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DEVELOPMENT OF HIGH PERFORMANCE CARBON FIBER BASED PREPREGS FOR HONEYCOMB STRUCTURE

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งานวิจัยนี้มีจุดมุ่งหมายพัฒนาวัสดุพรีเพลกส์คุณภาพสูงจากเส้นใยคาร์บอนเพื่อใช้ทำโครงสร้างรังผึ้งโดยมีระบบเรซินสามส่วน คือ เบนซอกซาซีนเรซิน อีพอกซีเรซิน และฟีนอลิกโนโวแลคเรซินเป็นเมตริกซ์ ทั้งนี้พรีเพลกส์ คือ เส้นใยเสริมแรงที่อาบด้วยเมตริกซ์เรซิน ซึ่งเมตริกซ์เรซินนั้นจะมีการพอลิเมอไรเซชั่นเพียงบางส่วนทำให้พรีเพลกส์อยู่ในรูปพร้อมใช้งาน การเก็บรักษาพรีเพลกส์จะอยู่ในรูปแผ่นหรือม้วน พรีเพลกส์เป็นวัสดุที่นิยมใช้งานมากในงานประเภทวัสดุในอวกาศยาน และวัสดุประกอบแต่งขั้นสูง ทั้งยังนำมาขึ้นรูปเป็นวัสดุแกนรังผึ้งได้อีกด้วย พอลิเบนซอกซาซีน (BA-a) เป็นพอลิเมอร์ในตระกูลฟีนอลิกมีคุณสมบัติที่ดีหลายประการ เช่น สังเคราะห์ได้ง่าย ค่าความหนืดก่อนการขึ้นรูปต่ำ ค่าการขยายตัวทางความร้อนใกล้ศูนย์ ค่าการดูดซึมน้ำต่ำและมีเสถียรภาพทางความร้อนสูง ระบบเรซินสามองค์ประกอบที่ได้มีความสามารถในการขึ้นรูปสูง คือช่วงอุณหภูมิของการขึ้นรูปที่กว้างและให้ค่าสมบัติหลังการบ่มที่ดี โดยในระบบมีอีพอกซีทำหน้าที่เป็นสารลดความหนืดและยังช่วยเพิ่มปริมาณการเชื่อมโยงของสายโซ่โมเลกุล ในขณะที่ฟีนอลิกโนโวแลคนอกจากจะเป็นตัวเร่งปฏิกิริยาการบ่มของเบนซอกซาซีนเรซินซึ่งทำให้อุณหภูมิการขึ้นรูปต่ำลงแล้วยังเป็นตัวทำแข็งของอีพอกซีอีกด้วย ในการทดลองนี้จะศึกษาผลกระทบของสัดส่วนของเรซินทั้งสามที่มีผลต่อสมบัติการขึ้นรูป สมบัติทางความร้อน และสมบัติทางกลของพอลิเมอร์ที่ได้ โดยมุ่งเน้นให้เหมาะสมกับการใช้เป็นเมตริกซ์ของพรีเพลกส์เป็นสำคัญ โดยที่ทำการปรับเปลี่ยนสัดส่วนของเรซินผสมต่างๆ เช่น เบนซอกซาซีน/อีพอกซี/ฟีนอลิก (BEP) ในอัตราส่วน 3:6:1 3:6:2 3:6:3 และ 3:6:4 โดยน้ำหนัก จากการทดลองพบว่าเมื่อปริมาณอีพอกซีเพิ่มขึ้นจะทำให้ความหนืดของเรซินผสมต่ำลง ในขณะที่เมื่อปริมาณฟีนอลิกเพิ่มขึ้นจะทำให้อุณหภูมิปฏิกิริยาการเชื่อมโยงของเบนซอกซาซีนเรซินลดลง โดยสามารถสังเกตได้จากการเปลี่ยนแปลงอุณหภูมิ ณ จุดสูงสุดของปฏิกิริยาการบ่มใน DSC thermograms ความสามารถในการขึ้นรูปและระยะเวลาในการเจลศึกษาด้วยหลักการ Fourier Transform Mechanical Spectroscopy (FTMS) จากการทดลองพบว่าเรซินสามระบบในสัดส่วนที่ศึกษามีช่วงอุณหภูมิการขึ้นรูปที่กว้างสามารถขึ้นรูปได้ตั้งแต่ 50 องศาเซลเซียส ไปจนถึง 200 องศาเซลเซียส และยังสามารถคงความหนืดที่ต่ำได้เป็นเวลานาน โดยที่สัดส่วน BEP362 ให้ความสามารถในการขึ้นรูปเป็นพรีเพลกส์ที่ดีที่สุด เช่น มีความหนืดต่ำ (1.4 Pa.s) และมีระยะเวลาเจลน้อยกว่า 5 นาที ค่าอุณหภูมิการเปลี่ยนสถานะคล้ายแก้วของระบบเรซินที่ศึกษามีค่าใกล้เคียงกันคืออยู่ระหว่าง 150 ถึง 165 องศาเซลเซียส อย่างไรก็ตาม BEP362 ให้ค่าอุณหภูมิการเปลี่ยนสถานะคล้ายแก้วที่สูงที่สุด คือ 165 องศาเซลเซียส นอกจากนี้ BEP362 ยังมีอายุการใช้งานที่นานโดยมีการเปลี่ยนแปลงความสามารถในการขึ้นรูปเพียงเล็กน้อย เช่น มีการเปลี่ยนแปลงน้อยกว่า 25% เมื่อเก็บรักษาไว้ที่อุณหภูมิห้องประมาณ 33 องศาเซลเซียสเป็นเวลามากกว่า 270 วัน ทั้งนี้สมบัติต่างๆเหล่านี้จะแสดงลักษณะเด่นที่ดีในระบบ BEP362 ดังนั้นอัตราส่วนผสมของเมตริกซ์ ที่เหมาะสมสำหรับทำคาร์บอนไฟเบอร์พรีเพลกส์คือ BEP362 สำหรับค่ามอดูลัสความดัดโค้งและความแข็งแรงในการดัดโค้งในระบบ BEP362 เมื่อปริมาณเส้นใยเป็น 55 เปอร์เซ็นต์โดยปริมาตรและทำการจัดเรียงเส้นใยแบบ cross-ply มีค่าประมาณ 68 จิกะปาสคาล และ 1,156 เมกกะปาสคาลซึ่งวัสดุประกอบแต่งที่ได้จากระบบ BEP362 นี้ให้ค่าความแข็งแรงที่เหมาะสม นอกจากนี้พรีเพลกส์ที่มี BEP362 เป็นเมตริกซ์เรซินยังสามารถนำมาขึ้นรูปเป็นโครงสร้างรังผึ้งได้ดี

ภาควิชา...........วิศวกรรมเคมี................ ลายมือชื่อนิสิต...

สาขาวิชา..........วิศวกรรมเคมี............... ลายมือชื่ออาจารย์ที่ปรึกษา......................................

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#4570460021: MAJOR CHEMICAL ENGINEERING
KEY WORDS: POLYBENZOXAZINE/ PREPREGS/ CARBON FIBER COMPOSITE

PASSARIN JONGVISUTTISUN: DEVELOPMENT OF HIGH PERFORMANCE CARBON FIBER BASED PREPREGS FOR HONEYCOMB STRUCTURE. THESIS ADVISOR: ASSISTANT PROFESSOR SARAWUT RIMDUSIT, Ph.D., 88 pp. ISBN 974-53-1279-7.

This research is aimed to develop a highly processable carbon fiber prepregs based on ternary mixture matrices of benzoxazine, epoxy, and phenolic resins. Prepregs is referred to a continuous fiber pre-impregnation with matrix resins. They are supplied in roll or sheet form, ready for immediate use at a composite manufacturing facility, and are widely used in the aerospace and other industries for high – performance structural applications as well as honeycomb core materials. Polybenzoxazine (BA-a), a polymer based on phenolic resin, possesses some outstanding properties such as ease of synthesis, low A-stage viscosity, near-zero shrinkage, low water absorption, and high thermal stability. Alloying with epoxy and phenolic novolac to form a ternary resin mixture can greatly broaden the properties of the polymer. The epoxy acts as a reactive diluent and crosslink enhancer of the ternary system while the phenolic resin can function as a polymerization initiator for the polybenzoxazine and/or a hardener for the epoxy resin. The effects of the resin mixture composition on processability, thermal, mechanical, and some physical properties for the composites such as cure temperature, flexural strength, and thermal stability are characterized. The resin composition was varied using different resin mass ratios i.e. benzoxazine/epoxy/phenolic (BEP) equals 361, 362, 363 and 364. It is observed that the viscosity of the matrices decreases with increasing epoxy mass fractions. In addition, the increase in phenolic novolac mass fraction effectively resulted in the decrease in curing temperature of the ternary systems. These results can be seen from the shift of an exothermic peak in the DSC thermograms to lower temperature. Processability and gel point of the matrices were investigated by using Fourier Transform Mechanical Spectroscopy (FTMS). It is found that the ternary system can provide a relatively wide range of processing window from 50 to 200^{O}C and can maintain low melt viscosity for a long period time. In addition, BEP362 show the highest processability for prepregging process due to low melt viscosity i.e. 1.4 Pa.s at 100^{o}C and can gel in less than 5 min at 180^{O}C. The glass transition temperatures of the above four ternary systems are relatively similar in values of approximately 150-165^{O}C with BEP362 showing the highest Tg of 165^{O}C. Furthermore, BEP362 can be kept at room temperature (~33^{o}C) with minimal effect on its processability i.e. a little change in Tg of the resin (less than 25% conversion of BEP362 up to 270 days). Therefore, the optimum composition of the ternary systems for making high processable carbon fiber prepregs is BEP362. The flexural modulus and flexural strength of the carbon fiber-reinforced BEP362 at approximately 55% volume of the fiber in cross-ply orientation and without any surface treatment render relatively high values of about 68 GPa and 1,156 MPa respectively. The honeycomb structure from carbon fiber-BEP362 prepregs is found to be relatively easy to fabricate as a results of the above mentioned characteristics.

Department…Chemical Engineering… Student's signature..................................

Field of study....Chemical Engineering… Advisor's signature...................................

Academic year ...…2004….. Co-advisor's signature…………………...

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CHAPTER I

INTRODUCTION

1.1 General Introduction

Advanced composite materials provide numerous useful in structural utilizations because they meet the strength, stiffness, and other mechanical property requirements for high performance applications (Buehler and Seferis, 2000; Ishida and Chaisuwan, 2003; Jang and Yang, 2000; Delmonte, 1981; Shalin, 1995; Shen and Ishida, 1996). Carbon fiber reinforced composites are often used where weight reduction and specific strength are required, i.e. in aerospace or extreme sports applications. During production of a composite, it is often required to form prepregs for easy handling and easy processing. Prepregs is referring as a continuous fiber pre-impregnation with matrix resins. They are supplied in roll or sheet form, ready for immediate use with a composite manufacturing facility, and are widely used in the aerospace and other industries for high–performance load-bearing applications.

Good prepregs characteristics include not only specific end–properties but also processability of the materials such as shelf life, pot life of the system at various temperatures, temperature range for completing cure and post-curing conditions etc. (Tyberg et al., 2000; Gan et al,2003; Goto et al.,2005; Delmonte, 1981; Markovitz, 1987; Saitou et al.,2004). There are two general prepregging methods i.e. solution and hot melt impregnation. Each method is depending on the processability of matrix resins to provide the appropriate resin viscosity to coat the reinforcing fiber. Since the composite quality is controlled by resin-fiber interfacial wetting and uniform resin content therefore the low viscosity resins are essentially required (Markovitz, 1987). In addition, at the prepregging temperature, the matrices resins are recommended to retain their low viscosity for provide some otherwise desirable end-products (1-3 Pa.s) (Gan et al., 2003). However, a time period for “B-staging” step should also minimized i.e. 1-15 minutes at 90-200°C (Sohoni et al., 1999; Goto et al., 2005). Various currently used matrices always have some shortcomings such as narrow processing window, short storage life, need of curing agent, required refrigeration for storage in epoxy and phenolic systems, and complicated processing methods of polyimide, making their utilization less user-friendly. The development of the thermally curable benzoxazine resin overcomes those drawbacks.

Polybenzoxazine a novel class of phenolic resins have a wide range of mechanical and physical properties that can be tailored to various needs. The polymer can be synthesized by ring-opening polymerization of the aromatic oxazines, no by-products released upon curing, no catalysts needed, no solvent elimination and no need of monomer purification (Ishida et al., 1996). The properties balance of the material good thermal, chemical, electrical, mechanical, and physical properties including very low A-stage viscosity, near-zero shrinkage, low water absorption, high thermal stability, good fire resistant characteristics and fast development of mechanical properties as a function of curing conversion. (Ishida et al., 1996). Hence this resin was chosen as a candidate for high performance and processability for making composites.

Furthermore, the ability of the resin to form alloys with various other resins or polymers often renders a novel class of a resin system with intriguing properties (Rimdusit and Ishida, 2000). Ishida and Allen investigated that alloys between benzoxazine resins (BA-a) and bisphenol A-typed epoxy exhibited greatly increase their cross-linked density, raising their glass transition temperature (141°C of neat polybenzoxazine to 155°C at 30% by weight of epoxy), increase flexural stress and flexural strain at break with only a minimal loss of stiffness.

Rimdusit and Ishida showed a broad range of processing and cured properties of ternary systems based on benzoxazine, epoxy and phenolic resins (BEP) can be obtained. Epoxy not only acts as a reactive diluent in the system but also contributed higher cross-linked density and flexibility compared with neat benzoxazine resins. The curing reaction is fastly happened by added phenolic in system. Therefore ternary system renders a high processability such as very low melt viscosity (0.3 Pa.s of BEP121 and BEP131 at 100°C), broader processing window (50°C to 160°C of BEP121) and thermal stability i.e. synergism in glass transition temperature BEP541 at 178°C, high char yield.

In addition for high-performance composites the excellent mechanical properties are required. However, the high degree of anisotropy and laminar structures causes most fiber-reinforced composites to delaminate by shear stress especially for composites with brittle matrices. Although polybenzoxazine shows lots of intrigued properties one shortcoming of this resin is its relatively high brittleness, particularly in basic typed polybenzoxazine such as bisphenol A-aniline species (BA-a). Many researches has been conducted to enhance the adhesion between carbon fiber and polybenzoxazine such as surfaces modification, surface treatment, rubber interlayer to yield good mechanical properties. Generally it is well recognized that epoxy resins substantially increase the adhesion in most systems. The presence of epoxy in our ternary systems is expected to be able to maintain or improve adhesion properties of the resulting resin mixture.

In this study, the suitable composition of ternary systems of benzoxazine, epoxy, and phenolic resins for utilizing as a matrix resin to form carbon fiber prepregs is evaluated. The characteristics of monomer such as viscosity, gel time, resin stability, and thermal properties are evaluated to determine the suitable matrix composition including the mechanical properties of neat resin and of carbon-fiber composites.

1.2 The Purposes of the Present Study

The major objective of this work is to develop high performance carbon fiber based prepregs based on ternary mixture matrices of benzoxazine, epoxy, and phenolic resin. The effects of the resin mixture composition of processability, thermal, mechanical, and some physical properties for the composites such as cure temperature, flexural strength, flexural modulus, and thermal stability will be characterized. The suitable composition of ternary systems of benzoxazine, epoxy, and phenolic resins for utilizing as a matrix resin to form carbon fiber prepregs is evaluated. The good adhesion between carbon fiber and BEP polymer alloys also be evaluated based on its fracture surface morphology using a scanning electron microscope.

CHAPTER II

THEORY

2.1 Advanced Composites Materials

Composite materials have a long history of usage. Depending on the types of matrices, composites can be categorized as polymer matrix composites, metal matrix composites, ceramic matrix composites, carbon – carbon composites, intermetallic composites or hybrid composites (Schwartz, 1997). In other hand based on the form of the dispersed phase, composite materials can be classified in to three commonly accepted types, fibrous composites, laminated composites, and particulate composites; respectively (Jones, 1975). Fiber reinforce composites consist of continuous or discontinuous fibers in a matrix, while laminated composites consist of layers of various materials and particulate composites are composed of particles dispersed within a matrix.

Modern structural composites frequently referred to as advanced composites. The term ‘advanced’ means the composites materials based on polymer materials with oriented, high-modulus carbon, aramid, glass or ceramic fiber (High performance composites, 1999). Composites materials are blends of two or more materials that are combined on a microscopic scale to form a useful material. A resinous binder or matrix will holds the fiber in place, distribute or transfer load, protect the dispersed either in the structure or before fabrication and control chemical and electrical properties. The fiber is strong and stiff relative to the matrix especially the fiber with a length-to-diameter ratio of over 100. The strength and stiffness of the fiber are much greater or multiples of those of the matrix material.

The structural properties of composite material are primarily from the fiber reinforcement while the binding matrix promotes processability and enhances properties i.e. stiffness, chemical and hygroscopic resistance. The useful application of advanced composite materials is aerospace application (60% capacity) (High performance composites, 1999). That is because of the advantages of advance composites such as high strength or stiffness-to-weight ratio, tailorable properties, weight reduction, longer life (no corrosion), lower manufacturing costs due to lower part count. However there are some disadvantages include difficulty in analysis, cost of raw materials and fabrication, possible weakness of transverse properties and environmental degradation of matrix. To solve the problem, proper design and material selection can avoid many of disadvantages.

In addition, the outstanding properties of composites material include exceptionally high strength and low weight; high impact resistance and dimensional stability under extreme stresses and temperatures; resistance to weathering, rot, water, chemicals, acids, oils, and solvent; and low thermal conductivity.

2.2 Material

2.2.1. Fiber

High-strength fibers used in advanced composites can be the same material or mixed (hybrid combination). The available fibers are not only carbon, glass and aramid, but also high-modulus polyethylene (PE), boron, quartz, ceramic, and newer fiber such as poly p-phenylene-2,6-benzobisoxazole (PBO) (www. compositesworld.com). These fibers can be grouped into three broad categories: carbon, organic resin, and inorganic compound. Within each group, several classes of high performance fiber materials have been developed that satisfy the basic criteria of low density, high strength and high stiffness to varying degrees. The mechanical properties of typical fiber reinforcements show in Table 2.1

Table 2.1 Properties of fiber reinforcement (encyclopedia of polymer science, 1985)

Reinforcement	Specific gravity	Tensile strength MPa	Specific strength 10^4 m	Tensile modulus GPa	Specific modulus 10^6 m
Glass					
E glass	2.54	3.4	13.8	72.4	2.9
S glass	2.48	4.6	18.7	85.5	3.5
Boron on tungsten substrate	2.63	3.1	12.0	400.0	15.5
Graphite					
High strength	1.80	2.7	15.6	262.0	14.8
High modulus	1.94	2.0	10.9	380.0	19.9
Intermediate	1.74	2.5	14.5	186.0	10.9
Organic fiber					
aramid	1.44	2.7	19.5	124.0	8.8

2.2.2. Matrix

There are several matrix choices available. Each type has an impact on the processing technique and the environmental properties of the finished composite. The first key choice is between a thermoplastic and a thermoset composite matrix. Thermoplastic composites are not in general use because high temperature (typically ranges from 300 to 400^{o}C) are required for processing, special autoclaves, processes, ovens, and bagging materials may be needed. A thermosetting matrix is widely used for advanced composites since their provided good processability, mechanical properties, and thermal properties. The following are common thermoset matrices for composites: polyesters, epoxy, bismaleimide, and polyimide respectively. (Harper, 1992)

Component unity is provided by matrix, which fulfils the following functions in a composite material (Trostyanskaya, 1995)

1. Provides shape and size stability of the article.
2. Fixes a given distribution of the fibers relative to each other.
3. Gives the material deformation stability under thermal and mechanical loading up to the level given by the performance specifications.
4. Redistributes the external action on all the elementary fibers in a composite material, including broken and distorted ones.
5. Gives the material outdoor resistance and stability in the medium for which it is intended.

The needs, or desired properties, of a matrix, depending on the purpose of the structure such as: easily processible, dimensional stability, excellent chemical resistance. A material can be the matrix of a composite material if it provides:

1. Limited complete wettability of elementary fibers in a fibrous filler at a temperature that is lower than the melt, thermal degradation or structural disorientation temperature of the fibers.
2. Lack of chemical reaction between matrix and fibers, which could modify the shape and fiber bulk properties.
3. Strong coupling over the whole surface of the elementary fiber as a result of chemical and polar interactions preserving a clear phase boundary.
4. Material monolithization and moulding of articles in regimes preventing thermodegradation and mechanical fracture or destruction of elementary fibers and disturbing their mutual arrangement (distribution)
5. Continuity of an uniform matrix distribution over the whole interstitial space at a filling degree up to 60-65 vol% and diameter of elementary fibers of 7-10 μm.

2.3 Fiber Matrix Systems

When developing a new part, designers of composites choose from a wide variety of fiber reinforcements and resin systems. Combining fiber and resin elements together to make a composite part can accomplish in numerous ways. One-step processes from the original labor-intensive wet lay-up, to highly automated method such as resin transfer molding (RTM), pultrusion and filament winding (High performance composites, 1999). In many cases the end user of the structure has fabricated the composite from prepregs. The three types of continuous fibers available as prepregs—roving, tape, and woven fabric—give the end user many options in terms of design and manufacture of a composite structure. Although the use of dry fibers and impregnation at the work (that is, filament-winding pultrusion or hand lay-up) is very advantageous in terms of costs, there are many advantages to the use of prepregs rather than wet impregnation, particularly for the manufacture of modern composites (Happer, 1992):

Prepregs reduce the handling damage to dry fibers.

Prepregs improve laminate properties by better dispersion of short fibers.

Prepregs allow the use of hard–to–mix or proprietary resin systems.

Prepregs allow more consistency because there, is a change for inspection before use.

Heat curing provides more time for the proper lay-down of fibers and for the resin to move and degas before cure.

Increased curing pressure reduces voids and improves fiber wetting.

Most prepregs have been optimized as individual systems to improve processing.

In general, the fabricators skilled in manufacturing from prepregs will not care to use wet processes.

Prepregs

Prepregs are material forms consisting of continuous unidirectional or woven fibers pre–coated with a controlled quantity of an uncured catalyzed resin formulation. They are supplied in roll or sheet form, ready for immediate use at a composite manufacturing facility, and are widely used in the aerospace and other industries for high performance structural applications.

Prepregs offer several advantages to the composite parts manufacturer over other product forms (T.Jonas, 1994) (e.g., wet lay-up):

1: The resin matrix is formulated by the prepregs supplier to give specific end–properties, such as hot/wet mechanicals, impact resistance, fire retardancy.

2: Resin formulation is consistent from batch to batch.

3: Prepregs resin content is controlled to se limits, which translates to controlled weight in the finished part.

4: Physical characteristics—resin flow, tack, drapeability, and gel time—of the prepregs can be tailored to meet end-user requirements. Resin flow is a measure of resin movement during the cure process. Flow requirements are determined by the type of process used.

Tack is a measure of the ability of a ply of prepregs to stick to another ply and to the tool surface. This is important in the lay up process.

Drapeability is a measure of the ability of the prepregs to conform to contoured tool surfaces without fiber damage, also important in the lay up process.

Gel Time is a measure of the time taken for the resin to reach an immobile state at a given temperature. This is a key parameter associate with the cure process used.

Manufacture of Prepregs

Prepregs are manufactured by taking continuous fibers and impregnating them with a precisely controlled amount of resin. Prepregs can be made from a single strand of fiber called “tow” that consists of 1K to 48K filaments. More commonly, tow is used to make unidirectional prepregs. There are two commonly used methods of manufacturing thermoset prepregs material: solution and hot melt impregnation. The prepregging process for thermoset matrices can be accomplished by feeding the fiber continuous tape, woven fabric, or roving through a resin-rich solvent solution, then removing the solvent by hot tower drying. The excess resin is removed via a doctor blade (a straight piece of material used to spread and control the amount of resin applied to roving, tow, tape, or fabric). Then the product is staged to the coldstable prepreg form (B stage). The newer technique for prepregs, a hot-melt procedure is gradually replacing the solvent method because of environmental concerns. A film of resin that has been cast hot onto release paper is fed, along with the reinforcement, through a series of heaters and rollers to force the resin into the reinforcement. Two layers of resin are commonly used so that a resin film is on both sides of the reinforcement. One of the release papers is then removed and the prepregs is trimmed, rolled, and frozen. (Happer, 1992) The solution or the melt of the polymer must have a low viscosity at prepregging stage to wet the whole surface of elementary fiber

Use and Properties (T.Jonas, 1994)

Composite parts are manufactured from prepregs by the basic steps of layup, and finishing.

Lay-up. As prepregs contains precatalyzed resins, it must be stored under refrigeration to prevent resin advancement. Before use, it is allowed to reach room temperature in the original sealed package to prevent any water condensation on the prepregs. Plies of prepregs are then cut and stacked in the required fiber orientation on the tool surface. This layup may be done manually or by robotic handling equipment. Depending on the cure process to be used, the tool and ply package is then vacuum bagged appropriately.

Cure. To cure the prepregs, heat and pressure must be applied. Standard processes for this are autoclave, press, and vacuum oven. Typical cure temperatures range from 150 to 650 ° F., with pressures ranging from vacuum to 200 p.s.i., depending on the type of resin matrix on the prepregs.

Finishing. After removal from the cure took, minimal finishing is needed. Prepregs can produce excellent surface finishes on the cured part, which needs no further work. Most of the finishing needed is for edge trimming to the final dimensions.

The properties of the major commercial prepregs types are as follows:

Unidirectional Prepregs Tape is available in widths ranging from 1 to 60 in., with finished cured ply thickness ranging from 0.002 to 0.012 inch. As the fibers are all in one direction, and not crimped as in the woven fabric prepregs, tape gives the best translation of the reinforcing fiber properties. However, the resultant cure part cost is higher, as there is an increased labor cost associated with the layup procedure compared to fabric. Because of this, there is increased use of robotic methods for layup of tape to try to reduce labor.

In the design of composite parts it is quite common to use a combination of unidirectional tape and woven fabric, with the tape used in areas that call for the higher mechanical values.

To eliminate some labor costs associated with unidirectional tape, it is possible to obtain pre-plied multilayer packages. These are used where the part has a repeat pattern of ply orientation and are combinations of 0 – 90-, and 45 - deg plies.

Woven Prepregs usually is supplied as broad goods with widths to 72 in. and cured ply thickness of 0.0005 to 0.030 inch. The weave styles can be varied to fit particular end needs. Typical examples are balanced weave, 45 deg., or bias weave and 90% unidirectional. Mechanical properties or fiber strength translation depends on the weave style, e.g., a square weave gives lower translation than an 8-harness sation because of the distance between fibers interweaves. Part layup costs are lower as typically less plies are used. However, there is a trade – off as the cost of woven prepregs material is higher than tape.

Prepregs tow is supplied as individual preimpreggnated fiber bundles on spools in the same type of package as the original dry fibers. They are used for filament winding where they offer the potential for low – cost manufacturing using high – performance matrix resins compared to typical wet wind systems. They also are used as local reinforcements or to fill in layed – up parts such as beams. Properties of the prepregs tow are similar to unidirectional tape material.

Applications

Prepregs are used extensively in the aerospace industry in military and commercial aircraft, satellites, and missiles where weight and performance are critical factors. For example, most aircraft interiors are produced using prepregs of glass and aramid, and there is increased use for structural components where metal is replaced by carbon composites. Other commercial applications include the recreational industry where prepregs are used in tennis racquets and golf clubs.

Ply Properties

Fiber Volume Fraction

Fiber-to-matrix ratio is a determining factor in the ultimate weight and cost of the component and governs the extent to which performance properties inherent in the fiber reinforcement. Fiber-to-resin ratio can range from 20:80 for low cost, nonstructural components to as high as 70:30 in some high-end pultrusion application for structural use. A fiber percentage that is easily achievable and repeatable in a composite for several fibers is 60 percent.

Fiber volume is used to relate the properties of the manufactured composites, the following equations can be used to convert between weight fraction and fiber volume:

$$W_f = \frac{w_f}{w_c} = \frac{\rho_f V_f}{\rho_c} \tag{1}$$

$$V_f = \frac{\rho_c}{\rho_f} W_f = 1 - V_m \tag{2}$$

Where W_f = weight fraction of fiber

w_f = weight of fiber

w_c = weight of composite

ρ_f = density of fiber

ρ_c = density of composite

ρ_m = density of matrix

V_f = volume fraction of fiber

V_m = volume fraction of matrix

In addition the fiber volume fraction can be calculated using the rule of mixtures.

$$V_f = \frac{\rho_c - \rho_m}{\rho_f - \rho_m} \tag{3}$$

Where ρ_f = density of fiber = 1.76 g/cm^3

ρ_c = density of composite

ρ_m = density of matrix

V_f = volume fraction of fiber

Fiber Orientation

Three additional factors must be considered when designing with fiber: fiber type, form and orientation. One of the advantages of using a modern composite is the potential to orient the fiber to respond to the load requirements

Unidirectional Properties The properties of unidirectional fiber laminates are listed in Tables 2.2 These values are for individual laminate of for a unidirectional composite (0^o aligned), and they represent the theoretical maxima (for that fiber volume) for longitudinal inplane properties. Flexural and compression properties will show maxima at different fiber volumes. These values may also be used to calculate the properties of a laminate which has fibers oriented in several directions. (Peters, 1992)

Table 2.2 Unidirectional Composite Properties: 60% Volume Fiber (Delmonte, 1981)

			Properties			
			0° Tension		Flexural	
Material	Epoxy Matrix Resin	Density (g/cm^3)	Strength (MPa)	Modulus (GPa)	Strength (MPa)	Modulus (GPa)
Graphite						
A-S	3501	1.54	1,516	137	1,551	117
HM-S	934	1.63	1,206	220	1,034	193
HT-S	5208	1.55	1,482	172	1,689	158
T-300	5208	-	1,447	137	1,782	137
GY-70	934	1.69	586	275	930	262
Aramid	-	1.38	1,516	82	620	75
49	1002S	1.82	1,241	43	1,172	41
S-2 class						

The strength and elasticity properties of composites can be calculates on the basis of the known properties and relation of the component The rule of mixtures holds for composites. The micromechanics formulas to arrive at Young's modulus for a given composite are (McCrum et. al., 1988).

1. Axial Stiffness (Voigt Model)

$$E_1 = V_f E_f + V_m E_m \tag{4}$$

Since $V_f + V_m = 1$

$$E_1 = V_f E_f + (1 - V_f) E_m \tag{5}$$

2. Transverse Stiffness (Reuss Model)

$$E_2 = \frac{1}{\left(\frac{V_f}{E_f} + \frac{(1 - V_f)}{E_m}\right)} \tag{6}$$

Where E_1 = composite or ply Young's modulus in tension for fiber oriented in direction of applied load

E_2 = transverse modulus of the lamina

V = volume fraction of fiber (f) or matrix (m)

E = Young's modulus of fiber (f) or matrix (m)

Cross Ply Properties (Shalin, 1995) Control over the properties of laminated composites is effected using cross lay-up of the layer along the full vertical extent of the material and changing the angle of fiber orientation in the individual layer (Table 2.3). The simplest and most widespread is cross lay-up, wherein the fibers in the material layers are oriented at an angle ±∅ relative to the principle axes of symmetry, whose special case is represented by the orthogonal lay-up of the layers at an angle of 0^o and 90^o when the relation of the layers arranged in the direction of principle axes changes. The increase of the angle between the directions of loading and orientation of the fibers in the adjacent layers is followed by the monotonic decrease of the strength and elasticity characteristics in the direction of axis x, whereas the above characteristic increase along axis y.

Table 2.3 Effect of fiber orientation on elasticity modulus in tension and extent of epoxy boron-fiber composite anisotropy(Shalin, 1995)

Relative arrangement of fiber	Angle between direction of fibers in adjacent layer (deg)	Young's Modulus (GPa)			
		E_x	E_y	$E_{\pi/4}$	E_z
Unidirectional					
1:0	0	162	18.6	15.4	18.6
Cross-planer					
1:1 (0:90)	90	86	85.0	16.2	18.7
1:1:1 (0:60)	60	92	93.0	89.3	18.5

The modulus of elasticity and breaking tensile stress of the orthogonally reinforced composites till loss of solidity are calculated by the formulae:

$$E^{+}_{x,ult} = E^{0}_{x} t + E^{0}_{y}(1-t) \qquad (7)$$

$$\sigma^{+}_{x,ult} = E^{0}_{x} t + E^{0}_{y}(1-t)\varepsilon^{+}_{x,ult} \qquad (8)$$

Where t = fraction of composite unidirectional layers in the loading Direction

E^o = the Young’s moduli of the composite unidirectional layer

On the breakdown of the lateral layer, the elasticity modulus and breaking tensile stress of the orthogonally reinforced composite are determined according to the expression

$$E^{+}_{x,ult} = E^{0}_{x}t \tag{9}$$

$$\sigma^{+}_{x,ult} = E^{0}_{x}t\varepsilon^{0}_{x} \tag{10}$$

Where $\sigma^0{}_x$ = breaking stress of the composite unidirectional layer

$\varepsilon^0{}_x$ = relative tensile strain of the composite unidirectional layer

2.4 Carbon Fiber

Carbon and its graphite derivatives have emerged prominently in twentieth century technology. Carbon fibers are fine filament composed largely or of carbon with structures and properties varying from those of amorphous carbon to those of well-developed crystalline graphite. The fibers have the widest variety of strengths and moduli. Carbon fibers are divided into high-strength and high modulus according to their mechanical properties. Possible strength of carbon fiber is estimated to be about 100 GPa. Though the theoretical tensile strength of single crystal of graphite is 150 GPa, highest of all the materials known. The commercial high-strength carbon fibers have a maximum strength of 7 GPa (Chand, 2000). The ratio of stiffness to density is very high for most carbon fiber because the density of carbon is low. For this reason, they are the most widely used and are notably effective as reinforcing elements in advanced composite materials.

The structure and properties of carbon fiber depend on the raw material used, generally a polymer fiber. Numerous precursors have been tried to produce carbon fiber. However three precursors which are being used for large-scale production of carbon fiber are PAN, rayon and pitch. The first high-stiffness carbon fibers were produced from rayon. However, rayon-based carbon fiber did not compete with the PAN-based carbon fiber that became commercially available by the late sixties due to higher carbon yields which is 50% against 30% of rayon.

PAN fibers are the most versatile and widely used. They offer an wide range of properties, including good-to-excellent strength to 1,000 Ksi and high stiffness. Later carbon fibers were also prepared from pitch an available by-product of the coal gasification and petrochemical industries. The properties of pitch carbon fibers are generally inferior to PAN carbon fiber. The properties of typical carbon fiber from three materials are shown in Table 3

Table 2.4 Axial tensile properties of carbon fiber (Smith, 1987)

Precursor	Tensile strength (GPa)	Tensile modulus (GPa)	Elongation at break (%)
PAN	2.5-7.0	250-400	0.6-2.5
Pitch	1.5-3.5	200-800	0.3-0.9
Rayon	~1.0	~50	~2.5

Processing of Carbon Fiber

Carbon fiber are made by the pyrolytic degradation of a fibrous organic precursor. By heating an organic polymeric fiber under tension to high temperatures in an inert atmosphere, the volatile constituents are driven off. The residual carbon atom tends to orient themselves along the fiber axis into graphitic crystallites and thus form a high strength, high modulus fiber. The properties of this fiber product are a function of the composition of the precursor and of the time-temperature profile of the pyrolytic process. The higher maximum processing temperature, the greater the extent of crystallite orientation parallel to the fiber axis, and thus the higher modulus of fiber.

Generally, carbonization is done above 1200°C in an inert atmosphere. A nitrogen environment is generally used up to 2000°C and argon is used as inert medium above this temperature because carbon reacts with nitrogen at this temperature to form cyanogens (Chard, 2000)

Surface and sizing treatment are usually necessary to realize higher compressive strengths in carbon fiber composites. Carbon fibers when used without surface treatment produce composites with low interlaminar shear strength. Surface treatments increase the surface area and surface acidic functional groups and improve bonding between fiber and resin matrix. In addition to achieve desirable properties in composite components, adhesion between fiber and matrix must be optimized. Adhesion requires sufficient saturation with resin (wetout) at the fiber-matrix interface. To ensure good adhesion, attention must be given to fiber surface finish or coupling agent, often term sizing. Sizing is not only enhances the fiber/matrix bond, but also eases processing and protects the fibers from breakage during processing. Developments in sizing formulations have variously resulted; most of carbon fiber was sized for compatibility with epoxy resin.

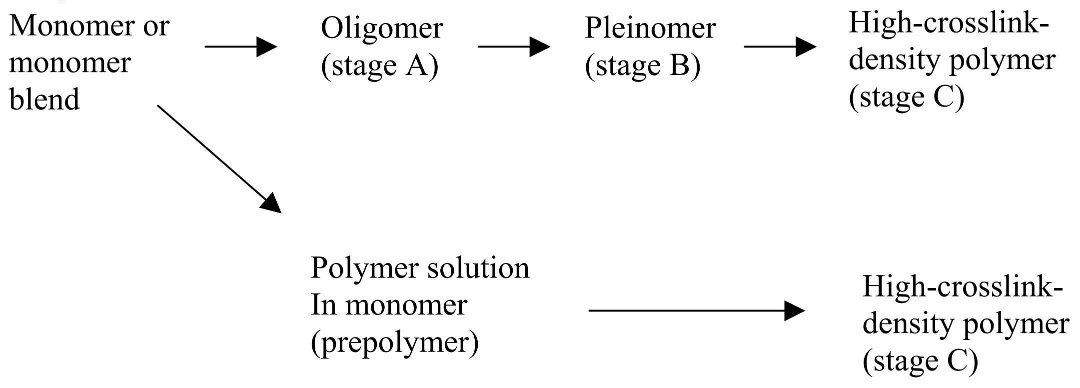
Applications of Carbon Fiber

` Large weight savings are possible when carbon fiber composites are used to replace more conventional materials; they are frequently applied in areas where weight reductions are valuable. Especially, they are used in variety of aerospace components. Typical aerospace-grade tow size range from 1K to 12K PAN- and pitch-based 12K carbon fibers are available with a moderate (33 to 35 Msi), intermediate (40 to 50 Msi), high (50 to 70 Msi), and ultrahigh (70 to 140 Msi) modulus. Heavy tow carbon fibers with filament counts from 48K up to 320K are available at a lower cost than aerospace-grade fibers. They typically have a 33 to 35 Msi modulus and 550-Ksi tensile strength and are used when fast part build-up is required, most commonly in recreational, industrial, construction and automotive markets. Carbon fibers and their composites exhibit many characteristics apart from their basic mechanical properties and weight saving. Electrical conductivity is coupled with excellent mechanical properties in thermoplastics molding compounds for structures in electronic equipment. Corrosion resistance is useful for making pipes, reactions or containers for chemical plants or in marine environment. Example of sports equipments that contain carbon fiber reinforcement include skis and ski poles, golf clubs tennis racquets, fishing rods, and racing cycles.

2.5 Thermosetting Resins

Plastic materials can be classified into two main categories based on their response to temperature: thermoplastics and thermosets. Thermosetting polymers differ from thermoplastics in that they become chemically crosslinked during final molding and curing. Thermosets (especially epoxy) have long been used as polymer matrices for carbon fiber composites. A distinctive characteristic of a thermosetting polymer is that one giant macromolecule consisting of covalently bonded repeating units is formed during the polymerization process. The giant macromolecule that percolates throughout the sample is called a gel. This sol-gel critical transition is a distinctive feature value of viscosity. At gelation, viscosity increases to infinite. After gelation an insoluble fraction (the gel fraction) is present in the system. At full conversion of functional groups, in stoichiometric formulation, the sol fraction disappears and the final thermosetting polymer is composed of one giant molecule of a gel (Pascault et al., 2002)

E.B. Trostyanskaya described synthesis of high-crosslink-density polymer are in this stages.



Transition from stage A to stage C, or from the prepolymer stage, is usually called ‘curing’. In the cure process, addition of multifunctional oligomer molecules is accompanied by an increase in the number of branches of different length. The branches are as a rule in interaction with each other, and lead to ring formation. The curing process can be followed by transmittance, viscosity or elasticity modulus increase, by the increase in the number of functional groups in reaction products.

In addition, the process of impregnation is carried out by immersion of fiber into melt or solution. Therefore the information about melt or solution viscosity and time of attaining on storage (shelf-life) of the resin or prepolymer melt is required.

2.6 Epoxy Resin

The need for ahigh degree of control over both network properties and resin processability make epoxychemistry appealing for many applications. Generally, the term ‘epoxy’ refers generally to a ring containing an oxygen, the materials called epoxy resins industrially contain specific 1,2-epoxides which are three membered oxirane rings (Figure 2-1). The term *glycidyl* may also be used when naming compounds with epoxy groups. Although the networks formed following the cure of these systems may no longer contain epoxide groups, they are referred to as epoxy networks.

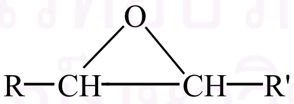


Figure 2.1: Oxirane ring found in common epoxy resins

There is no universal agreement on the nomenclature of the three-membered epoxy ring. There is division even on the term epoxy itself. They have also been known by other names, for example, epoxides, ethoxylines, oxiranes, glycidyl polyethers and diepoxide polymers.

Cured epoxy resins form the prime matrix for high performance glass, aramid and carbon fiber composites, while the unsaturated polyester resins are primarily used in industrial applications. This is because an epoxy resin has an excellent combination of mechanical properties and corrosion resistance, dimensionally stable, exhibits good adhesion, and relatively in expensive. Moreover, the low molecular weight of uncured epoxide resins in the liquid state results in exceptionally high molecular mobility during processing. This mobility enables the resin to quickly wet the surface of carbon fiber.

Diglycidyl Ether of Bisphenol (Standard Epoxy)

Most widely used epoxy resins are made from diglycidyl ether of bisphenol A. The chemical structure of bisphenol A is illustrated in Figure 2.2.

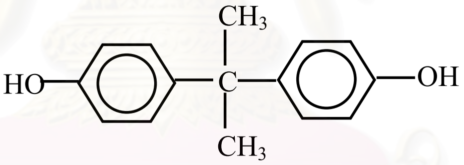


Figure 2.2: The chemical structure of bisphenol A.

Bisphenol A epoxy resins find large volume application in protective coating, and significant uses as adhesive, sealants impregnate, bonding, and laminating materials. In addition epoxy resin used in this study is diglycydyl ether of bisphenol A (DGEBA). The formation of DGEBA from bisphenol A and epichlorohydrin is shown in Figure 2.3. From the reaction, DGEBA is obtained by reacting epichlorohydrin with bisphenol A in the presence of sodium hydroxide. The reaction takes place in two steps; they are the formation of a chlorohydrin intermediate and the dehydrohalogenation of the intermediate to the diglycydyl ether, respectively. Each molecule of the diglycydyl ether will react with that of the bisphenol A at the epoxide group, forming eventually the higher molecular weight DGEBA at last.

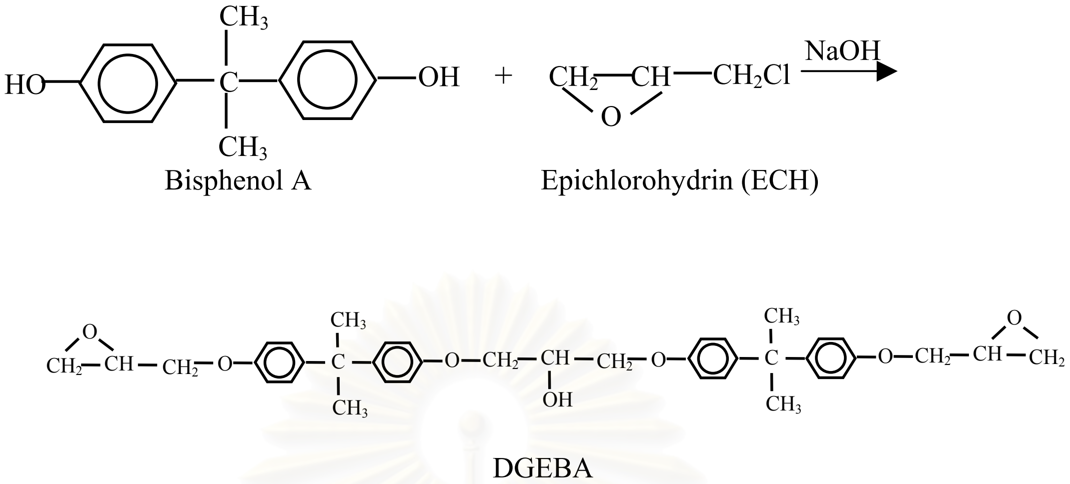


Figure 2.3: Formation of diglycydyl ether of bisphenol A (DGEBA)

Basic Characteristics of Epoxy Resins (Kamponpan, 2002)

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

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

2. Easy cure. Epoxy resins cure rapidly and easily at practically any temperature from 5 to 150'C, depending on the selection of curing agents.

3. Low shrinkage. Their low shrinkage during cure are one of the mast advantageous properties of the epoxy resins. Furthermore, epoxy resins react with very little rearrangement and without volatile by-products being evolved.

4. High adhesive strengths. Owing to the chemical makeup, mainly the presence of the polar hydroxyl and ether groups, the epoxy resins are excellent adhesives. They can be cured with low shrinkage, thus the various surface contacts set up between the liquid epoxy resins formulation and the adherents are not disturbed during cure.

Adhesive strengths without the need for both open time and high pressure are perhaps the best available in the contemporary plastic technology.

5. High mechanical properties. The strength of appropriately formulated epoxy resins usually surpasses that of other types of casting epoxy resins. This is due to their low shrinkage and comparatively unstressed structure after curing.

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

7. Good chemical resistance. The chemical resistance of the cured epoxy resin relies considerably on the curing agent used. Generally, most epoxy resins possess extremely high resistance to caustics and good to cxcellent resistance to acids.

8. Versatility. The epoxy resins are likely the most versatile of the modern plastics. The basic properties may be modified in many ways such as by blending of resin types, by selection of appropriate curing agents, and by application of modifiers and fillers.

2.7 Benzoxazine Resin

Polybenzoxazine is a newly developed thermosetting resin with interesting properties. As a novel class of phenolic resins, it has been developed and studied to overcome the shortcomings of the traditional novolac and resoles. Polybenzoxazine resins are expected to replace traditional phenolic, polyesters, vinyl esters, epoxies, BMI, cyanate esters and polyimides in many respects. The physical and mechanical properties of polybenzoxazine are shown to compare very favorably with those of conventional phenolic and epoxy resins. The resin permits development of new applications by utilizing some of their unique features such as low viscosity, near-zero shrinkage upon polymerization, low water absorption, Tg much higher than cure temperature, fast mechanical property build-up as a function of degree of polymerization, and high char-yield. Polybenzoxazine can be synthesized from inexpensive raw materials and can be cured without the use of strong acid or base catalyst The crosslinking reaction of the resin is through thermally activated ring-opening reaction; therefore, do not release by-products during the polymerization (Takeichi et al., 2002). The molecular structure of polybenzoxazine offers superb design flexibility that allows properties of the cured material to be controlled for specific requirements of a wide variety of individual requirements.

Benzoxazine resin based on bisphenol-A and anline is synthesized according to the following reaction scheme (Figure 2.4) (Ning and Ishida, 1994).

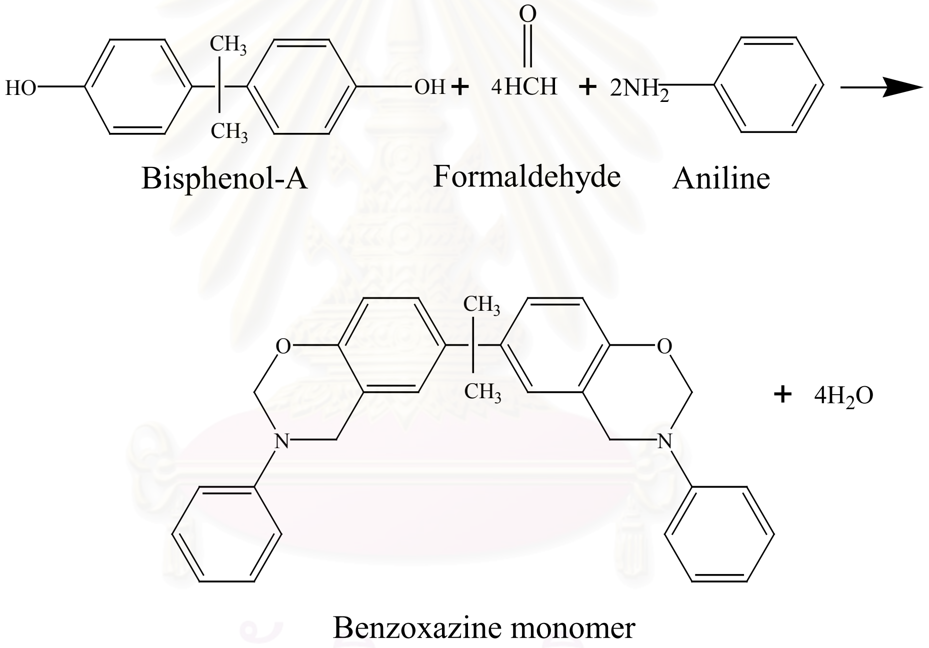


Figure 2.4: Synthesis of benzoxazine resin.

Moreover, the reactive blending of benzoxazine with epoxy resins allows the network to achieve higher crosslinking. The co-reaction proceeds via the ring-opening polymerization of BZ followed, by reaction of the generated phenol with the epoxy, probably catalyzed by the amine group. PBZ–EPOXY system has been projected as a high performance matrix for several applications. These systems are processable by traditional techniques such as prepregs, RTM and VRTM etc. for composite fabrication. The system, not requiring any refrigeration, is stable at ambient conditions indefinitely.(Kimure et. al.,1999)

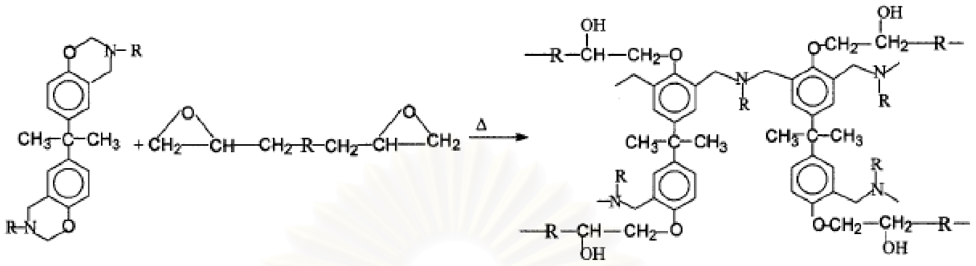


Figure 2.5: General expected reaction sequence for curing of benzoxazine and epoxy (Ishida and Allen, 1996)

2.8 Phenolic Resin

Phenolic resins constituted the first type of thermosetting resin to be synthesized when they were first introduced in 1907. This type of resin has become the subject of further studies because of its excellent fire resistant properties. Phenolic resins have recently been used in the manufacture of transportation systems (Young-Kyu Lee, 2002). The resins are usually made from the condensation polymerization of phenol and formaldehyde, thus give them another name, phenol formaldehyde resins.

The two most common types of phenolic resins (resols and novolacs) are derived from the reaction of phenol with formaldehyde. The reaction mechanism to form the prepolymers is controlled by the pH and the reactant ratio of phenol to formaldehyde.In strongly acidic conditions with an excess of phenol, novolacs are formed; whereas, in basic conditions with an excess of formaldehyde, resols are formed. Novolacs are soluble and fusible, and require an external curing agent, such as HMTA, to form the phenolic network. On the other hand, resols will crosslink with heat to form insoluble, infusible networks (Tyberg, 2000) The molecular structure of the phenolic novolac is shown in Figure 2.6.

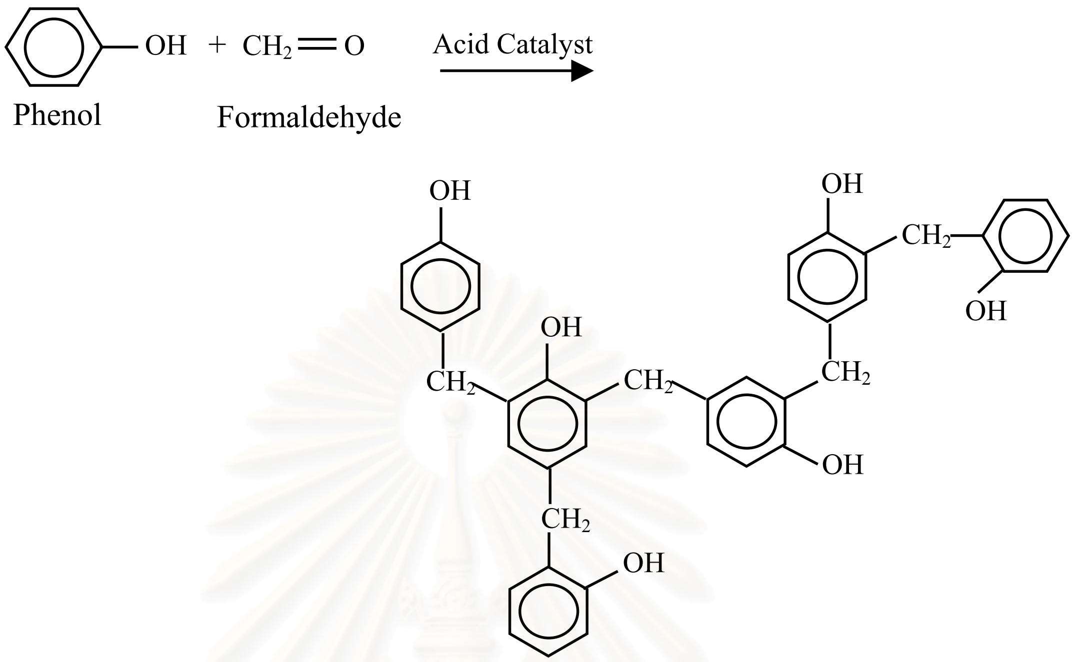


Figure 2.6: Synthesis and molecular structure of phenolic novolac resin

As a result of the low smoke generation of phenolic networks upon burning, they are the materials of choice in non-structural applications such as aircraft interiors. Phenolics have a broad range of applications varying from construction to electronics and aerospace. However upon polymerization phenolic produces volatile by-products such as formaldehyde and ammonia, which lead to voids in the materials. This has been a negative feature in forming phenolic matrix composites because the high void content results in brittle components. In other hand , phenolics have been used as curing agents for epoxy resins where the epoxy is usually the major component. In many cases, these systems make up the base resins for semiconductor packaging due to their improved hydrophobicity relative to amine-cured epoxies and their low cost (Tyberg, 2000).

2.9 Honeycomb (Bitzer, 1997)

Honeycomb consists of an array of open cells, from very thin sheets of material attached to each other. Usually the cells form hexagons (Figure 2.10), but there are other cell configurations. It can be made from any thin flat material, and in the past over 500 different kinds of honeycomb have been manufactured. The first honeycomb core patent, covering a manufacturing method for the production of Kraft paper honeycomb, is probably the Budwig Patent, issued in 1905 in Germany.

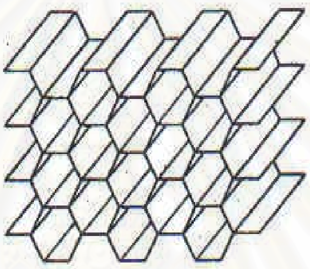


Figure 2.7: Hexagonal honeycomb cells

Since 1919 the first aircraft sandwich panel was fabricated. Figure shows a typical honeycomb sandwich structure which consists of facings, adhesive and honeycomb core.

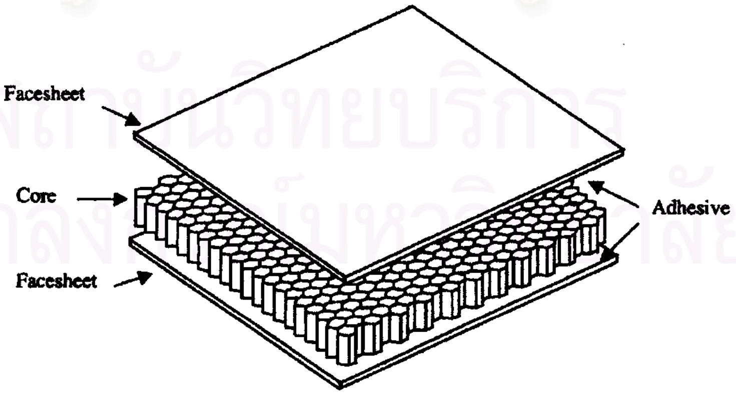
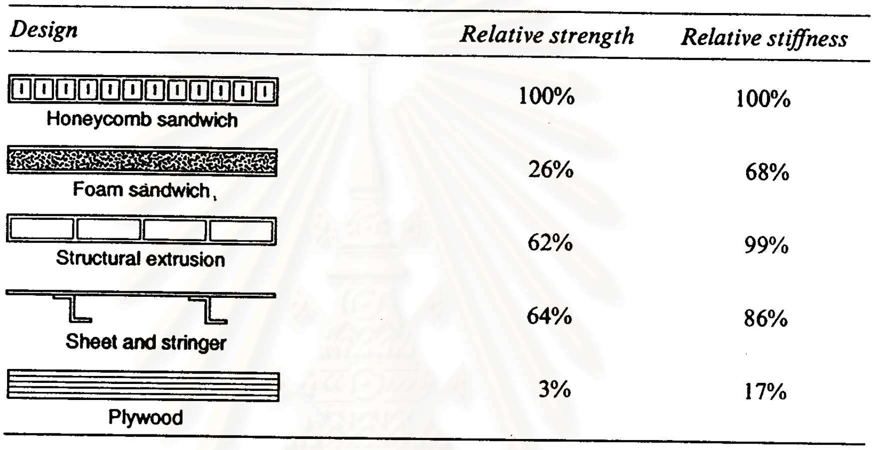


Figure 2.8: Honeycomb sandwich panel

The main reason for using honeycomb is to save weight. Table 3 compares some of the standard panel constructions for a given loading. All these panels are 1 in.

(2.5 mm) thick and weight the same 3.0 psf (1.46 kg/m^2), replacing the solid plywood beam. Foam has a lower shear strength and modulus than honeycomb; thus the beam has a lower load capacity and gives more deflection. The sheet and stringer and extrusions have thin skins which buckle; therefore they cannot carry as much load as the honeycomb beam.

Table 2.5 Structural comparisons for structures of equivalent weight (Bitzer, 1997)



Design	*Relative strength*	*Relative stiffness*
Honeycomb sandwich	100%	100%
Foam sandwich	26%	68%
Structural extrusion	62%	99%
Sheet and stringer	64%	86%
Plywood	3%	17%

Web Materials

Since, the 1940s honeycomb has been made from many different web materials, as honeycomb can be made from just about any thin flat sheet material. Some of the more common web materials currently in use are:

Metallic- aluminum, stainless steel, titanium
Nonmetallic- fiberglass, Nomex, Kraft paper

A few of the more unusual web materials are copper, lead, asbestos, Kapton, Mylar and Kevlar. One new material is carbon fabric, which produces honeycomb that has extremely high mechanical properties. Based on a need in the space community for an extremely low density, high stiffness and excellent thermal conductivity honeycomb carbon fiber honeycomb was developed (Figure 2.9)

.

Figure 2.9: Carbon fiber honeycomb core

CHAPTER III

LITERATURE REVIEWS

For prepregging process low viscosity matrices resins are required. The relatively low viscosities are less critical for preparing pre-impregnated because the impregnation temperature can be increased to decrease viscosity. The high viscosity resins are typically difficult to process such as high temperature processing, use of solution method. The high temperature and solvent were necessary to give a low enough viscosity to process the material. Low viscosities of the resins are critical to permit good wet-out of the reinforcing fiber tows and yield uniform resin content. (Tyberg et al., 2000).

Shin et.al.(2002) studied a systematic chemical, physical, thermal, and mechanical properties of the poor resin fiber interfacial wetting polyimide composites. The two prepregging process was compared i.e. solution and hot melt. The experiments indicated that the critical controlling mechanism identified for the composite quality was resin-fiber interfacial wetting. Poor wetting resulted in lower composite mechanical properties and poor thermostability. The interfacial wetting is primarily controlled by solution viscosity. In addition resin and solvent content in prepregs are important factors for producing high quality composites, where in high viscosities resin, a solvent is needed for fiber wetting. Too much residual solvent will induce void formation. Subsequently, the effect of resin viscosity and wetting behavior on composites quality and properties were examined. The effect of the prepregging method and different composite cure methods were discussed. The viscosities of polyimide solution were roughly 0.015, 1.5, 3, and ~9Pa.s. For product quality, the wetting at prepregging stage is more important than any other process condition or other curing condition. Composite quality and properties improved significantly by lowering resin viscosity.

A new class of polymeric resin polybenzoxazine have shown various unique properties. Benzoxazine monomers can be synthesized from inexpensive raw materials and polymerized by a ring opening addition reaction yielding no reaction byproduct. Like epoxies and polyimides, the flexible chemistry of benzoxazines has allowed structural tailoring (Ning and Ishida, 1994), including excellent processability, low melt viscosity (5 Pa.s at 100°C), lack of void formation. Ishida and Allen (1996) investigated mechanical and physical properties of polybenzoxazine comparable to phenolic and advance epoxy resins. The polybenzoxazine was found to exhibit excellent mechanical and thermal properties with good handling capability for material processing and composite manufacturing, e.g. having the glass transition temperature above 190°C, a tensile modulus of 5.2 GPa, and tensile strength of 64 MPa which were higher than epoxy (165°C, 2.7 GPa and 59 MPa) and phenolic resin (121°C, 3.8 GPa and 48 MPa, respectively).

Moreover benzoxazine has reported capability to be alloyed with various existing resin systems. Ishida and Allen (1996) reported the copolymerization of benzoxazine resin with epoxy resin. Copolymerization leads to a significant increase in the glass transition temperature. Reaction of DGEBA with BPA-based benzoxazine (BA-a) increased the Tg of the latter from about 143 to about 153°C for an epoxy-content of 35%. Further increase in epoxy decreases Tg to below that of pure PBZ. The copolymer also showed improvement in flexural strain at break and flexural strength. The flexural strength increased from 125 to 170 MPa on enhancing the epoxy-content to 50%. Kimura et al. (1999) reported the similar binary systems. The curing reaction proceeded without any accelerator. Molding compound showed good thermal stability under 150°C, this corresponds to the injection molding temperature. Above 150°C, the curing reaction proceeded rapidly. The cured epoxy resin showed good heat resistance, water resistance, electrical insulation, and mechanical properties compared with the epoxy resin cured by the bisphenol-A type novolac.

Tyberg et al. (2000) has investigated the The structure–property relationships of phenolic–epoxy networks. Network densities have been explored by measuring the moduli in the rubbery regions and these experimental values were compared with those predicted from stoichiometry. The T_gs decreased, and toughness increased, as the phenolic Novolac content in the network was increased. Both results could be correlated to the decrease in network densities along this series. Analysis of the cooperativity of the networks suggests a crossover in properties from two competing factors, network density and intermolecular forces (hydrogen bonding) networks. In addition, an increase in phenolic novolac content improves the flame retardance rather dramatically. The maximum flame retardance was achieved for networks with 80 wt% of the phenolic component. Thus, by increasing the phenolic novolac content to reach a phenol to epoxy ratio of about 3:1, the combination of mechanical properties and flame retardance is improved simultaneously.

The improvement of the processability of benzoxazine resins has been reported. Rimdusit and Ishida (2000) investigated ternary systems of benzoxazine, epoxy, and phenolic resins. The ternary mixtures were found to have a wide range of desirable properties. The benzoxazine imparts to a combination of good thermal curability, high mechanical properties, and low water uptake. The epoxy reactant provides improved crosslink density, low melt viscosity, flexibility, and possibly enhanced adhesion to polar substrates. The phenolic provides a lower polymerization temperature for the benzoxazine monomer and improved thermal stability for the epoxy component. The blend renders homogeneous and void-free cured specimens with an outstanding characteristic. Low melt viscosity with suitable period of time was achieved e.g. 0.3 Pa.s constant up to 1000 seconds at 100°C. The gel time at 140°C ranges from 5 min to 30 min and less than 5 min at 180°C. Which is suitable to the “B-stage” time or gel time for prepregs (1 min to 15 min at a temperature range 90°C to 210°C []), and a glass transition temperature as high as 170°C. The fully cured polymer mixtures show relatively high degradation temperature, reported at 5% weight loss, i.e. up to 370°C. The char yield of the ternary systems increase significantly compared with the pure epoxy resin. That is due to the fact that both polybenzoxazine and phenolic novolac are known to give higher char yield compared with epoxy resin. The tendency for benzoxazines and phenolic resins not to support flame propagation makes the ternary blend a desirable material in applications where flammability is to be avoided such as interior parts.

Frigione and Kenny (2002) focused on the stability of epoxy matrix carbon fiber prepregs affected by exposure to controlled environmental conditions. Effects of the aging on glass transition temperature, reactivity and processability have been investigated. At higher aging times, the heat of reaction continuously decreases, reaching from 141 to about 90 J/g after 5 months of exposure (35%conversion). The resin stored has not achieved a fully crosslinked structure. The curing reaction, slowed down since diffusion controlled, can start anew once the curing temperature is raised up to values higher than the attained Tg.

Carbon fiber-reinforced composites materials have been used extensively in many engineering fields, especially civilian and military aircraft on account of their high specific strength and specific modulus. The composites used for structural applications require excellent mechanical properties. Although polybenzoxazine showed excellent properties such as low viscosity, and non volatile by-products in the curing process. However, polybenzoxazine is still brittle.

For high performance composites, strong interfacial adhesion strength must be achieved to improve the mechanical properties of composites as it plays an important role in mechanical properties. Jang and Yang (2000) has improved the mechanical properties of CF/polybenzoxazine composites using carbon fiber surface treatments. The influences of oxygen plasma treatment and nitric acid treatment on the mechanical properties were studied. The flexural strength of 60 min oxidized CF/polybenzoxazine composites is 2.4 times as high as that of untreated ones and is even more than that of plasma-treated ones (~850 MPa of nitric acid treatment, ~600 MPa of oxygen plasma treated, and ~380MPa of untreated). They observed the cohesive failure occurred in the matrix region due to the improvement of the interfacial adhesion strength between CF and matrix by the nitric acid treatment.

Moreover, the high degree of anisotropy and laminar structures cause most fiber-reinforced composites to delaminate by the shear stress. Therefore, to improve the delamination resistance improvements is needed in the mechanical properties, especially for composites with brittle matrices. Jang and Yang (2000) modified polybenzoxazine with liquid rubber (ATBN and CTBN) to improve the delamination toughness of carbon-fiber/polybenzoxazine composites. They conclude that ATBN improved the delamination toughness and interfacial bonding in the composites more effectively. Despite such improvement, there are some disadvantages from this rubber modified resin approach including the considerable reduction of strength, modulus, and glass transition temperature such as decrease in flexural strength with increase in CTBN (~380 MPa of 0% CTBN to ~200MPa of 20%CTBN).

Ishida and Chaisuwan (2003) improved the mechanical properties of carbon fiber-reinforced polybenzoxazine composites by rubber interlayering. The resin used is BA-35X because it shows the highest thermal stability achieved from neat benzoxazine based on bisphenol-A and unfunctionallized aniline derivatives (Tg = 236^{o}C of BA-35X and Tg = 170^{o}C of BA-a). Carbon fiber woven fabric (T300) was used either as-received or desized condition. The fiber content of the composite is about 60% by volume. They reported the optimizing concentration of ATBN rubber provided the mechanical properties comparable or superior to those of modified epoxy and phenolic matrices i.e. flexural strength: ~800 Mpa of rubber interlayered BA-35X, 780 of modified epoxy, and 650 of modified phenolic; flexural modulus: 58 Gpa of rubber interlayered BA-35X, 58 GPa of modified epoxy, and 56GPa of modified phenolic.

CHAPTER IV

EXPERIMENT

4.1 Materials

The materials used in this research are benzoxazine resin, epoxy resin, phenolic novolac resin, and carbon fiber. Benzoxazine resin is based on bisphenol-A, aniline, and formaldehyde. Thai Polycarbonate Co., Ltd. (TPCC) kindly supplied bisphenol-A (Commercial grade). Para-formaldehyde (AR grade) was purchased from Merck Company and aniline (AR grade) was obtained from APS Finechem Company. Phenolic novolac resin is prepared by reacting phenol with formaldehyde (37% aqueous) in a presence of an acid catalyst (oxalic acid). The reactants (AR grade) were purchased from Apec Chemical Co., Ltd. Oxalic acid (AR grade) was purchased from Suchapanpanit Company. Epoxy resin, EPIKOTE 828-EL was purchased from The East Asiatic (Thailand). All chemicals were used without further purification. Three types of carbon fiber were used. Beslon HTA-N-6000 was kindly supported by Prof. Takeshi Kitano (retired) of AIST, Tsukuba, Japan, Besfight HTA-12K-E30 from Toho Co., Ltd, and carbon fiber woven fabric (K100) was purchased from Asia Kangnam Company Limited (Thailand). All fibers was used as-received.

4.2 Benzoxazine Resin Preparation

Benzoxazine resin is synthesized using bisphenol-A, formaldehyde, and aniline at the stoichiometric mole ratio of 1:4:2. This resin was prepared based on a patented solventless method (Ishida, US Patent 5,543,516). The preparation reaction is shown in Figure 4.1. The obtained benzoxazine monomer is clear-yellowish solid powder at room temperature. The product is then ground into fine powder and can be kept in a refrigerator for future-use.

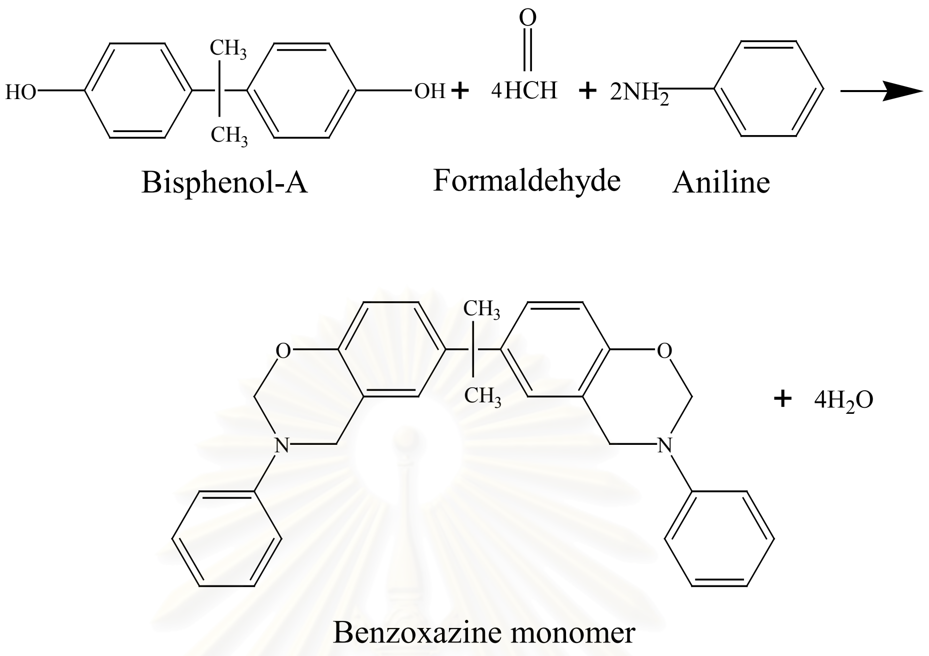


Figure 4.1: Preparation of bifunctional benzoxazine resin (BA-a).

4.3 Phenolic Novolac Resin Preparation

Phenolic novolac resin is based on phenol and formaldehyde. In the synthesis process, a phenol:formaldehyde mole ratio of 1.12:1 was used with oxalic acid as a catalyst (Sandler, 1994). The preparation scheme of phenolic novolac resin is shown in Figure 4.2. The ingredients were then stirred mechanically for 1 hr followed by heating at 100°C for 2 hr and vacuum dried at 100°C The obtained product is yellow to orange solid at room temperature.

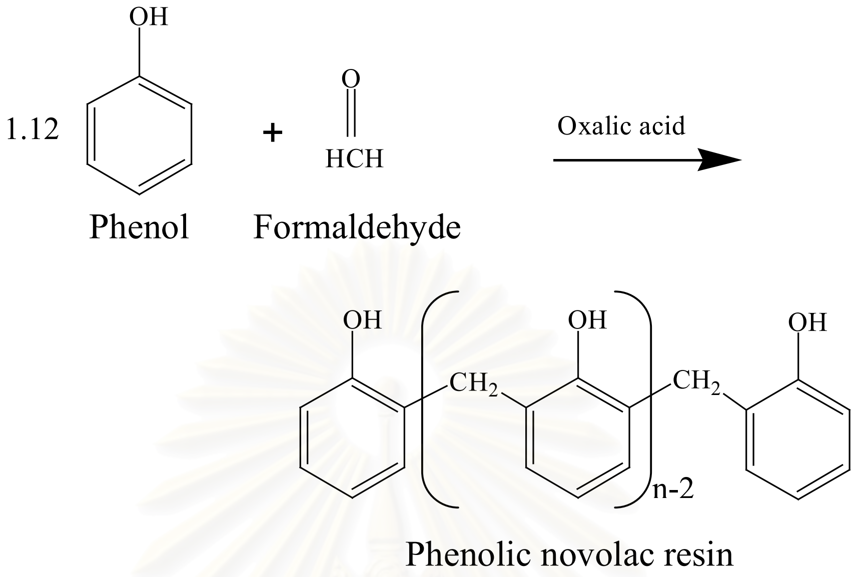


Figure 4.2: Preparation of phenolic novolac resin.

4.4 Benzoxazine/Epoxy/Phenolic Novolac Ternary Mixture Preparation (BEP Resins)

Ternary system matrices were made by measurement the amount of each resin at the desirable mass fraction. The mixture was heated to about 90°C in an aluminum pan and was mixed thoroughly to yield a homogeneous resin mixture. The mixtures can also be kept at room temperature for future-use.

4.5 Composite manufacturing

Unidirectional carbon fiber reinforced prepreg tape were prepared by brushing the ternary mixture matrix solution (50 wt% in tetrahydrofuran) onto a drum-wound unidirectional carbon fiber tape. After brushing, the prepregs were removed and cutting to appropriate sizes followed by conditioning at 45°C for 10 hr in a vacuum oven to ensure that no solvent was left. The composite panels were fabricated by hot pressed in a hydraulic press. Eight plies of the prepregs were laminated in a (0°/90°) arrangement and were cured at 180°C for 3 hr. After the cured cycle all sample was post-cured in circulating oven at 200°C for 2 hr. The curing cycle of this carbon fiber composite is shown in Figure 4.3

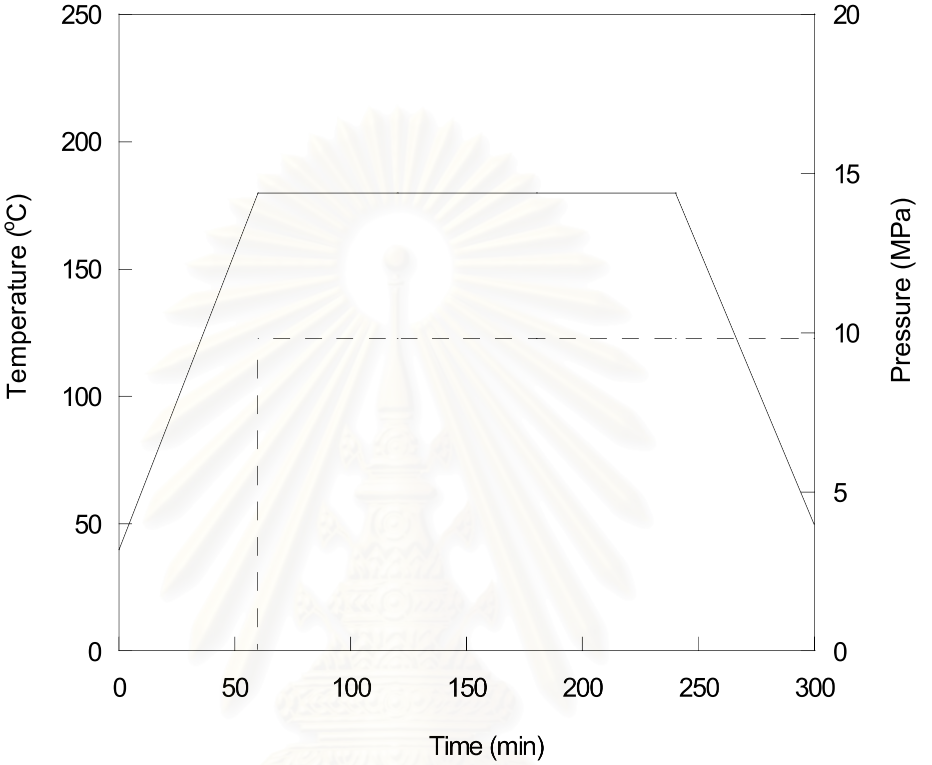


Figure 4.3: Curing cycle of carbon fiber reinforced composites based on BEP resins.

4.6 Rheological Properties Determination

Rheological properties of each alloy were examined using a Rheometer (Physica Parr) model MCR300 equipped with parallel plate geometry. The diameter of the upper plate is 25 mm. The measuring gap was set at 0.5 mm. The void free monomer mixture, which was liquefied at 80°C, was then poured on to the lower aluminum plate. The pre-heated upper plate was then lowered to a set gap of 0.5 mm. The temperature was immediately equilibrated at the set point for 1 min and the test was then started. The melt viscosity of the ternary mixture was performed under shear sweep mode at 100°C, with the shear rate range of 1-1000 (s^{-1}).

Processing window of the resin mixture was determined under an oscillatory shear mode. The composite waveform was obtained by the superposition of mechanical waves with three different frequencies i.e.1, 3, and 10 rad/s. The testing strain amplitude is maintained at 2.5% for each frequency. A sample mass about 3 g was used in each test. The testing temperature program was ramped from room temperature at a heating rate of 2°C/min to a temperature beyond the gel point of each resin and the dynamic viscosity was recorded.

Gel time based on the frequency independent of tanδ of each mixture was examined using a Rheometer (Thermo Haake) model RS600 with parallel plate geometry the diameter of the upper plate is 60 mm and the measuring gap was set at 0.5 mm.The superposition of mechanical waves was five different frequencies ranging from 1 to 100 rad/s at constant stress of 20 Pa. The gel time is obtained from the point where the loss tangent of different frequencies intersects each other.

4.7 Differential Scanning Calorimetry (DSC)

Curing temperature of each matrix was examined using a differential scanning calorimeter (model 2910) from TA Instuments in a temperature range of 30-300°C. A sample mass of 5-10 mg was placed in a non-hermetic aluminum pan with lid. The experiment was performed at a heating rate of 10°C/min under nitrogen purging. Curing temperature and time, and glass transition temperatures were obtained from the thermograms.

4.8 Thermogravimetric Analysis (TGA)

Degradation temperature (T_d) and char yield of our carbon fiber composites were studied using a thermogravimetric analyzer (model TGA/SDTA 851^e) from Mettler-Toledo (Thailand). The temperature was scanned from room temperature to 850°C with a heating rate of 20°C/min under dried nitrogen purge. The initial mass of a tested sample was 15-20 mg. The degradation temperature at 5% weight loss and the char yield at 800°C were recorded for each specimen.

4.9 Density Measurement

A density of each specimen was determined by a 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 1 mm). The density was calculated by the following equation:

The average value from at least three specimens was calculated.

$$\rho = \left(\frac{A}{A - B}\right) \times \rho_o \qquad (1)$$

where ρ = Density of the specimen (g/cm^3)

A = Weight of the specimen in air (g)

B = Weight of the specimen in liquid (g)

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

4.10 Fiber Volume Fraction

All tested specimens were evaluated for fiber volume fraction by measuring the density of the composites (water displacement method). The fiber volume fraction was then calculated using the rule of mixtures

$$\nu = (\rho_c - \rho_{resin})/(\rho_{fiber} - \rho_{resin}) \qquad (2)$$

where ν = fiber volume fraction

ρ_{fiber} = density of the carbon fiber = 1.76 g/cc

ρ_{resin}= cured resin density of each composition

ρ_c = composite density .

4.11 Flexural Property Measurement

Flexural modulus and flexural strength of composite specimens were determined utilizing a Universal Testing Machine (model 5567) from Instron Instrument. The test method used was a three-point bending mode with a support span of 32 mm at the crosshead speed of 1.7 mm/min. The dimension of the specimens was 50 mm x 25 mm x 1 mm. The flexural properties were determined using ASTM D 790M-93 according to the following equations:

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

$$S = \frac{3PL}{2bd^2} \tag{4}$$

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)

4.12 Interfacial Bonding Examination

Interfacial bonding of a filled sample was investigated using a ISM-5400 scanning electron microscope at an acceleration voltage of 15 kV. All specimens were coated with thin film of gold using a JEOL ion sputtering device (model JFC-1100E) for 4 min to obtain a thickness of approximately 30Å and the micrographs of the specimen fracture surface were taken. The obtained micrographs were used to qualitatively evaluate the interfacial interaction between the matrix resin and the carbon fiber.

CHAPTER V

RESULTS AND DISCUSSION

5.1 Neat Resin Characterization

5.1.1 Processability of Ternary Systems

The processability of ternary mixtures based on benzoxazine, epoxy, and phenolic resins were evaluated based on variation of their viscosity with temperature i.e. the processing window as well as their curing temperature. The curing exotherms of the neat benzoxazine resin (BA-a) and the binary mixtures (BE) between benzoxazine (B) and Epoxy resin (E) were shown in Figure 5.1. The DSC thermograms was in the temperature range of 30-300^{o}C at the heating rate of 10^{o}C/min. The curing exotherm of all these composition has been shown the ability of thermally curability without adding initiator or catalyst of the resin mixtures. However the shift of the exotherm peak to the higher temperature occurred for all composition when the amount of the epoxy in the mixtures increased, i.e. the curing peak of the neat BA-a at 225^{o}C was shifted to 247^{o}C in BE55. The reaction was expected to contain at least two mechanisms; the first exotherm at lower temperature can be interpreted as reaction among benzoxazine monomers while the second one at higher temperature was assigned to the reaction between benzoxazine resin and epoxy resin. All these characteristics are pronounced by the splitting of the curing peak with increasing the amount of epoxy resin. For examples, the first peak at 247^{o}C and the second peak at 270^{o}C was determined for BE 55. This result is in good agreement with those reported by Rimdusit and Ishida, 2000. However, the shift of curing reaction to higher temperature made the mixture more difficult to be cured. Higher curing temperature may not be suitable in terms of prepregs processability, i.e. for prepregs the “B-staging” step usually carried out at a temperature range from 90-210^{o}C within 1-15 minutes (Gan et al, 2003 and Saitou et al, 2004).

In other report, (Rimdusit and Ishida, 2000) the addition of phenolic novolac (P) into the BE mixture was found to help reduce the curing temperature since phenolic novolac resin can act as an initiator for benzoxazine resin. That is clearly seen in our experiment in Figure 5.2 using the composition of benzoxazine resin and epoxy resin binary mixture with the mass fractions of BE 11, BE 12, BE 13, respectively. The binary mixtures showed the sign of the shift of their exotherm peaks to the higher temperature with the splitting of the curing peaks with the amount of the epoxy as indicated before. However, the addition of phenolic novolac to form ternary mixtures of benzoxazine, epoxy and phenolic novolac resins (BEP) such as at the mass fractions of BEP 111, BEP 121 and BEP 131 found to lower the curing temperature. For example, BE13 exhibited the first peak at 250^{o}C and the second peak at 295^{o}C while the addition of the phenolic novolac to form BEP131 reduced the exotherm to 195^{o}C and 245^{o}C respectively.

Considering the curing exotherms of BEP111 and BEP121 in Figure 5.2, the curing reaction of the mixtures can start at relatively low temperature (near 100^{o}C) which means greater economical processing condition can be achieved. The melt viscosity characteristics of these ternary systems have been reported by Rimdusit and Ishida, 2000. Their experiment was performed at 100^{o}C under steady shear mode using parallel plate rheometer. In their reports, over 50% by weight of epoxy mass fraction led to the substantially low viscosity (0.3 Pa.s for BEP121) and remained constant up to 1000 seconds, while the viscosity of BEP111 was higher (7 Pa.s) and rapidly increase with time signifying the curing reaction occurred even at this relatively low temperature. The recommended fraction of epoxy was 30%-60% by weight for a suitable period of time at mixing or compounding condition.

Regarding the processability of the matrices as prepregs, the matrices must be capable of wetting and penetrating into the bundle of reinforcing fibers. The higher wettability often leads to the greater mechanical performance of the composites. Additionally, resin proportions added to the fibers in the prepregging will be readily controlled with low viscosity and suitable processing window systems (Rimdusit and Ishida, 2000). As a consequence, BEP121 (i.e. equivalent to BEP 363) was selected to as a binder due to its appropriate viscosity and chemorheological properties (Rimdusit and Ishida, 2000).

Figure 5.3 illustrates the curing behaviors of the ternary mixtures. In this case, the composition of benzoxazine and epoxy in the ternary mixtures was fixed at 1:2 mass ratio and the amount of phenolic novolac was systematically varied. The investigated ternary compositions were BEP361, BEP362, BEP363, and BEP364 respectively. From our investigation, the increase in phenolic novolac content in the above systems tended to lower the curing peak temperature in DSC thermograms, i.e. from 240^{o}C in BEP 361 to about 222^{o}C in BEP364. From the thermograms of BEP363 –BEP364, the curing reaction can be initiated at relatively low temperature of 100^{o}C. In some cases of fiber-reinforced composites, it is essential for the prepregs to be capable of being cured at a relatively low temperature to achieve releasable curing products with high heat resistance by secondary curing at high temperature and to ensure excellent composite stability (Goto et al., 2005).

However, in prepregging process such as hot melt method, low and fairly constant viscosity is required. The low melt viscosity gives good resin wetting prepregs formation as well as void free final product while constant viscosity renders enough time for prepregs processing (Goto et al., 2005). The viscosity of four different matrix compositions compared with that of pure benzoxazine monomer is presented in Figure 5.4. The measurement was performed under shear sweep mode with the shear rate range of 0.001-1000 1/s within experiment time of 600 seconds. From the curve, almost all exhibit a constant viscosity at the range of shear rate above implying Newtonian flow behavior of the resins as the resins maintained low-molecular-weight liquids at the period of time. The values of melt viscosity was increased by increasing the amount of phenolic novolac due to less fraction of the epoxy diluent in the mixture i.e. 0.4 Pa.s of BEP361 to 3.8 Pa.s of BEP363. Additionally, the viscosity of BEP364 was increase as the shear rate increased. This behavior can be explained as due to the proceeding of the curing reaction of BEP364 even at the relatively low testing temperature.

During heating the materials, two opposing processes took place. The viscosity of the resin was reduced by raising melting temperature while increased when cross-linking reaction started. Therefore, it was important to identify the temperature limits for product processing where the resins could be molten and fabricated into composites. Figure 5.5 revealed processing windows of BEP ternary mixtures. The complex viscosity of the resin as a function of temperature was recorded. The uncured monomer characteristics at room temperature were semi-solid in BEP361 to solid in BEP363. The point that dynamic viscosity of the ternary mixtures rapidly decreased with increasing temperature was related to the softening point of the resin. In the following stage, the ternary mixtures provided the lowest viscosity at certain temperature range. This lowest viscosity region rendered a processing window for a compounding process of each resin. Finally, at higher temperature the ternary mixtures underwent crosslinking reaction past the gel point thus resulting in a rapid increase in the viscosity beyond this transition (Rimdusit and Ishida, 2002).

Furthermore, the dynamic viscosity of the ternary mixtures tended to increase with increasing phenolic novolac mass fraction. The liquefying temperature of these ternary mixtures also increased with increasing amount of the phenolic novolac resin. The liquefying temperature was 35° C for BEP361, 45°C for BEP362, and 60°C for BEP363. However the liquefying temperature of all these mixtures was still lower than the unmodified BA-a resin which possessed the liquefying temperature of about 80°C. These liquefying behaviors are due to the presence of the epoxy diluent, which was a liquid at room temperature while benzoxazine resin and phenolic novolac resin are solids at room temperature. On the contrary, the gel point of these ternary mixtures tended to decrease with increasing the amount of the phenolic novolac resin. The BA-a resin and BEP361 showed approximately the same gel point at a temperature of 210°C while those of BEP362 and BEP363 are 180°C and 160°C respectively. This characteristic corresponds with the DSC results (Figures 5.2 and 5.3) that phenolic novolac resin can substantially reduce the curing temperature of the mixtures between benzoxazine and epoxy resins. As a result, it can be concluded that BEP364 and BEP363 had a rather narrow processing window due to the excess phenolic novolac mass fraction. If the processing window for the hot melt prepregging is considered, BEP361 and BEP362 are thus more suitable as a binder for the process. Generally, the B-staging step is carried out within 1-15 minutes in the prepreg processing. Consequently, gel time of each matrix should be in the above range. Many workers utilized ASTM D4473 method to determine gel point of each resin system which is the crossover of G' and G" i.e. at the gel point the storage modulus equals the loss modulus. However, the crossover point is frequency. Therefore, gel time determined by this technique is not exact (Winter and Mours, 1997). Holly et al. (1988) proposed using the loss angle (δ) for locating gel point. At the gel point tanδ becomes frequency independent. Therefore, the exact gel point is determined by the intersection of the various curves in a plot of tanδ versus time at various frequencies.

Figure 5.6 showed the intersection of tanδ at different frequencies of BEP362 at 120^{o}C. In the case of a control stress rheometer, the range of stress that is applied to the materials must be evaluated. The stress must be ensured to affect the gel time and the gel must exhibit a linear relationship in the whole stress range used. The results are shown in Figure 5.7 based on BEP362 using the gelation temperature of 120^{o}C. From this figure, no sign of the nonlinear behavior was observed within this range of stress.

Figure 5.8 expressed the effect of phenolic novolac mass fraction on the gelation behaviors of the ternary mixtures. The mass fraction of the phenolic novolac was varied systematically i.e.BEP360, BEP360.5, BEP361, BEP361.5, BEP362, BEP362.5, BEP363, BEP363.5, and BEP364. Gel time of every composition is obtained from the point where the loss tangent of different frequencies intersects each other as indicated previously. From the plot, increasing phenolic novolac mass fraction lowered the gelation time in the exponential decay manner. The gel time of the ternary mixtures ranged from 25 minutes in BEP360.5 to about 1 minute in BEP364. However, BEP360 showed no sign of gelation at 180^{o}C. This characteristic corresponded with the DSC results (Figure 5.2) that BEP360 (BE12), could not be cured at 180^{o}C.

From these processability results, it can be concluded that the suitable ternary mixtures for prepreg processing is BEP362 due to its relatively low curing reaction temperature with wide range of processing window 50-200^{o}C. The conversion of BEP362 at the gel point is determined to be 35%. This result is in good agreement with other resin systems i.e. BEP121 = 34%, and some epoxy molding compound 22-35% (Rimdusit and H. Ishida, 2002).

5.1.2 Properties of Ternary Systems Alloys

The effect of epoxy and phenolic novolac on the glass transition temperature in ternary system was previously reported by Rimdusit and Ishida using EPON825. When the amount of epoxy resin was less than 60% by weight, the glass transition temperature of ternary system were dependent on the mixed composition of benzoxazine, epoxy, and phenolic novolac resins. Too much amount of phenolic novolac leaded to significantly decrease in glass transition temperature since the number of chain which did not contribute to networking increased i.e. the number of dangling ends increased (Tyberg, 2000). In addition too much epoxy has a significant amount of unreacted epoxy groups and renders the lower T_g (Rimdusit and Ishida, 2000). The effect of both amount of phenolic novolac and epoxy was clearly observed in T_g when isothermally cured at 180^{o}C for 3 hours. In our series of the ternary systems, the highest T_g in BEP362 was obtained because of the optimum in both epoxy and phenolic mass fraction rendering the highest crosslinked density for the range of the ternary system compositions under investigation. Table 5.1, Figure 5.9, and Figure 5.10 showed the glass transition temperatures (T_g) of the fully cured ternary alloys between benzoxazine, epoxy, and phenolic novolac resins compared with other reported. All polymer alloys showed only single T_g implying the miscibility of the three resins. Figure 5.10 shows the effect of the curing condition on the glass transition temperature. From the plots, it was clearly seen that BEP362 exhibited the highest T_g in all examined curing condition. Thus BEP362 was suitable to utilize as matrix.

The network formation capability of the ternary system alloys can also be evaluated by a solubility test. In this test, all resin compositions were heated isothermally in a compression molder at 180^{o}C for 3 hours and post-cured in air-circulated oven at 200^{o}C for 2 hours to achieve the fully cured condition. The polymer alloy samples i.e. BEP361, BEP362, BEP363, and BEP364 were immersed in tetrahydrofuran (THF) to extract the unreacted fraction in the alloys. The extracting time was 45 days. Figure 5.11 reveals that BEP363 and BEP364 could not resist the solvent used while BEP362 and BEP361 can maintain their integrity. The solubility test of these alloys also support our previous results that phenolic novolac fraction in both BEP363 and BEP364 was overly presented and was not useful in the network formation of the final products.

Normally, degradation temperature (T_d) is one of the key parameters that needed to be considered for high temperature applications. Thermogravimetry (TG) is one technique which the change in sample mass lost is monitored as a function of temperature and/or time. The decomposition temperature, in this case, is defined as the temperature at 5% weight loss of the specimen. The TGA curve of the ternary alloys cured at 180^{o}C for 3 hours with a heating rate of 20^{o}C/min in nitrogen atmosphere is presented in Figure 5.12 and the numerical results were tabulated comparatively with other systems in Table 5.2. All alloys demonstrated an improvement in their thermal stability over the polybenzoxazine homopolymer. The decomposition temperature at 5 % weight loss was approximately 370-380^{o}C compared with 334^{o}C of polybenzoxazine (BA-a) and 352^{o}C of polybenzoxazine (BA-35X). This is due to, the enhanced cross-linked density from the incorporation of the epoxy resin in the systems was encouraging the degradation temperature of alloys.

The char yields of the ternary polymer alloys reported at 800^{o}C under N_2 atmosphere was also evaluated. The char yield of polymer alloys was increased with increasing in phenolic novolac mass fraction this is due to the fact that phenolic novolac resin possessed the highest char yield (55%) while both benzoxazine resin and epoxy resin rendered lower char yield i.e. 25-30% and 10% respectively

(Kampangsaeree, 2005). The characteristic was due to the more prevalent benzene rings in the phenolic novolac structure.

The flexural properties of the ternary alloys are also illustrated in Figure 5.13 and Table 5.3. The flexural strength of the alloys was slightly higher than those of polybenzoxazine and of typical epoxy. Epoxy provides flexural strength of about 110-145 MPa depending on the type of its curing agent. The increasing of epoxy resin fraction resulted in the higher flexural strain at break due to the flexibility in molecular structure of epoxy resin compared with the other two polymers (Rimdusit and H. Ishida, 2000). The flexural modulus of the ternary systems slightly increased when phenolic novolac mass fraction increased. To understand this behavior, it should be noted that crosslink density is not the only factor affecting the physical properties of the network. Although BEP363 and BEP364 had lower network densities, the prevalent unreacted phenols rendered the increasing chance of hydrogen bonding formation which also can raised the T_g (Tyberg, 2000).

5.1.3 Reactivity and Processability of Aging Resin

Storing resin monomer for prolonged times at ambient temperature has an effect to the curing called "chemical aging". The chemical aging of monomer will lead to permanent changes in the structure and posses some effects such as an increase of viscosity, reduction of reactivity, and processability. Thus prepregs are usually stored at low temperatures, below -20^{o}C, to ensure that there is no loss in its ability to react up to an appropriate degree of crosslinking. However, storing for prolonged time does not completely enable the aged prepregs or monomer for processing (Frigione and Kenny, 2002). Therefore, in this work the stability of ternary resin systems with prolonged storing time at ambient temperature has been observed.

The stability of BEP362 was examined from being aged at room temperature in desiccators for a prolonged time. The resin samples were taken at different time and were analyzed using DSC. Figure 5.14 shows the change in T_g of BEP362. At first, the rate of T_g development was a function of aging time. After approximately 1 month, there was a slight change in T_g. Figure 5.15 shows the heat of reaction as a function of aging time. Increasing degree of conversion of the resin led to an increase of T_g from the network formation in the resin. Consequently, T_g of aged samples was slightly higher than un-aged sample. It can be summarized that at low temperatures the curing reaction proceeds at very slow rates. However, the prolonged time does not significantly affect the processability of the ternary mixture after 1 month. There were only marginal changes in both heat of reaction and T_g.

The heat of reaction for unaged resin and the 9-month aged resin was calculated to be about 232 J/g and 175 J/g, respectively. The latter corresponded to the conversion of about 24%, lower than the conversion of BEP362 at the gel point (35%) and also lower than that of epoxy system (35% for 5 months) (Frigione and Kenny, 2002) . Therefore BEP362 resin can maintain reactivity and processability with prolonged storing time at ambient temperature making its prepregs to have long shelf life even at ambient conditions.

5.2 Composite Mechanical Properties

Jang et al. (2000) used carbon fiber surface treatments method to improve the mechanical properties of carbon fiber/BA-a composites. Oxygen plasma treatment and nitric acid oxidation were applied, both methods were effective to improve the resulting composite mechanical properties. Ishida and Chaisuwan (2003) proposed an alternative method. ATBN rubber was chosen as the rubber interlayer to improve the mechanical properties of CF/BA-35X composites. Good mechanical properties were reported, and the flexural strength from optimizing the concentration of ATBN rubber showed superior strength to the modified epoxy, modified phenolic resin, and modified BA-a composites.

From the previous experiment, our ternary systems showed some outstanding processability, thermal stability, and mechanical properties; therefore, in this work the ternary system was used as a matrix to produce prepregs of carbon fiber composites.

Flexural properties of carbon fiber-reinforced BEP alloys as a function of matrix composition are shown in Table 5.4. Two different types of carbon fiber were used as-received without any additional surface modification to evaluate their cross-ply composites i.e. beslon HTA-N-6000 and besfight HTA-12K-E30. These cross-ply were also compared with other reported systems. The fiber content of the composite was about 50% by volume. Where as, the 60% woven fiber volume fraction was done using KN 100 plain wave carbon cloth.

From the table, both flexural strength and flexural modulus of the ternary systems composites are relatively high compared with other carbon fiber composite systems. For example, the flexural modulus of BEP362/HTA-12K-E30 fiber composites was 69 GPa whereas that of polyimide PMR-15/T-650/35 was 60 GPa (cross-ply system). The flexural modulus of PMR-15/T-650/35 was calculated to be cross-ply orientation by the following equation.

$$E^{+}_{x,ult} = E^{0}_{x} t \qquad (1)$$

Where t = fraction of composite unidirectional layers in the loading direction

E^{o}_{x} = the flexural moduli of the composite unidirectional layer

$E^{+}_{x,ult}$ = the flexural moduli of the cross-ply composite

Flexural modulus of the carbon fiber reinforced BEP362 alloys as a function of the fiber volume fraction was illustrated in Figure 5.16. The flexural modulus of our composites followed the rule of mixture relatively well. The moduli of the axial stiffness and transverse stiffness were calculated by Voigt and Reuss models respectively while the modulus of the cross-ply composites was calculated by equation 1. The flexural moduli of BEP362 composites increase with increasing fiber volume fraction. Calculating modulus in BEP362 composites using equation 1 had approximately the same values as those from the experiment i.e. 70 GPa of the calculated value with 55% fiber volume fraction compared to 73 GPa from the experiment. However, the modulus of the woven composites from KN 100 fiber showed significantly lower values than the calculated modulus possibly due to the difference in fiber alignment such as form fiber netting, etc. From the table, our BEP362 composites showed higher flexural strength and flexural modulus values compared with other modified polybenzoxazine composites i.e. at 60% fiber volume fraction the flexural strength of BEP362/KN 100 equaled 1,011.06 MPa, that of nitric acid treatment CF/BA-a composites was 850 MPa, that of ATBN rubber interlayer CF/BA-35X composite was 820 MPa, and the higher flexural modulus of BEP362/KN 100 as 71 GPa, whereas ATBN rubber interlayer CF/BA-35X composite was 58 GPa.

The nature of the bending failure of CF/BEP362 composite was formed at the tensile-stressed side of the specimen through the fiber fracture and delamination of each ply of the prepregs. Scanning electron micrograph of the specimens failed under the flexural test showed in Figure 5.17a. The sample was BEP362/HTA-12K-E30 with 50% fiber volume fraction. Figure 5.17b and Figure 5.17c present the SEM micrographs of the fracture surface of BEP362 composites with cross-ply and woven fiber orientation after flexural test. The flexural surface was clearly embedded with the ternary matrix. This suggested that the cohesive failure occurred in the composites implying good interfacial adhesion between CF and our ternary matrices. A sign of fiber pull-out was also observed.

In addition, the honeycomb structure was made successfully using BEP362 prepregs. The honeycomb product was shown in Figure 5.18. The corrugation method was used to convert the BEP362 prepregs into honeycomb. The BEP362 prepregs was corrugated by metal mold using hot press at 180^{o}C in 3 hour, after that BEP362 was applied to the nodes to stack the sheet and cured in an oven for 3 hour. The prepregs showed good ability to form as honeycomb structure i.e. dimensional stability.

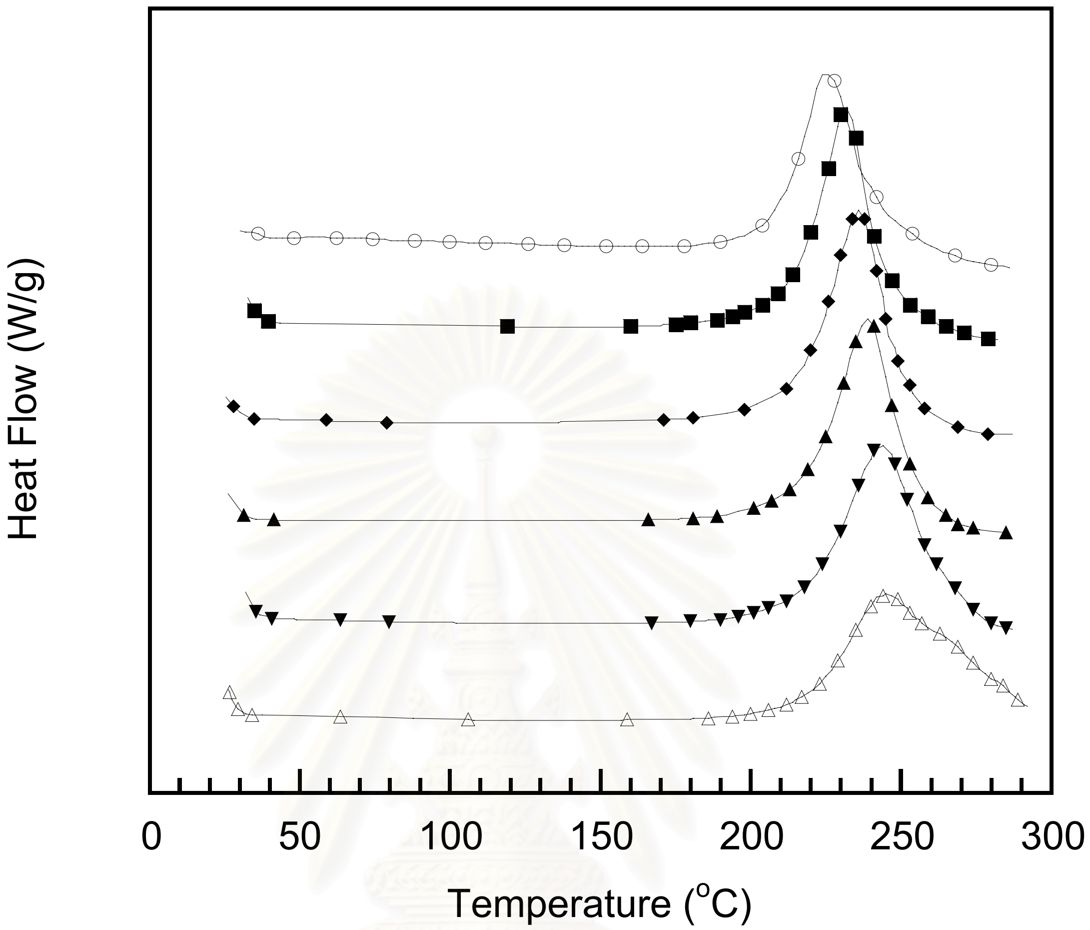


Figure 5.1: DSC thermograms of BE mixtures: (o) BA-a, (■) BE91, (♦) BE82, (▲) BE73, (▼) BP64, (Δ) BP55

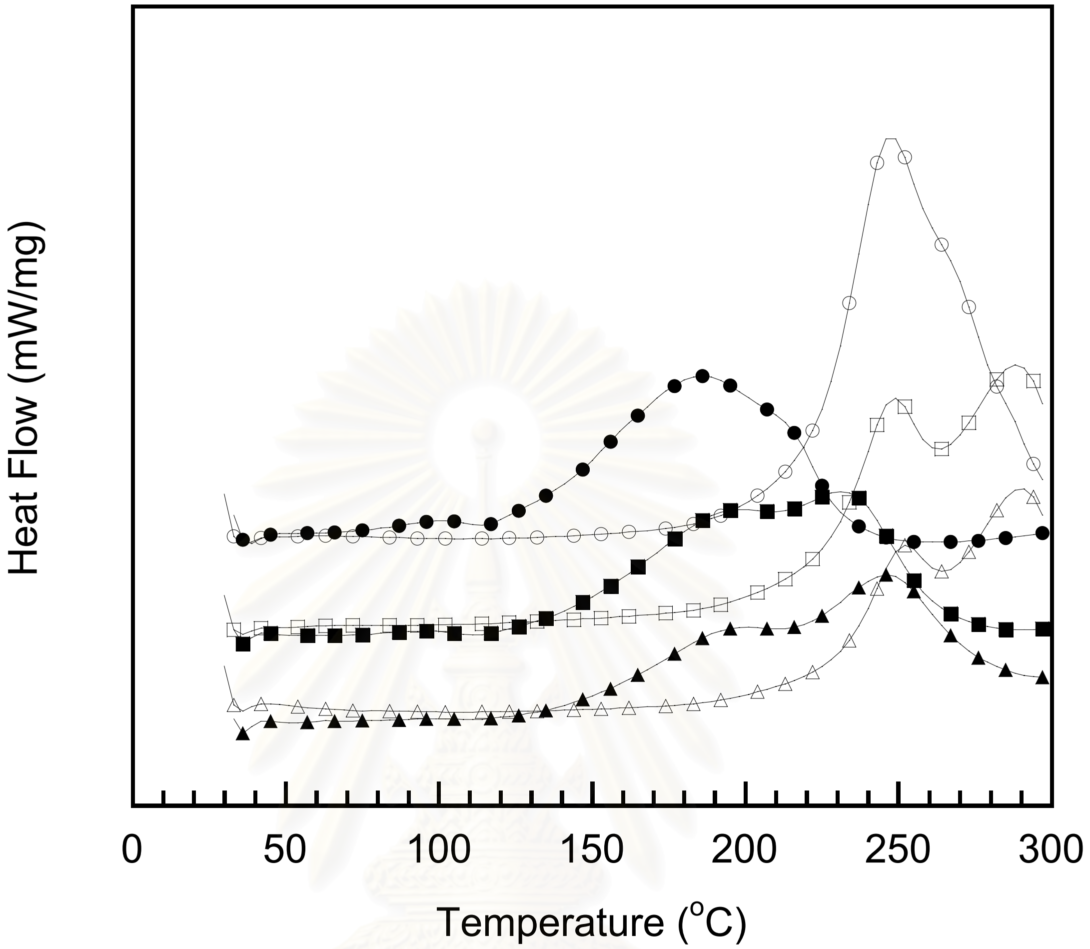


Figure 5.2: DSC thermograms of BEP mixtures: (o) BE11, (●) BEP111, (□) BE12, (■) BEP121, (Δ) BE13, (▲) BEP131.

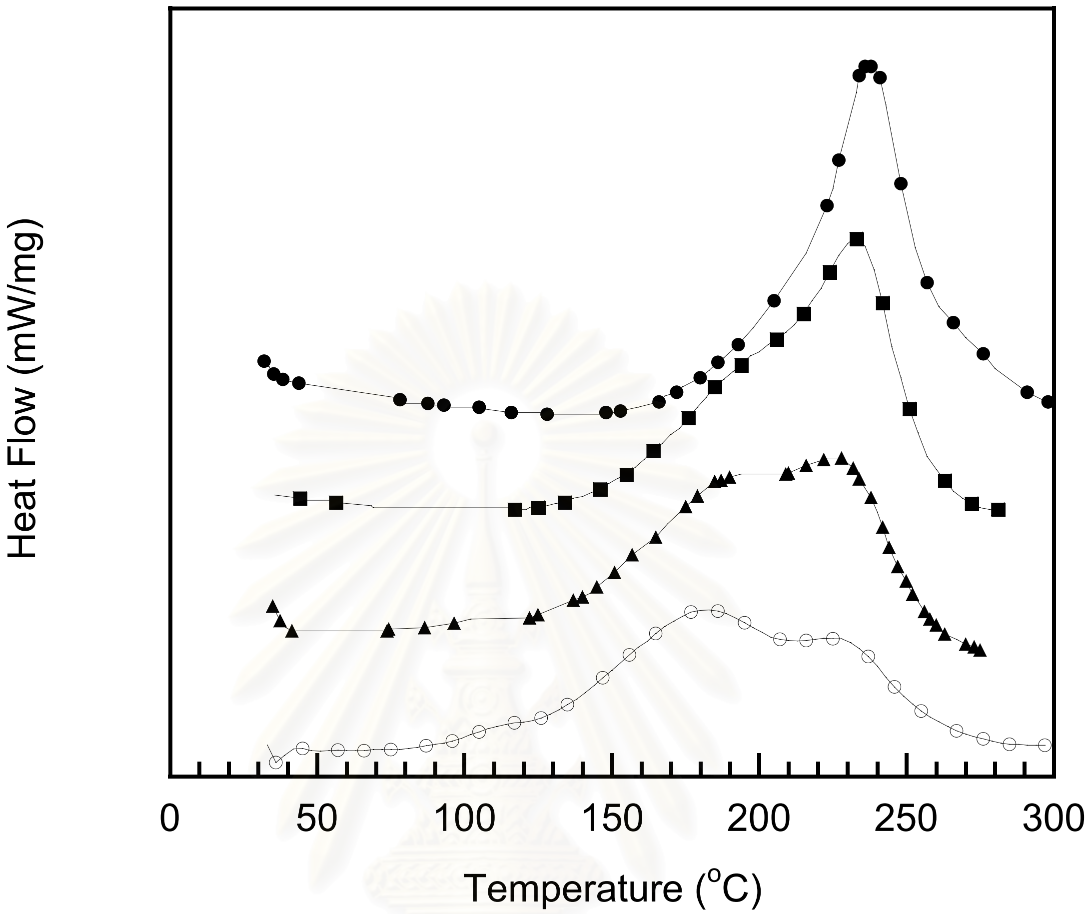


Figure 5.3: DSC thermograms of BEP mixtures: (●) BEP361, (■) BEP362, (▲) BEP363 (o) BEP364.

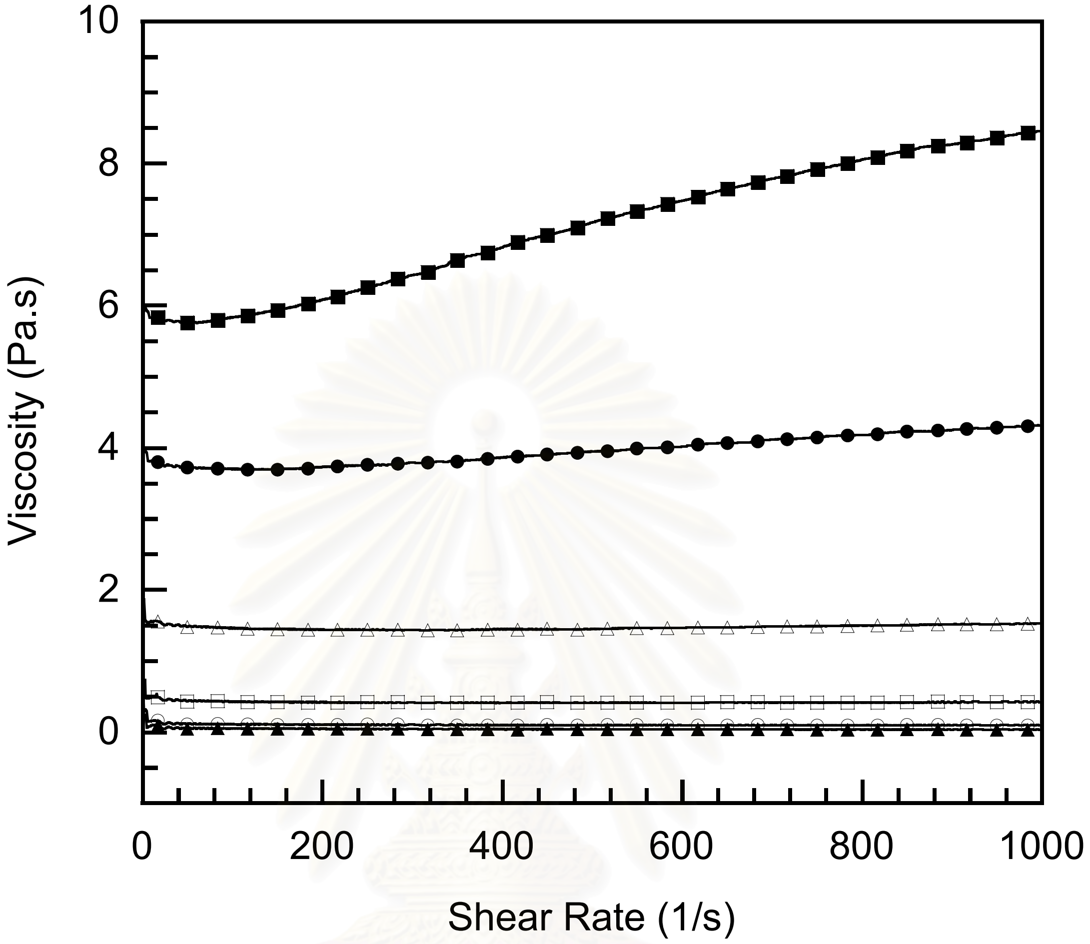


Figure 5.4: Viscosity of ternary systems at 100^{o}C: (o) BEP360, (□) BEP361, (Δ) BEP362, (●) BEP363, (■) BEP364, (▲) EPOXY828.

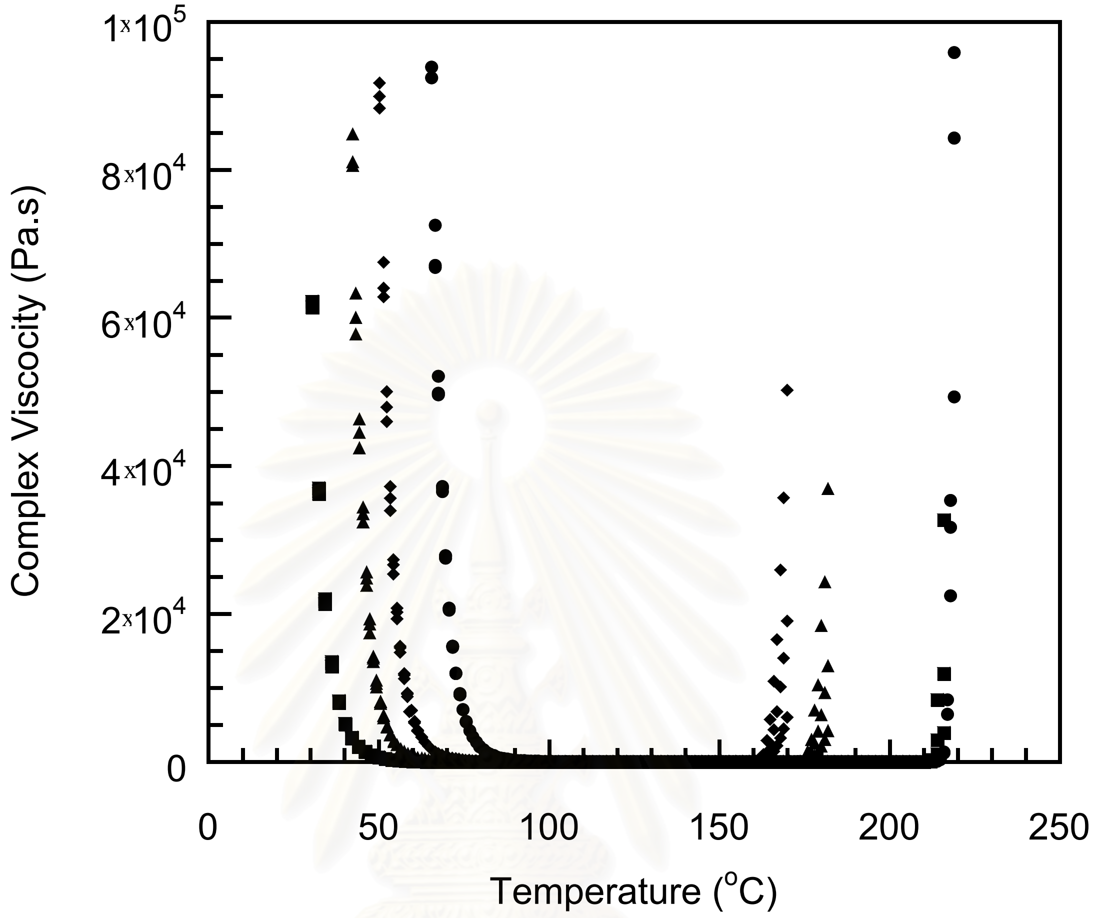


Figure 5.5: Processing window of Ternary mixtures at heating rate of 2°C/min: (●) BA-a, (■) BEP361, (▲) BEP362, (◆) BEP363.

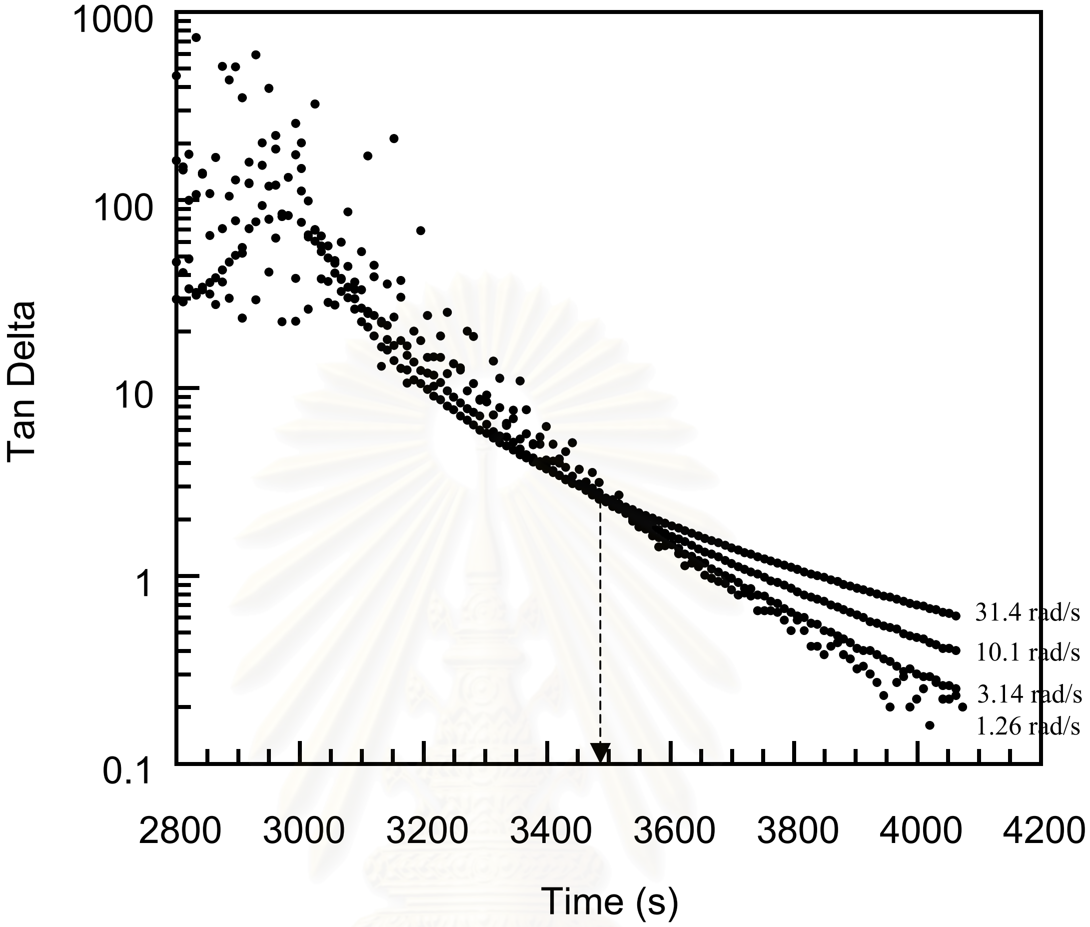


Figure 5.6: The gel time of BEP362 using frequency independent of loss tangent as a gel point at 120°C.

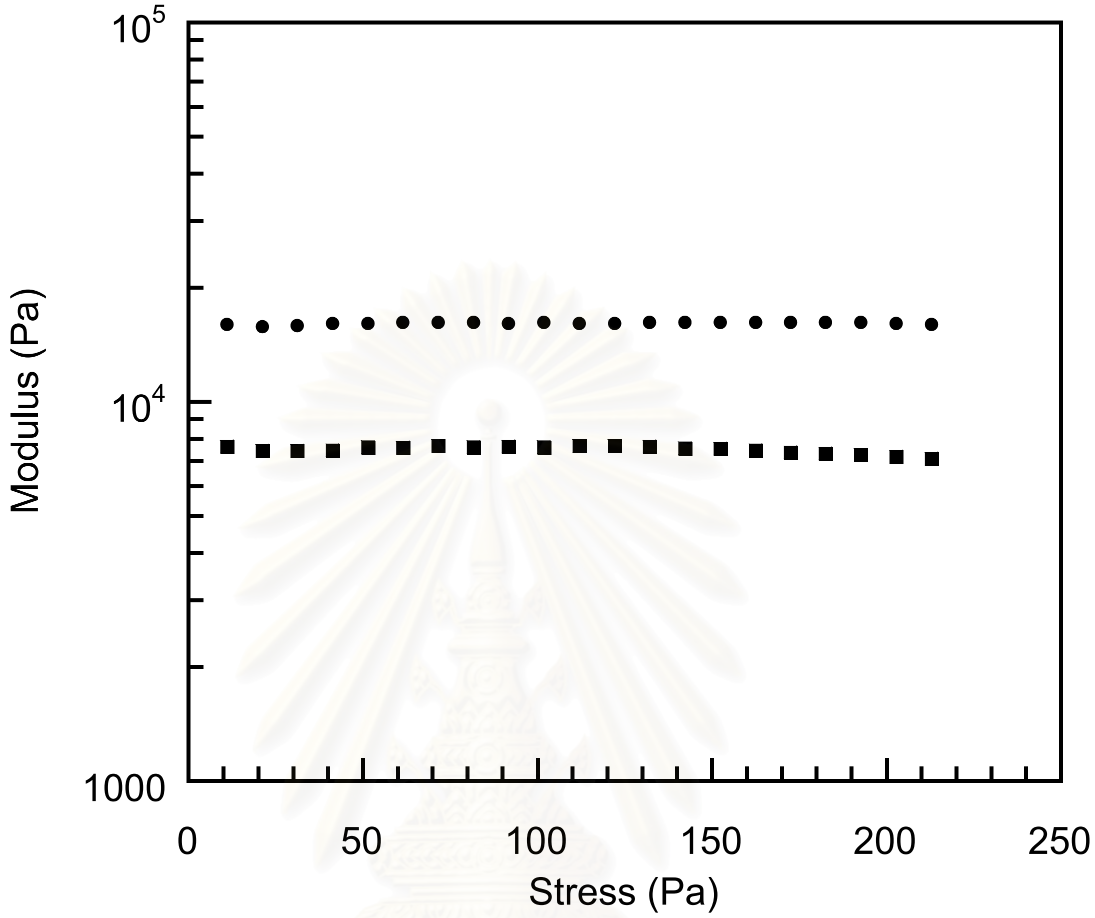


Figure 5.7: Stress sweep experiment at the gel point of BEP362: (●) Storage Modulus, (■) Loss Modulus.

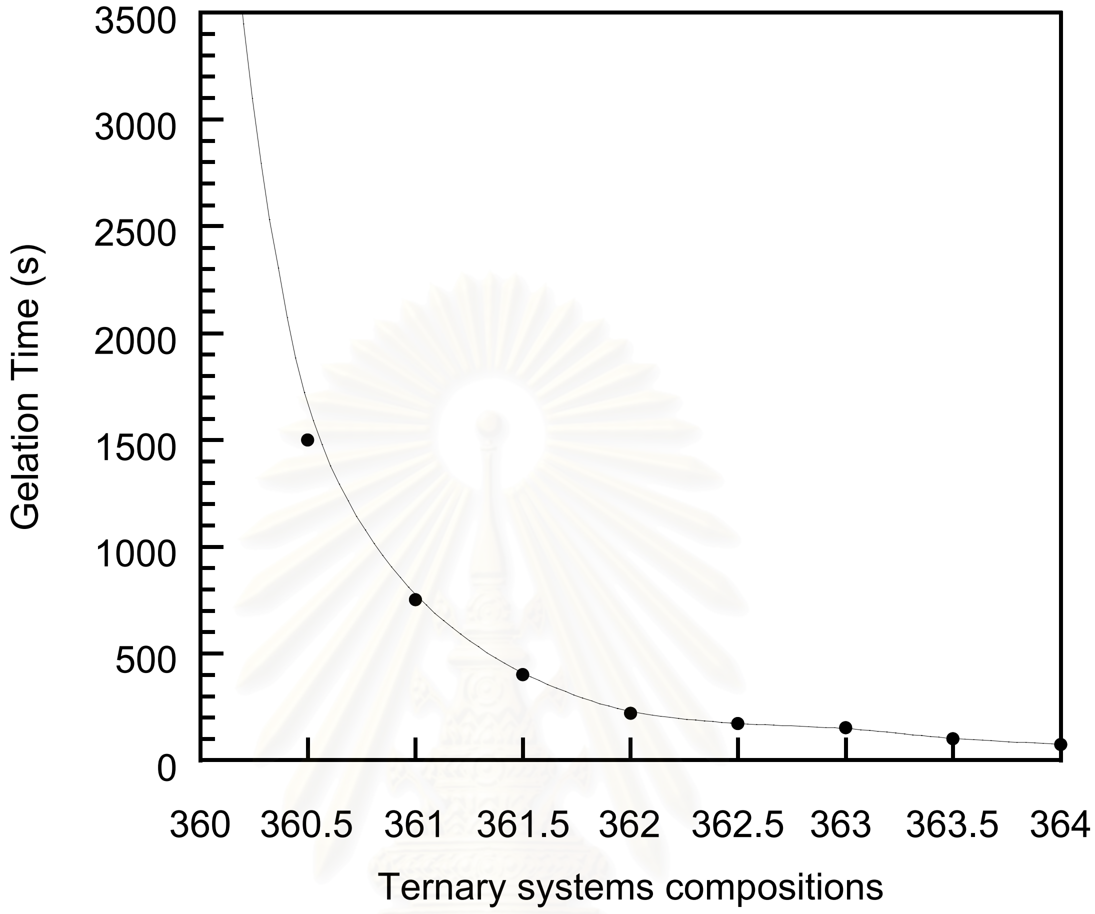


Figure 5.8: The plot of gel time as a function of ternary systems compositions at 180°C.

Table 5.1: Glass transition temperature of ternary systems cured in air and in non-hermetic DSC pans compared with previously reports.

Resins	DSC T_{g}s (^{o}C)	Air-cured T_{g}s at curing condition	
		180^{o}C 3 hour	180^{o}C 3 hour + 200^{o}C 2 hour
BA-a*	139	-	-
BEP361*	135	-	-
BEP361	130	143	160
BEP362	136	157	165
BEP363	123	136	147
BEP364	126	129	135

* Ref.: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.

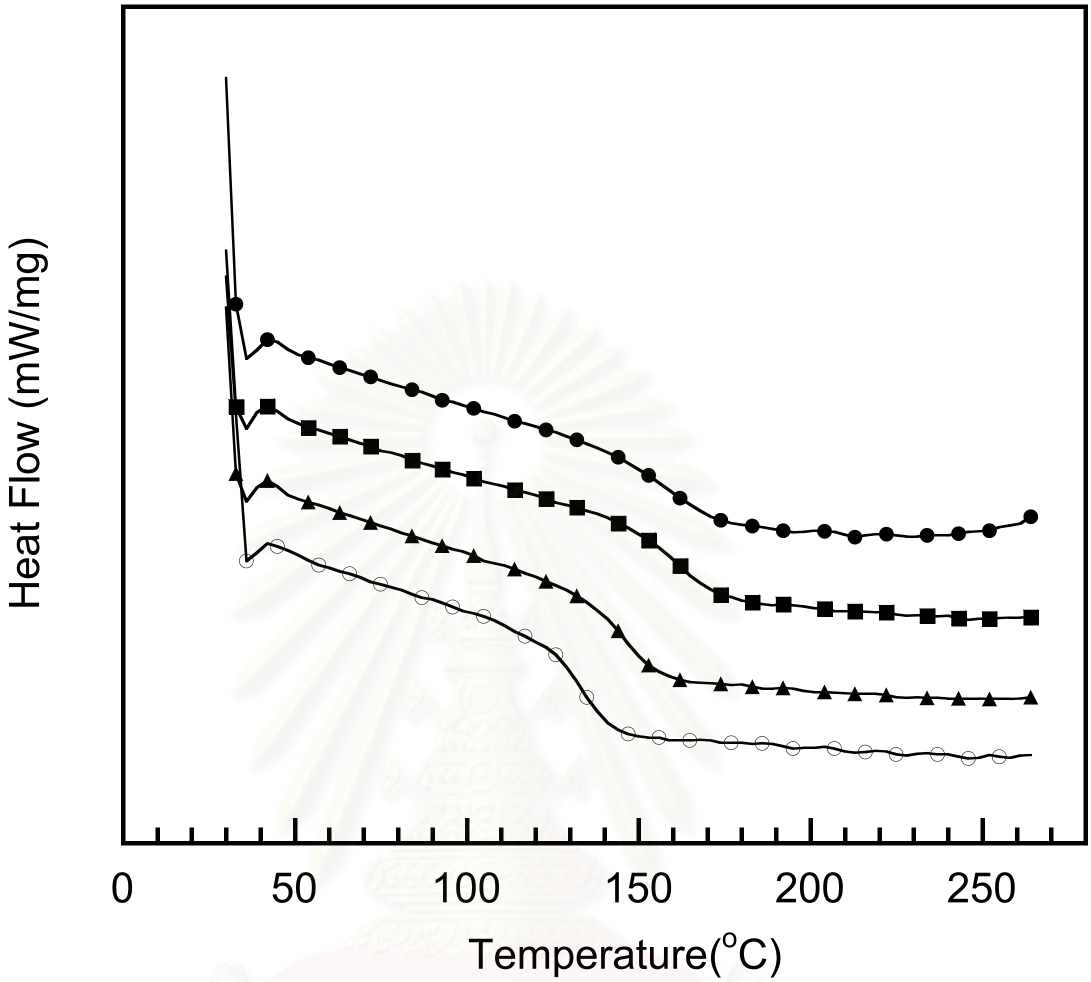


Figure 5.9: DSC thermograms showing glass-transition temperature of Ternary systems alloys: (●) BEP361, (■) BEP362, (▲) BEP363 (o) BEP364.

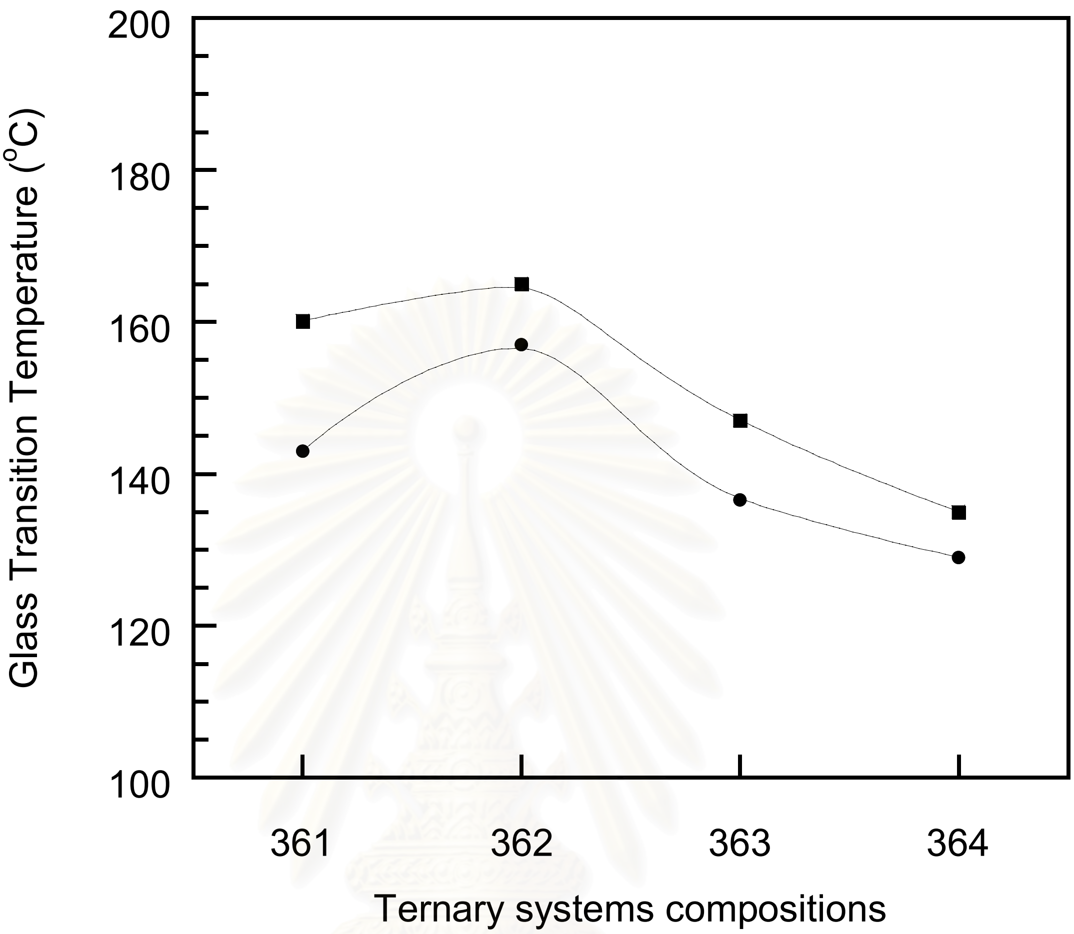


Figure 5.10: The Glass transition temperature of Ternary systems alloys with two different curing conditions: (●) 180°C 3 hour, (■) 180°C 3 hour + 200°C 2 hour.

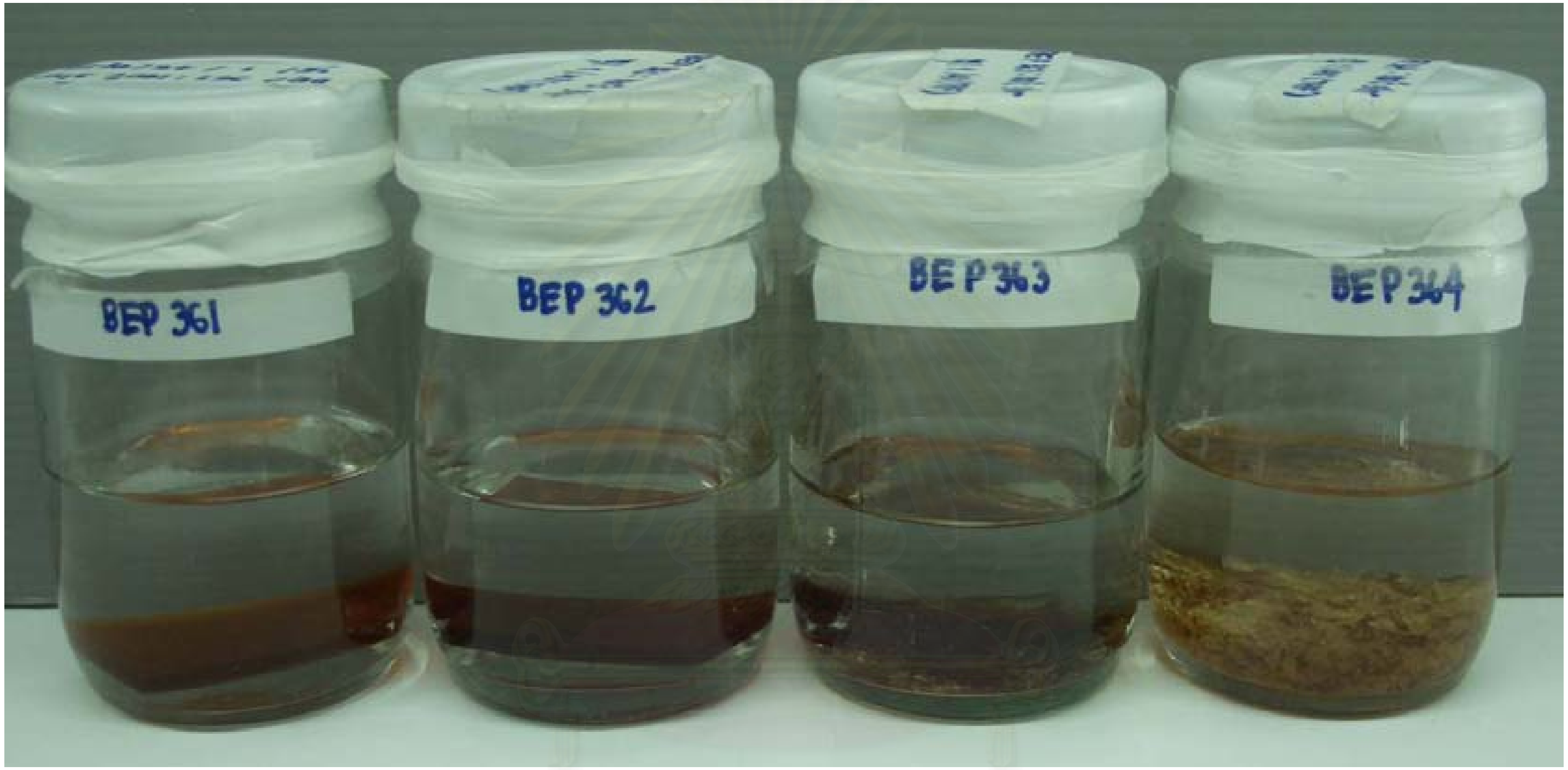


Figure 5.11: Solvent extraction of BEP alloys using THF at 45 days.

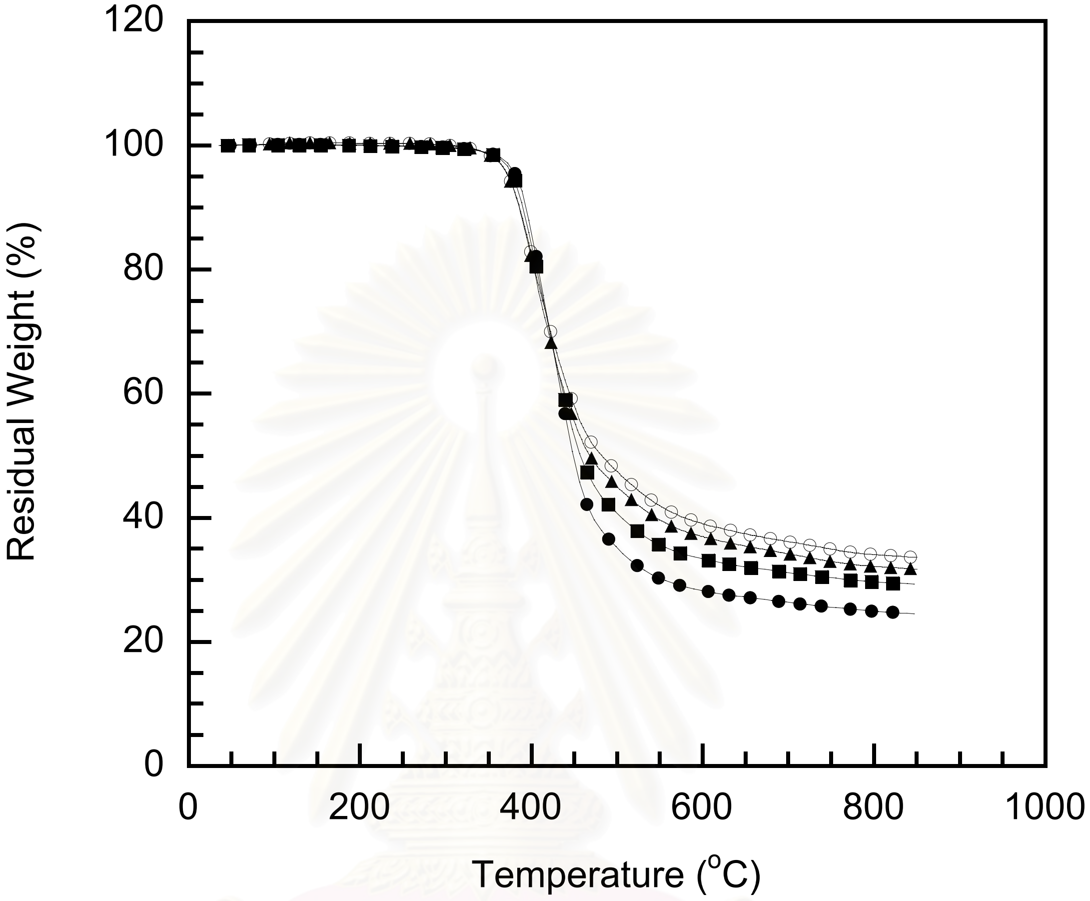


Figure 5.12: TGA thermograms of BEP alloys: (●) BEP361, (■) BEP362, (▲) BEP363 (○) BEP364.

Table 5.2: The Thermal Characteristics of Polybenzoxazine and Polybenzoxazine alloys compared with typical Epoxy and Phenolic.

Resins	Degradation Temperature (°C)		Char Yield (%)
	5% weight loss	10% weight loss	
BEP361	382	393	24.8
BEP362	378	389	29.6
BEP363	373	388	32.1
BEP364	372	385	34.0
BA-a[1]	334	355	25.0
BA-35X[2]	352	-	30.0
BEP361[3]	348	-	19.3
Epoxy[1]	-	-	10.5
Phenolic[1]	-	-	55.0

[1] Ref.: Kampangsaeree N. Development of Fire resistant Wood-substituted Composites from Polybenzoxazine Alloys. Master's degree. Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, 2004.

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

[3] Ref.: 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.

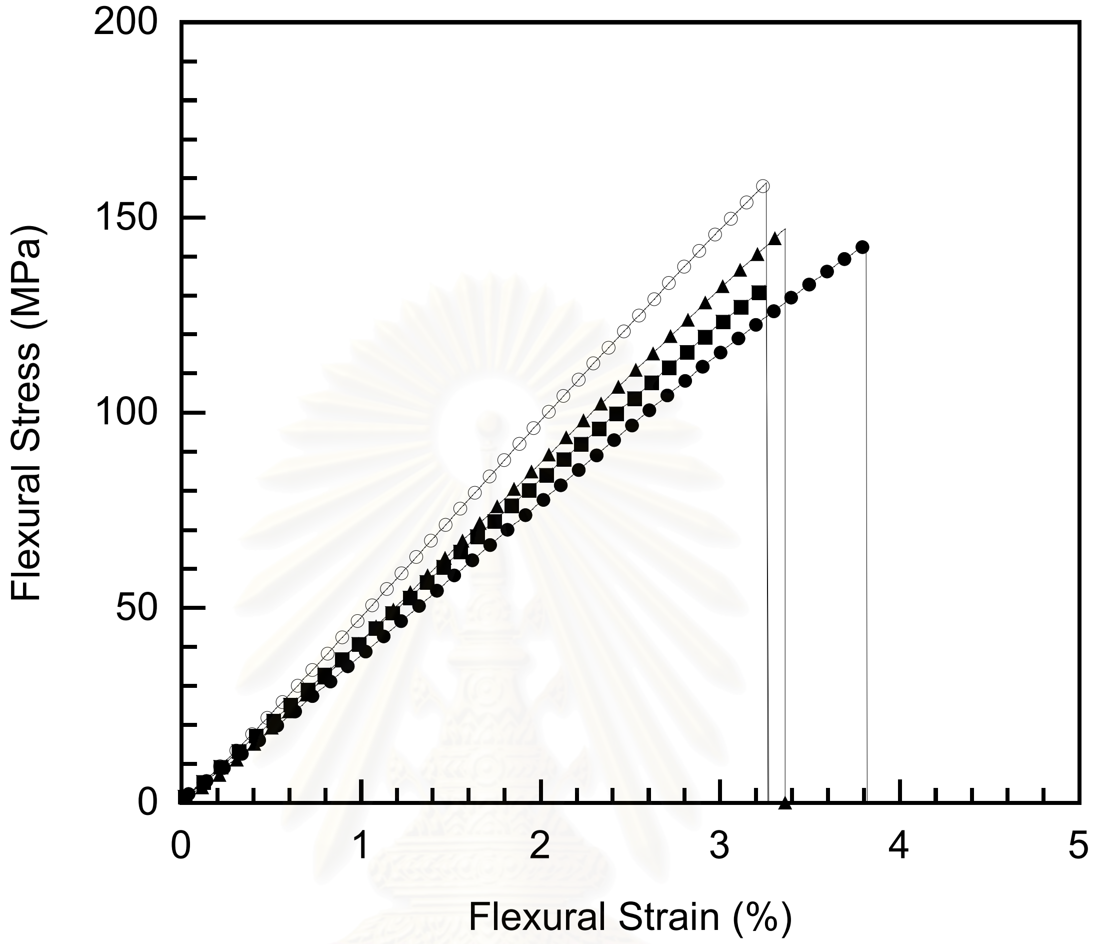


Figure 5.13: Flexural stress & strain of BEP alloys at various compositions: (●) BEP361, (■) BEP362, (▲) BEP363 (○) BEP364.

Table 5.3: Flexural properties of BEP alloys

Composition	Flexural Strength (MPa)	Flexural Modulus (GPa)
BA-a[1]	117	4.27
BEP361	141.5± 2.2	3.8±0.2
BEP362	134.7± 3.3	4.2±0.0
BEP363	145.0± 2.7	4.5± 0.1
BEP364	158.6± 0.1	5.0± 0.1
Epoxy828[2]	145	3.86
Phenolic[3]	-	3.8

[1] Ref.: Rimdusit S., Pirstpindvong S., Tanthapanichakoon W., and Damrongsakkul S. Toughening of polybenzoxazine by alloying with urethane prepolymer and flexible epoxy: a comparative study. Polym. Eng. and Sci. 45 (2005): 288-297.

[2] Ref.: www.resins.com, 2001 Resolution Performance Products.

[3] Ref.: Ishida H. and Allen D.J. Physical and mechanical characterization of near-zero shrinkage polybenzoxazines. J. Polym. Sci. Pol. Phys. 34 (1996) 1019-1030.

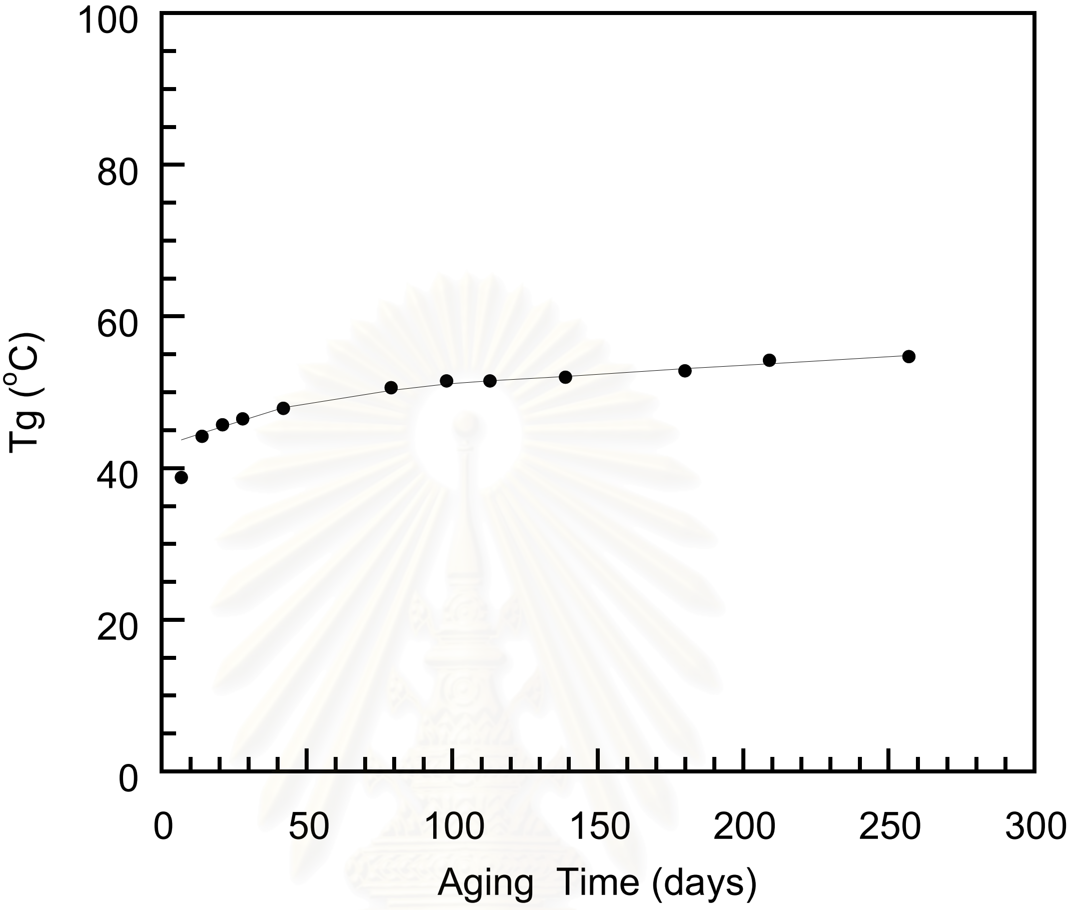


Figure 5.14: Changes in glass transition temperature (T_g) as a function of aging time for BEP362

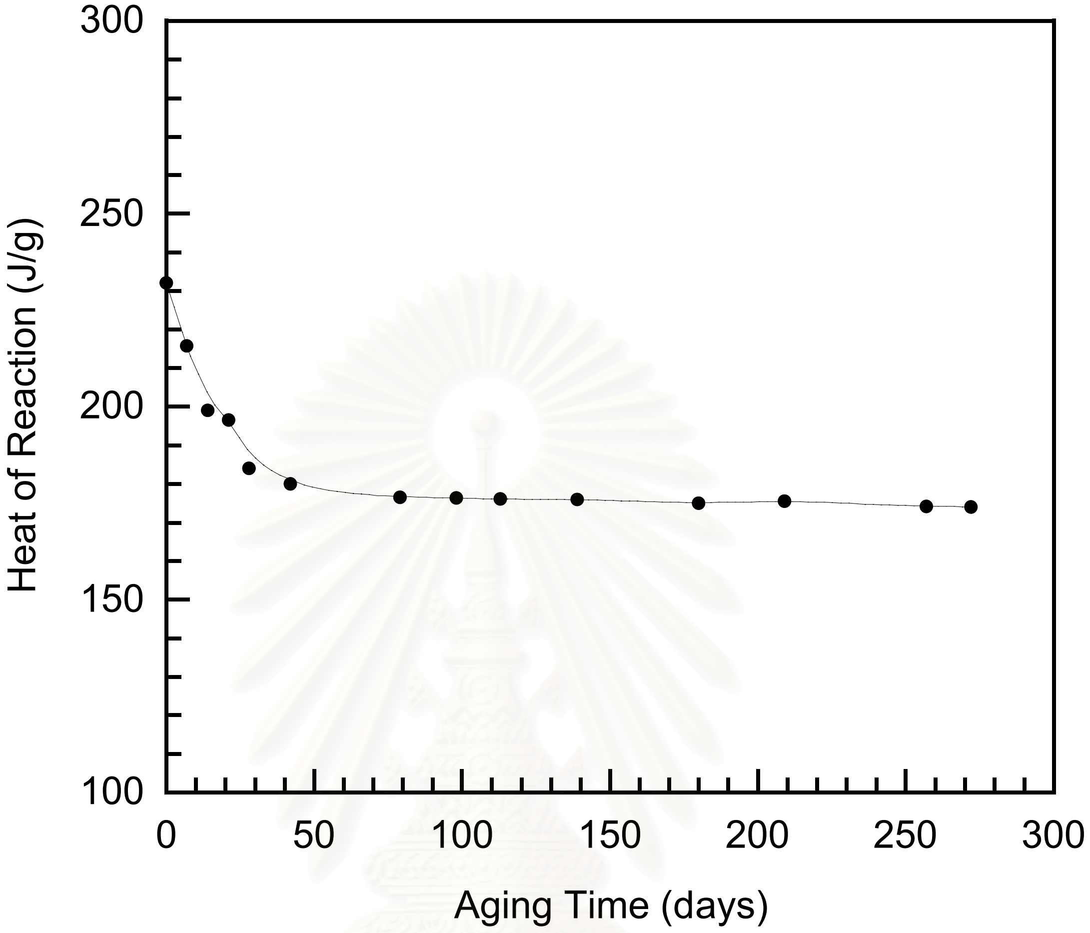


Figure 5.15: Changes in total heat of reaction as a function of aging time for BEP362

Table 5.4 : The mechanical properties of ternary systems composites and other high-performance composites.

Resins	Fiber Types	Treatment Method	Fiber Volume fraction (%)	Flexural properties	
				Strength (MPa)	Modulus (GPa)
BEP361	HTA-N-6000	-	50	940	69
	HTA-12K-E30	-	50	921	57
	KN 100	-	60	706	68
BEP362	HTA-N-6000	-	50	809	59
	HTA-12K-E30	-	50	1,072	68
	KN 100	-	60	1,011	71
BEP363	HTA-N-6000	-	50	850	58
	HTA-12K-E30	-	50	996	54
	KN 100	-	60	734	69
BA-a[1]	Woven T-300	-	N/A	400	N/A
BA-a[1]	Woven T-300	Plasma 3min	N/A	600	N/A
BA-a[2]	Woven T-300	Acid 60min	N/A	850	N/A
BA-35X[3]	Woven T-300	Rubber layer	60	820	58
EPOXY[4] (TGBAP/BEP)	Woven T-300	PEI Coating	60	800	N/A
PMR-15[5]	T-650/42-6K	-	69	1,800	60
EPOXY828[6]	Morganite II	-	69	1,655	N/A
	Calanese GY-70	-		696	N/A

[1] Ref.: Jang J. and Yang H. Toughness improvement of carbon-fibre/polybenzoxazine composites by rubber modification. Compos. Sci. and Tech. 60 (2000): 457-463.

[2] Ref.: Jang J. and Yang H. The effect of surface treatment on the performance improvement of carbon fiber/polybenzoxazine composites. J. of Mater. Sci. 35(2000): 2297.

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

[4] Ref.: Shin S., Jang J. The effect of thermoplastic coating on the mechanical properties of woven fabric carbon/epoxy composite. J. of Polym. Sci. 35 (2000): 2047-2054.

[5] Ref.: Shen S. and Ishida H. Development and characterization of high-performance polybenzoxazine composites. Polym. Compos. 17 (1996): 710.

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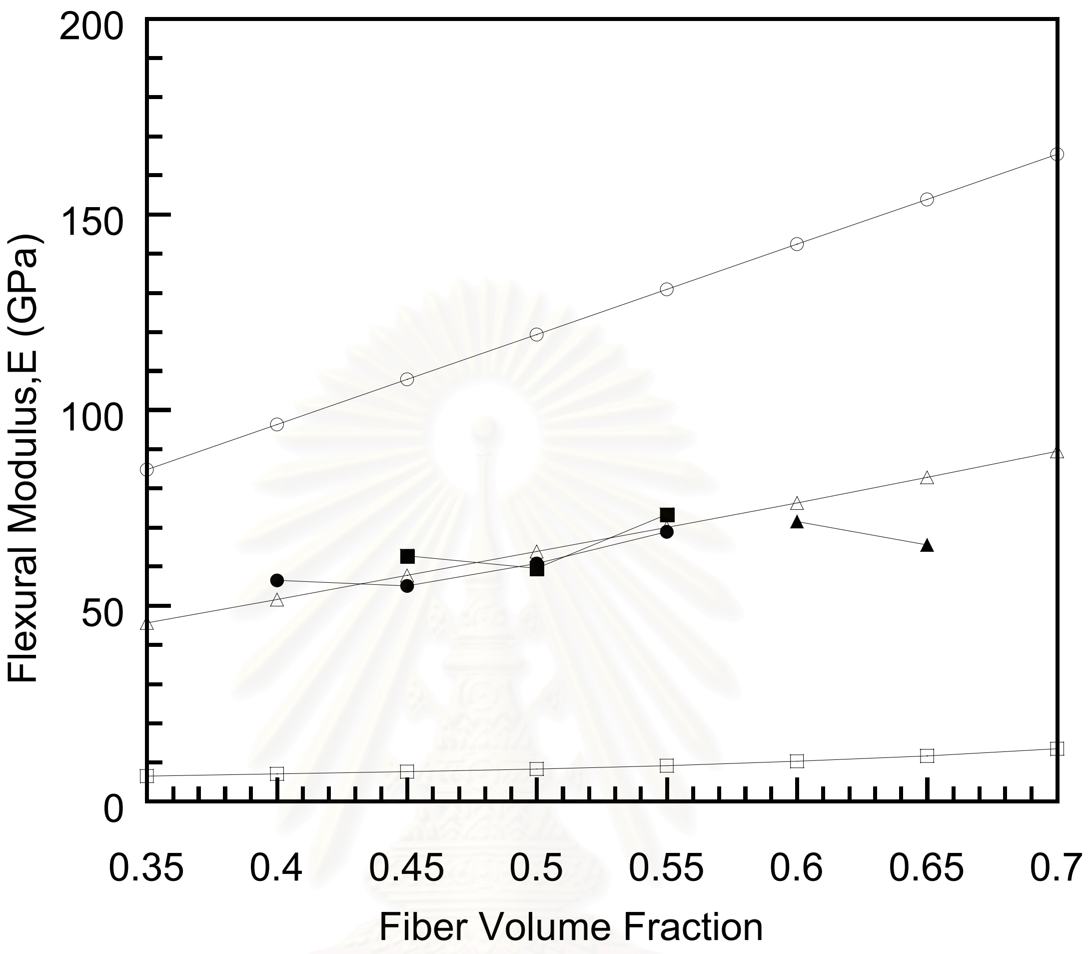
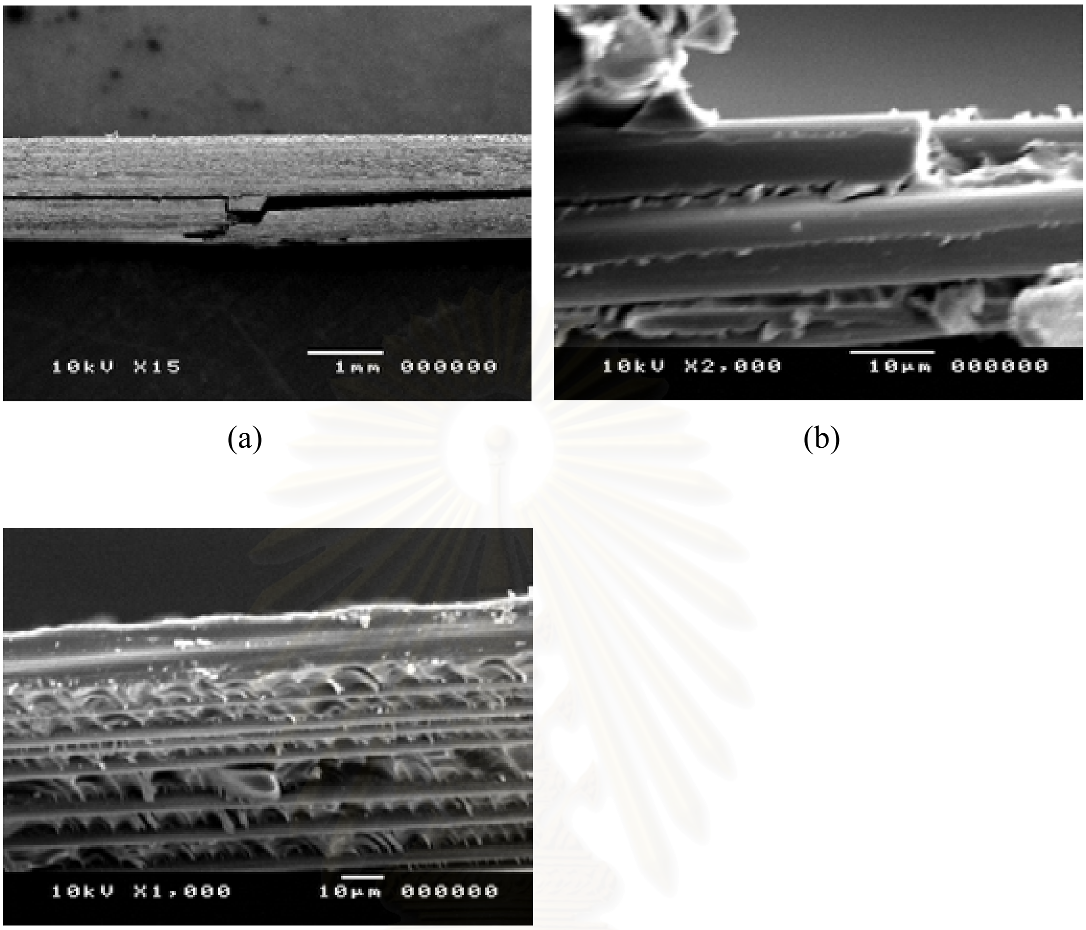


Figure 5.16: The effect of fiber volume fraction on Flexural modulus of BEP362/CF composites: (o) Voigt Model, (□) Reuss Model, (Δ) Cross-ply Calculation, (●) HTA-12K-E30, (■) HTA-N-6000, (▲) KN 100.



(a) (b)

(c)

Figure 5.17: SEM micrographs of the fracture surface after flexural test: (a) cross-ply laminate damage pattern of BEP362/HTA-12K-E30 , (b) cross-ply laminate fracture surface of BEP362/HTA-12K-E30, and (c) woven laminate of BEP362

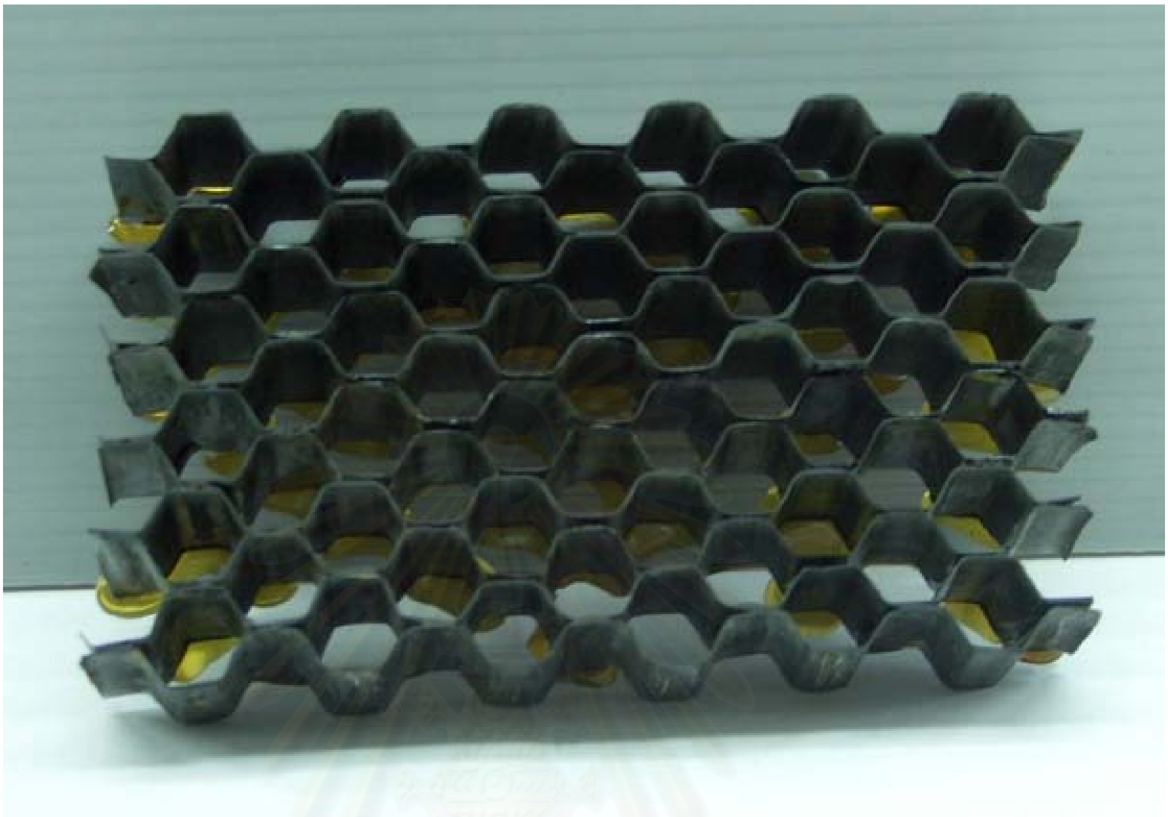


Figure 5.18: Honeycomb product from BEP362 prepregs.

CHAPTER VI

CONCLUSIONS

The suitable ternary matrix composition based on benzoxazine, epoxy, and phenolic novolac resins for carbon fiber prepregs fabrication was determined. The optimal composition was based on processability, thermal stability, mechanical properties of the matrices, and mechanical properties of composite materials. From the results, BEP362 was capable of prepregging via methods either hot melt or solvent impregnation methods. The excellent wettability of BEP362 was observed due to its low melt viscosity (1.2 Pa.s at 100^oC) with suitable pot-life with wide range of a processing temperature $50\text{-}200^oC$. The ternary system can be kept at ambient temperature for several weeks and still maintained its processability of its prepregs. The optimal curing condition of BEP362 is 180^oC 3 hour and post cure at 200^oC 2 hour, T_g of fully cured alloys is 165^oC.

Thermal stability and mechanical properties of BEP362 showed the highest value among the series of the ternary systems under investigation with, high degradation temperature, high char yields, as well as good mechanical properties due to the balance in ternary system composition. Benzoxazine provided the molecular rigidity and thermal-curability while epoxy contributed as reactive diluents to the mixture while phenolic novolac acted as an initiator in the ternary systems. Moreover, the good carbon fiber/BEP362 adhesion was also achieved. Therefore, the matrix resin for carbon fiber prepregs was achieved though BEP362 ternary system.

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APPENDICES

APPENDIX A

Processability of Benzoxazine/Epoxy/Phenolic Novolac Mixture

Appendix A-1 Gel time of ternary systems mixture at 180°C.

Ternary Systems Compositions	Gelation Time (min)
360	-
360.5	25.0
361	12.5
361.5	6.6
362	3.6
362.5	2.8
363	2.5
363.5	1.6
364	1.3

Appendix A-2 Glass transition temperature of BEP362 as a function of aging times.

Aging Time (Days)	Glass transition temperature (°C)
0	36.03
7	38.73
14	44.20
21	45.72
28	46.47
42	47.84
79	50.57
98	51.48
113	51.48
139	51.93
180	52.84
209	54.21
257	54.66
272	54.88

Appendix A-3 Heat of reaction of BEP362 as a function of aging times.

Aging Time (Days)	Heat of reaction (J/g)
0	232.10
7	215.80
14	199.00
21	196.60
28	184.00
42	180.00
79	176.50
98	176.30
113	176.00
139	175.90
180	175.00
209	175.50
257	174.20
272	174.00

APPENDIX B

Characterization of Benzoxazine/Epoxy/Phenolic Novolac Alloys

Appendix B-1 Glass transition temperature of BEP alloys.

Ternary Systems Compositions	DSC T_gs (^{o}C)	Air-cured T_gs at curing condition	
		180^{o}C 3 hour	180^{o}C 3 hour + 200^{o}C 2 hour
BEP361	130	143	160
BEP362	136	157	165
BEP363	123	136	147
BEP364	126	129	135

Appendix B-2 Degradation temperature of BEP alloys.

Ternary Systems Compositions	Degradation Temperature (^{o}C)	
	5% weight loss	10% weight loss
BEP361	382	393
BEP362	378	389
BEP363	373	388
BEP364	372	385

Appendix B-3 The char yield of BEP alloys.

Ternary Systems Compositions	Char Yield (%)
BEP361	24.8
BEP362	29.6
BEP363	32.1
BEP364	34.0

Appendix B-4 Flexural properties of BEP alloys

Ternary Systems Compositions	Flexural Modulus (GPa)	Flexural Strength (MPa)
BEP361	3.8±0.2	141.5±2.2
BEP362	4.2±0.0	134.7±3.3
BEP363	4.5±0.1	145.0±2.7
BEP364	5.0±0.1	158.6±0.1

APPENDIX C

Mechanical Characterization of Carbon fiber reinforced Benzoxazine/Epoxy/Phenolic Novolac Alloys

Appendix C-1 Flexural properties of Carbon fiber reinforced BEP alloys (fiber type: HTA-N-6000).

Ternary Systems Compositions	Flexural Modulus (GPa)			
	40% V_f	45% V_f	50% V_f	55% V_f
BEP361	60±0.3	-	69±0.7	-
BEP362	-	62±1.5	59±3.1	73±0.0
BEP363	-	57±0.0	58±3.0	60±0.0

Ternary Systems Compositions	Flexural Strength (MPa)			
	40% V_f	45% V_f	50% V_f	55% V_f
BEP361	871±49.2	-	940±66.0	-
BEP362	-	842±85.2	809±75.0	1081±0.0
BEP363	-	779±0.0	850±38.37	791±0.0

Appendix C-2 Flexural properties of Carbon fiber reinforced BEP alloys (fiber type: HTA-12K-E30).

Ternary Systems Compositions	Flexural Modulus (GPa)			
	40% V_f	45% V_f	50% V_f	55% V_f
BEP361	50±3.3	52±7.9	57±2.6	67±2.4
BEP362	56±1.3	55±3.3	60±3.7	68±0.0
BEP363	-	53±7.7	55±3.1	-

Ternary Systems Compositions	Flexural Strength (MPa)			
	40% V_f	45% V_f	50% V_f	55% V_f
BEP361	757±109.4	859±234.3	921±58.9	1,187±55.9
BEP362	962±136.1	969±123.7	1,073±129.8	1,156±0.0
BEP363	-	984±83.9	996±39.6	-

Appendix C-3 Flexural properties of Carbon fiber reinforced BEP alloys (fiber type: HTA-12K-E30).

Ternary Systems Compositions	Flexural Modulus (GPa)		
	55% V_f	60% V_f	65% V_f
BEP361	64±0.0	68±0.0	67±2.8
BEP362	-	71±4.0	65±3.2
BEP363	66±0.3	69±0.4	-

Ternary Systems Compositions	Flexural Strength (MPa)		
	55% V_f	60% V_f	65% V_f
BEP361	970±0.0	706±0.0	894±100.0
BEP362	-	1,011±65.8	850±130.0
BEP363	814±39.0	734±65.2	-

VITA

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