : 1929-1941.

Satapathy, L.N.; Ramesh, P.D.; Agrawal, D.; and Roy, R. Microwave synthesis of phase-pure, fine silicon carbide powder. Mater. Res. Bull. 40 (2005) : 1871-1882.

Sawyer, L.C. and Grubb, D.T. Polymer Microscopy. New York: Chapman and Hall, 1987.

Schwartz H.F., Bosisio R.G., Wertheimer M.R., and Couderc D. Microwave curing of SR compounds. Rubber Age. 107(10) (1975) : 27-38.

Stuart, B. H. Polymer Analysis. New York: John Wiley & Sons, Inc., 2002.

Sutton, W.H. Key issues in microwave process technology. Ceramic Transactions. 36(1993) : 3-18.

Thostenson, E.T. and Chou, T.W. Microwave processing: fundamentals and applications. Composites. A 30 (1999) : 1055-1071.

Takeichi, T.; Zeidam, R.; and Agag, T. Polybenzoxazine/clay hybrid nanocomposites: influence of preparation method on the curing behavior and properties of polybenzoxazine. Polymer. 43 (2002) : 45-53.

Van, Q.L. and Gourdenne A. Microwave curing of epoxy resins with diaminodiphyenylmethane – I. general features. Eur. Polym. J. 23 (10) (1987) : 777-780.

Wang, Y.-X. and Ishida, H. Cationic ring-opening polymerization of benzoxazine. Polymer. 40(1999) : 4563-4570.

Warrior, N.A.; Turner T.A.; Robitaille F.; and Rudd, C.D. Effect of resin properties and processing parameters on crash energy absorbing composite structure made by RTM. Compos. Part A. 34 (2003) : 543-550.

Wypych, G. Handbook of Fillers, 2nd edition. Chem Tech Publishing. Toronto, (2000).

Xu, H.H.K.; Quinn, J.B.; Smith, D.T.; Antonucci, J.M.; Schumacher, G.E.; and Eichmiller, F.C. Dental resin composites containing silica-fused whiskers-effects of whisker-to-silica ratio on fracture toughness and indentation properties. Biomaterials. 23 (2002) : 735-742.

Xu, Y.; Chung, D.D.L.; and Mroz C. Compos. Part A. 32(2001) : 1749-1757.

Yarlagadda, K.D.Y.P. and Hsu, S.H. Experimental studies on comparison of microwave curing and thermal curing of epoxy resins used for alternative mould materials. J. Mater. Process. Tech. 155-156 (2004) : 1532-1538.

Zhang, Y.; Pickles, C.A.; and Cameron J. The production and mechanical properties of SiC whisker-reinforced epoxy composites. J. Reinf. Plast. Comp. 11 (1992) : 1176-1186.

Zhang, Z.; Liu, Y., Huang, Y.; Liu, L.; and Bao, J. The effect of carbon-fiber surface properties on the electron-beam curing of epoxy-resin composites. Comp. Sci. Technol. 62 (2002) : 331-337.

Zhou, J.; Shi, C.; Mei, B.; Yuan, R.; and Fu, Z. Research on the technology and the mechanical properties of the microwave processing of polymer. J. Mater. Process. Tech., 137 (2003) : 156-158.

APPENDICES

APPENDIX A

Density Determination

Appendix A-1 Density of the distilled water at the give temperature (g/cm^3).

T (°C)	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
10	0.99973	0.99972	0.99971	0.9997	0.99969	0.99968	0.99967	0.99966	0.99965	0.99964
11	0.99963	0.99962	0.99961	0.9996	0.99959	0.99958	0.99957	0.99956	0.99955	0.99954
12	0.99953	0.99951	0.99950	0.99949	0.99948	0.99947	0.99946	0.99944	0.99943	0.99942
13	0.99941	0.99939	0.99938	0.99937	0.99935	0.99934	0.99933	0.99931	0.99930	0.99929
14	0.99927	0.99926	0.99924	0.99923	0.99922	0.99920	0.99919	0.99917	0.99916	0.99914
15	0.99913	0.99911	0.99910	0.99908	0.99907	0.99905	0.99904	0.99902	0.99900	0.99899
16	0.99897	0.99896	0.99894	0.99892	0.99891	0.99889	0.99887	0.99885	0.99884	0.99882
17	0.99880	0.99879	0.99877	0.99875	0.99873	0.99871	0.9987	0.99868	0.99866	0.99864
18	0.99862	0.99860	0.99859	0.99857	0.99855	0.99853	0.99851	0.99849	0.99847	0.99845
19	0.99843	0.99841	0.99839	0.99837	0.99835	0.99833	0.99831	0.99829	0.99827	0.99825
20	0.99823	0.99821	0.99819	0.99817	0.99815	0.99813	0.99811	0.99808	0.99806	0.99804
21	0.99802	0.99800	0.99798	0.99795	0.99793	0.99791	0.99789	0.99786	0.99784	0.99782
22	0.99780	0.99777	0.99775	0.99773	0.99771	0.99768	0.99766	0.99764	0.99761	0.99759
23	0.99756	0.99754	0.99752	0.99749	0.99747	0.99744	0.99742	0.99740	0.99737	0.99735
24	0.99732	0.99730	0.99727	0.99725	0.99722	0.99720	0.99717	0.99715	0.99712	0.99710
25	0.99707	0.99704	0.99702	0.99699	0.99697	0.99694	0.99691	0.99689	0.99686	0.99684
26	0.99681	0.99678	0.99676	0.99673	0.99670	0.99668	0.99665	0.99662	0.99659	0.99657
27	0.99626	0.99623	0.9962	0.99617	0.99614	0.99612	0.99609	0.99606	0.99603	0.99600
28	0.99597	0.99594	0.99591	0.99588	0.99585	0.99582	0.99579	0.99576	0.99573	0.99570
29	0.99597	0.99594	0.99591	0.99588	0.99585	0.99582	0.99579	0.99576	0.99573	0.99570
30	0.99567	0.99564	0.99561	0.99558	0.99555	0.99552	0.99549	0.99546	0.99543	0.99540

Appendix A-2 Density of SiC whisker-filled polybenzoxazine composite.

SiC$_w$ Mass fraction	Actual density (g/cm^3)	Theoretical density (g/cm^3)
0	1.1882 ± 0.0005	1.19
0.02	1.2033 ± 0.0009	1.2051
0.04	1.2188 ± 0.0003	1.2205
0.06	1.2346 ± 0.0004	1.2363

APPENDIX B

Comparison of Processing Condition between
Thermal Cured and Microwave Cured

Appendix B-1 Heat of reaction of thermal cured 4 wt% SiC$_w$ in polybenzoxazine
composite at 200°C as a function of times.

Time (min)	Heat of reaction (J/g)
0	326.4
5	325.7
30	47.4
60	23.2
90	2.7
120	1.4
150	1.8

Appendix B-2 Heat of reaction of microwave cured 4 wt% SiC$_w$ in polybenzoxazine
composite at 270W as a function of times.

Time (min)	Heat of reaction (J/g)
0	326.4
5	323.7
10	40.18
15	13.3
20	1.66

APPENDIX C

Characterization of SiC$_w$-filled Polybenzoxazine Composites

Appendix C-1 Glass transition temperature of SiC$_w$-filled PBZ composites.

Curing method	SiC$_w$ content	Glass transition temperature (°C)	
		DSC	DMA
Thermal heating	0	156	154
Thermal heating	2	157	149
Thermal heating	4	160	152
Thermal heating	6	159	156
Microwave heating	4	160	153

Appendix C-2 Degradation temperature of SiC$_w$-filled PBZ composites.

Curing method	SiC$_w$ content	Degradation temperature (°C)	
		5% weight loss	10% weight loss
Thermal heating	0	341	372
Thermal heating	2	350	374
Thermal heating	4	350	374
Thermal heating	6	349	375
Microwave heating	4	352	373

Appendix C-3 The residual weight of SiC_w-filled PBZ composites.

Curing method	SiC_w content	Residual weight (%)	
		TGA	600^oC 12 hr in furnace
Thermal heating	0	0	0
Thermal heating	2	0.8	1.92
Thermal heating	4	2.5	3.94
Thermal heating	6	4.3	5.96
Microwave heating	4	2.5	4.00

Appendix C-4 Flexural properties of SiC_w-filled PBZ composites.

Curing method	SiC_w content	Flexural modulus (GPa)	Flexural strength (MPa)
Thermal heating	0	4.4 ± 0.38	101.79 ± 32.61
Thermal heating	2	4.94 ± 0.85	109.54 ± 16.33
Thermal heating	4	5.27 ± 0.48	118.93 ± 28.18
Thermal heating	6	5.87 ± 1.31	115.29 ± 18.71
Microwave heating	4	5.74 ± 0.24	117.93 ± 6.67

Appendix C-5 Fracture energy and specific energy absorption under compression
load of SiC_w-filled PBZ composites.

Curing method	SiC_w content	Fracture energy (kJ/m2)	Specific energy absorption (kJ/kg)
Thermal heating	0	294.37 ± 24.56	24.87 ± 1.97
Thermal heating	2	349.44 ± 32.33	25.89 ± 4.15
Thermal heating	4	465.65 ± 64.63	36.68 ± 5.24
Thermal heating	6	598.98 ± 96.78	49.35 ± 7.84
Microwave heating	4	467.08 ± 32.31	37.73 ± 5.66

Appendix C-6 The storage modulus of SiC_w-filled PBZ composites.

Curing method	SiC_w content	Storage modulus (GPa)
Thermal heating	0	5.50
Thermal heating	2	5.92
Thermal heating	4	6.10
Thermal heating	6	6.18
Microwave heating	4	6.79