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นายปฐมกร คุโณภาส

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THERMOMECHANICAL PROPERTIES OF ARYLAMINE-BASED BENZOXAZINE RESINS ALLOYED WITH EPOXY RESIN

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Field of Study	Chemical Engineering
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ปฐมกร คุโณภาส : คุณสมบัติทางกลเชิงความร้อนของเบนซอกซาซีนเรซินกลุ่มแอริลเอมีนที่ทำอัลลอยกับอีพอกซีเรซิน. (THERMOMECHANICAL PROPERTIES OF ARYLAMINE-BASED BENZOXAZINE RESINS ALLOYED WITH EPOXY RESIN) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. ศราวุธ ริมดุสิต, 89 หน้า.

ในงานวิจัยนี้ ผลกระทบของการเติมอีพอกซีเรซินลงในเบนซอกซาซีนเรซินที่มีกลุ่มของแอริลเอมีนที่แตกต่างกันเป็นองค์ประกอบ เช่น อะนิลีน, เมตา-โทลูอิดีน และ 3,5-ไซลิดีน ซึ่งถูกเรียกว่า BA-a, BA-mt และ BA-35x ตามลำดับ ได้ถูกทำการตรวจสอบ ช่วงอุณหภูมิในการขึ้นรูปของ BA-35x, BA-mt และ BA-a ถูกพบว่ามีช่วงอุณหภูมิในการขึ้นรูปกว้างขึ้นตามปริมาณของอีพอกซีเรซิน จุดเกิดเจลของของผสมเบนซอกซาซีน-อีพอกซีเรซินสามารถทำนายได้แม่นยำโดยสมการอาร์เรเนียส เช่น เวลาการเกิดเจลของ BA-35x ที่ถูกอัลลอยด้วยอีพอกซีเรซิน ที่สัดส่วนมวล 70:30 สามารถทำนายได้โดย $t_{gel}=0.7012\times10^{-7}\exp(10.563/T)$ ในการเติมอีพอกซีลงในพอลิเบนซอกซาซีน ส่งผลให้ปริมาณความหนาแน่นในการเชื่อมขวางของพอลิเมอร์อัลลอยเพิ่มขึ้น ซึ่งจะมีอิทธิพลต่อคุณสมบัติส่วนใหญ่ของลูกผสม จากการวิเคราะห์ทางกลเชิงไดนามิกส์ ค่าอุณหภูมิการเปลี่ยนสถานะคล้ายแก้วหาได้จากตำแหน่งสูงสุดของมอดูลัสสูญเสีย ในระบบ BA-a และ BA-mt ที่ทำอัลลอยกับอีพอกซีเรซิน ถูกพบว่าแสดงการเกิดพฤติกรรมงานร่วม ซึ่งให้ค่าอุณหภูมิการเปลี่ยนสถานะคล้ายแก้วสูงสุดที่สัดส่วนมวลเบนซอกซาซีนต่ออีพอกซีที่ 80:20 ซึ่งมีค่าเท่ากับ 182 องศาเซลเซียส สำหรับระบบBA-a และ 213 องศาเซลเซียส สำหรับระบบBA-mt อย่างไรก็ตาม ในระบบ BA-35x ค่าอุณหภูมิการเปลี่ยนสถานะคล้ายแก้วมีแนวโน้มลดลงจาก 241 องศาเซลเซียส ถึง 223 องศาเซลเซียส ในปริมาณอีพอกซีเรซิน 40% โดยน้ำหนัก ในพอลิเมอร์อัลลอยเบนซอกซาซีน-อีพอกซี ที่มี เมตา-โทลูอิดีน เป็นองค์ประกอบ มีค่าอุณหภูมิการสลายตัวของมวลที่สูญเสียไป 5% สูงสุดท่ามกลางพอลิเบนซอกซาซีน-อีพอกซีอัลลอย เช่น ที่สัดส่วน 80:20 โดยมวล ระบบ BA-mt มีค่าอุณหภูมิการสลายตัวเท่ากับ 357 องศาเซลเซียส, ระบบ BA-35x มีค่าเท่ากับ 352 องศาเซลเซียส และระบบ BA-a มีค่าเท่ากับ 345 องศาเซลเซียส นอกจากนี้ ความต้านแรงดัดโค้ง และความเครียด ณ จุดขาดภายใต้การดัดโค้งของทั้ง 3 ระบบ ถูกพบว่ามีการเพิ่มขึ้นตามปริมาณการเพิ่มของอีพอกซีเรซิน เช่น ความต้านแรงดัดโค้งสูงถึง 182 MPa สำหรับ BA-a/Epoxy ที่สัดส่วนมวล 60:40 เมื่อเปรียบเทียบกับค่า 140 MPa ของ BA-a, 161 MPa ของ BA-mt/Epoxy จาก 129 MPa ของ BA-mt และ 155 MPa ของ BA-35x/Epoxy จาก 112 MPa ของ BA-35x

ภาควิชา.......วิศวกรรมเคมี....... ลายมือชื่อนิสิต.......ปฐมกร.......
สาขาวิชา.......วิศวกรรมเคมี....... ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก.......
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PATHOMKORN KUNOPAST: THERMOMECHANICAL PROPERTIES OF ARYLAMINE-BASED BENZOXAZINE RESINS ALLOYED WITH EPOXY RESIN. ADVISOR: ASSOC. PROF. SARAWUT RIMDUSIT, Ph.D., 89 pp.

In this research, effects of addition of epoxy resin into various arylamine-based benzoxazine resins, i.e. aniline, m-toluidine, and 3,5-xylidine systems, which designated as BA-a, BA-mt, and BA-35x, respectively, have been investigated. Processing windows of BA-35x, BA-mt, and BA-a were found to be widened with the amount of the epoxy resin. Gel points of benzoxazine-epoxy resin mixtures can be well predicted by an Arrhenius equation e.g. the gel time of BA-35x alloyed with epoxy resin at composition 70:30 mass ratio can be estimated by $t_{gel}=0.7012\times10^{-7}\exp(10.563/T)$. An addition of the epoxy to the polybenzoxazines increased the crosslinked density of the resulting polymer alloys which influenced their major properties. From dynamic mechanical analysis, T_g values obtained from the peaks of loss moduli of BA-a and BA-mt alloyed with epoxy resin were found to show a synergistic behavior with the maximum T_g value at the benzoxazine-epoxy composition of 80:20 mass ratio with the T_g values of 182°C for BA-a and 213°C for BA-mt systems. However, in the BA-35x and epoxy binary mixture, the decreasing trend in T_g from 241°C to 223°C with an addition of epoxy resin up to 40wt% was observed. In benzoxazine-epoxy polymer alloys based on m-toluidine, the degradation temperature at 5% weight loss was found to be the highest value among polybenzoxazine-epoxy alloys, i.e. at composition 80:20 mass ratio, T_d was found to be 357°C for BA-mt system, 352°C for BA-35x system, and 345°C for BA-a system. In addition, the flexural strength and the flexural strain at break of all three binary systems were found to increase with increasing amount of the epoxy i.e. the flexural strength up to 182 MPa for BA-a/Epoxy at 60:40 mass ratio (compared with about 141 MPa of the neat BA-a) 161 MPa of BA-mt/Epoxy from 129 MPa of the neat BA-mt, and 155 MPa of BA-35x/Epoxy from 112 MPa of the neat BA-35x.

Department: CHEMICAL ENGINEERING	Student's Signature
Field of Study: CHEMICAL ENGINEERING	Advisor's Signature
Academic Year : 2008	

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CHAPTER I

INTRODUCTION

1.1 General Introduction

Thermoset polymers are plastics that have been generated using heat or chemicals to crosslink the molecular chains. Once a thermoset is cured, it cannot be re-heated and reshaped. Thermoset materials are generally stronger than thermoplastic materials due to the formation of 3-D network of chemical bonds, and are also better suited to high temperature applications up to the degradation temperature of the materials [1]. Despite the emergence of several new classes of thermosets, high performance polymers and several other new generation materials that are superior in some respects, phenolic resins retain industrial and commercial interest. Phenolic resins are widely used in various applications because of their several desirable properties, such as good mechanical strength, electrical insulation, and dimensional stability, resistance against various solvents, flame retardation, and low smoke generation. However, a number of short-comings are also associated with these materials. For example, they are rather brittle, have poor shelf life, acid or base catalysts are often used for the preparation of the resins, which potentially corrode the processing equipments. They usually release by-products such as water, ammonium compounds, and so forth during curing which sometimes affects the properties of cured resins because of the formation of voids. To overcome these problems recently a new type of addition cure phenolic system, polybenzoxazines, has been developed [2-4].

Benzoxazine resins are a novel kind of thermosetting phenolic resin that can be synthesized from phenol, formaldehyde and amine group. The curing of the resins involves ring-opening polymerization without a catalyst or a curing agent and does not produce by-products during cure which result in no void in the products. Polybenzoxazines have some reported outstanding properties such as high glass-transition temperature (T_g), high thermal stability, near-zero volumetric shrinkage or expansion upon polymerization, low melt viscosity before cure resulting in its high processability, low water absorption. Furthermore, polybenzoxazines possess high electrical properties, excellent mechanical performance and a wide molecular design flexibility [5-9].

A series of benzoxazine resins can be synthesized that upon polymerization produce a varying amine group. In this research, we use benzoxazine resins based on bisphenol-A, formaldehyde and three types of aromatic amines (aniline, m-toluidine, 3,5-xylidine). Ishida and Sanders, 2000 [10] reported that for benzoxazine resins based on m-toluidine and 3,5-xylidine, its thermal degradation temperature (T_d) at 5% weight loss was reported to be 350°C which is higher than aniline-based polybenzoxazine, i.e. about 315°C, with no significant effect on the final char yield.

However, one shortcoming of these resins for some particular application is the rather high rigidity. Alloying, blending or compositing can be utilized to improve mechanical properties or thermal stability of polybenzoxazines. As a result, in recent years other polymers e.g. epoxy resin, phenolic resin, urethane prepolymer etc. were used to form alloys with benzoxazine resins to improve their properties [11, 12, 13]. From the study of Ishida and Allen, 1996 [11] on benzoxazine-epoxy copolymers, it was revealed that the significant increase in crosslink density of the thermosetting matrix strongly influences to its mechanical properties. That leads to significant increases in the glass transition temperature, flexural stress, and flexural strain at break over those of the polybenzoxazine homopolymer, with only a minimal loss of stiffness.

Epoxy resin is a kind of thermosetting polymers which has been used in various industries such as adhesives and coatings. This resin can be used in an electronic part assembly, electronic circuit board, and electronic encapsulation. Generally, epoxy resin shows good mechanical strength and chemical resistance, and its properties strongly depend on the type or quantity of hardeners, curing agents or curing conditions used. There are many kinds of epoxy hardeners such as amine, acid anhydride, polyamide and so on [14, 15]. Those curing agents are selected according to various uses. The major curing agents for epoxy at present can be classified into 4 major groups including amine compounds, acid anhydrides group, lewis acids and polyamides group. These curing agents have their own advantages and disadvantages. The amine groups are volatile, smelly and rather toxic to the user but can provide room-temperature cure for epoxy while the acid anhydrides and Lewis acid group may cause corrosion to the processing apparatus. Finally the polyamide groups can adversely affect the processability of epoxy resin due to its rather high viscosity of the high molecular weight polyamide though high performance cured system can be obtained [16].

As a result, in this research, we propose to utilize a novel class of epoxy crosslinkers based on self-polymerizable benzoxazine resins to solve the problems of the currently used curing agents and this research will examine the effect of the various types of aromatic amines (arylamine) on the thermal and mechanical properties of the obtained arylamine-based benzoxazine resins alloyed with epoxy.

1.2 Objectives

1. To investigate effects of types of arylamines (aniline, m-toluidine, 3,5-xylidine) in benzoxazine resins on the alloying ability with epoxy.
2. To study the suitable composition ratios of polymeric alloys between benzoxazine resins (BA-a, BA-mt and BA-35x) and epoxy on curing and processing conditions.
3. To compare the effect of types of arylamines in benzoxazine resins on thermal and mechanical properties of the resulting benzoxazine-epoxy alloys.

1.3 Scopes of the Study

1. Synthesis of arylamine-based benzoxazine resins (BA-a, BA-mt and BA-35x).
2. Preparation of polymeric alloys between benzoxazine resins (BA-a, BA-mt and BA-35x) and epoxy at various weight ratios of benzoxazine and epoxy resins i.e. 60:40, 70:30, 80:20, 90:10 and 100:0.
3. Evaluation of the curing condition or cross-linking process of the alloys
    - Rheometer
    - Finding curing condition by Differential Scanning Calorimeter (DSC)
    - Determining functional groups by Fourier Transform Infrared Spectroscope (FTIR)
4. Examination of thermal and mechanical properties of the alloys
    - Differential Scanning Calorimeter (DSC)
    - Dynamic Mechanical Analyzer (DMA)
    - Thermal Mechanical Analyzer (TMA)
    - Thermogravimetric Analyzer (TGA)
    - Universal Testing Machine (flexural mode)
    - Hardness (shore D)

CHAPTER II

THEORY

2.1 Benzoxazine Resin

Benzoxazine resin is a novel kind of phenolic resin that can be synthesized from phenol, formaldehyde, and primary amine. It can be prepared by using solvent or non-solvent systems depending on initiator and heating [5]. The resin was invented to provide optimal properties for electronics and high thermal stability applications. As a novel class of phenolic resins, it has been developed and can be easily modified to overcome the shortcomings of the traditional phenolic novolac and resoles. Polybenzoxazines are expected to replace traditional phenolics, polyesters, vinyl esters, epoxies, and polyimides in many respects.

Benzoxazine resins can be classified into monofunctional, bifunctional as well as multifunctional types depending on a type of phenol used. Examples of monofunctional and bifunctional benzoxazine resins are shown in Figure 2.1 and 2.2, respectively.

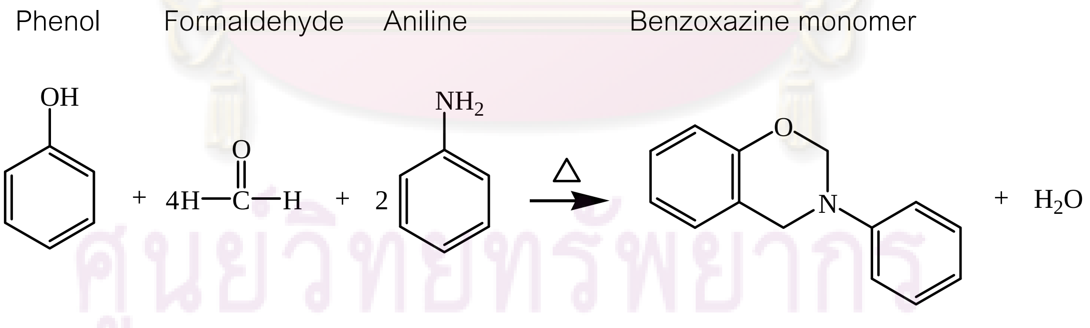


Figure 2.1 Synthesis of monofunctional benzoxazine monomer.

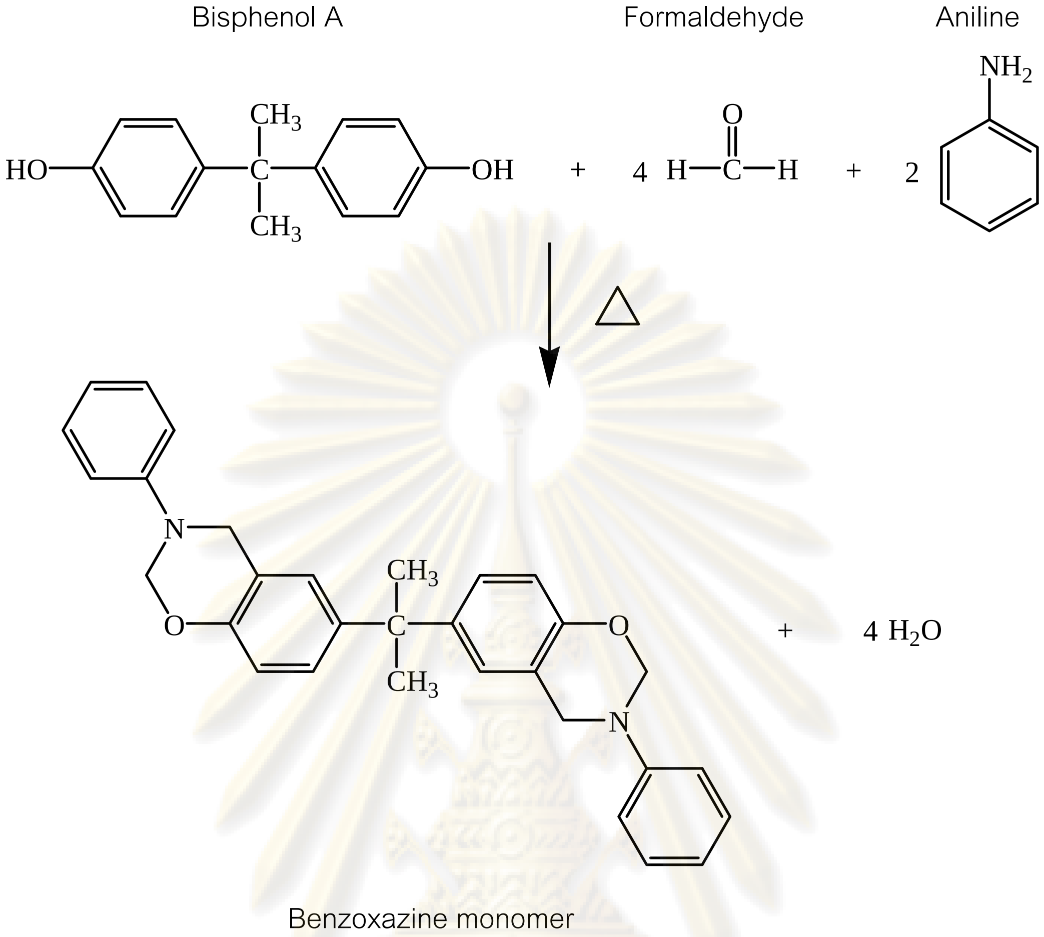


Figure 2.2 Synthesis of bifunctional benzoxazine monomer.

Benzoxazine resin can be self-polymerized by heating and does not need a catalyst or curing agent for its curing process. These two kinds of polybenzoxazines are different in types of reactants. The monofunctional benzoxazine monomer uses phenol while the bifunctional benzoxazine monomers use bi-phenol for the synthesis. Their properties are also different. The bifunctional benzoxazine monomer can be polymerized to yield a crosslinked network structure whereas the latter can be polymerized, in principle, to yield a linear structure.

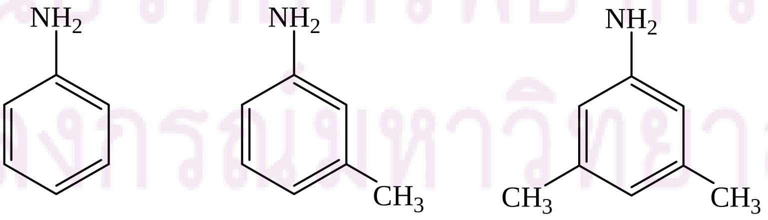
Polybenzoxazine has been reported to provide excellent thermal, mechanical, electrical, chemical and physical properties such as high moduli, high glass-transition temperature, high char yield, near-zero volumetric shrinkage upon polymerization, low water absorption, low melt viscosity, excellent resistance to chemicals and UV light, and no by-product during cure [3, 6-9].

The other advantages of polybenzoxazine include easy processing ability, lack of volatile formation which is highly attractive for composite material manufacturing. Furthermore, benzoxazine resin has been reported to be able to form alloy with several other polymers or resins. For example, Ishida and Allen reported that the addition of epoxy to the polybenzoxazine network greatly increased crosslinked density of the resulting thermosetting matrix thus significantly affected its mechanical properties. In the binary system, benzoxazine resin with epoxy resin can be polymerized to obtain a high crosslink density and glass transition temperature than polybenzoxazine homopolymer [11, 17].

In this research, benzoxazine resins synthesized from bisphenol-A, para-formaldehyde and three different types of arylamines i.e. aniline, m-toluidine, 3,5-xylidine are used as potential crosslinkers for epoxy resins. Properties and structures of these arylamines are shown in Table 2.1 and Figure 2.3, respectively. Figure 2.4 and Table 2.2 show structures and properties of the resulting arylamine-based benzoxazine resins.

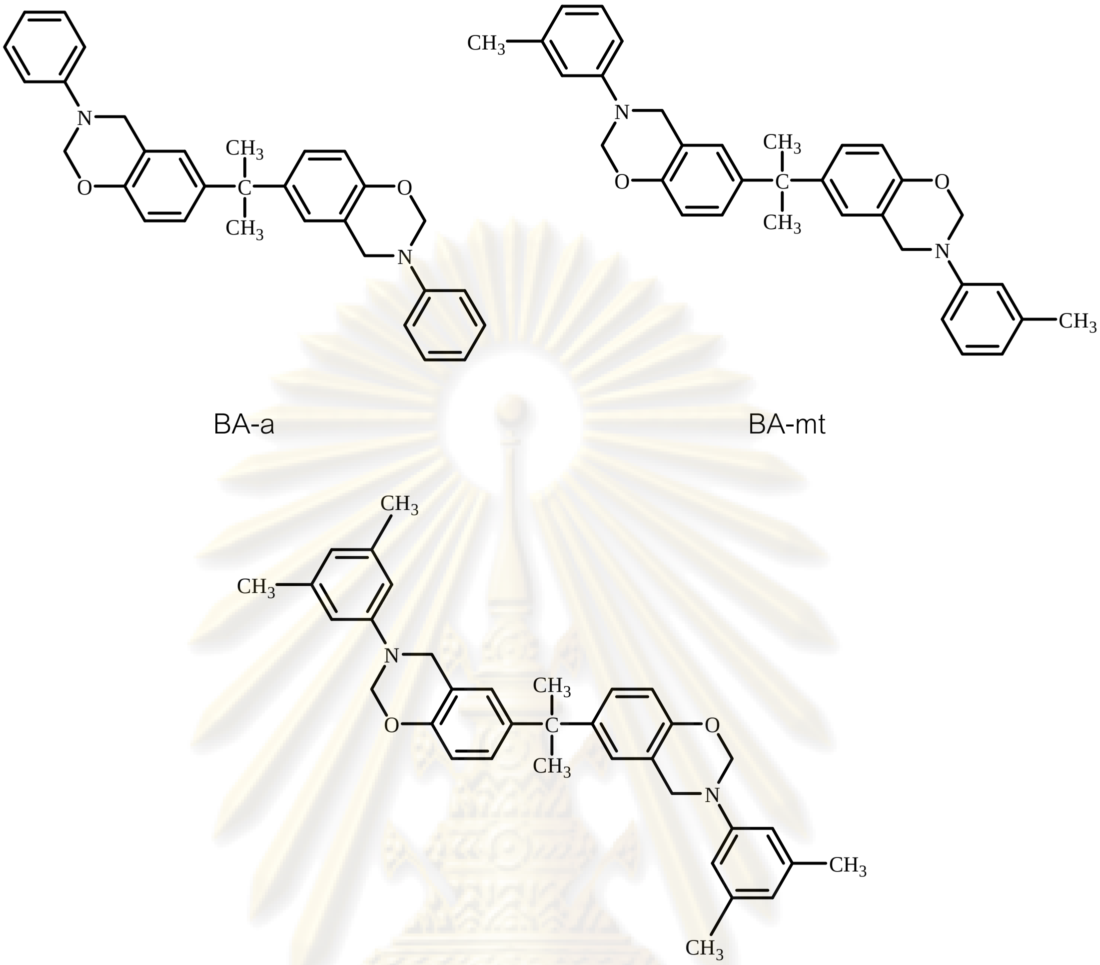
Table 2.1 Properties of the three arylamines used for benzoxazine resin synthesis [18].

Properties	Aniline	m-Toluidine	3,5-Xylidine
Molecular weight (g/mol)	93.13	107.15	121.18
Melting point (°C)	-6.0	-31.3	9.8
Boiling point (°C)	184.2	203.3	220.5
Density (g/cm^3)	1.022	0.989	0.971
Purity (%)	99	$\geq$ 99	$\geq$ 97



Aniline m-Toluidine 3,5-Xylidine

Figure 2.3 Structures of the three arylamines used in this work [18].



BA-a

BA-mt

BA-35x

Figure 2.4 Benzoxazine monomers from three different arylamines [10].

Table 2.2 Major properties of the three arylamine-based polybenzoxazines [10].

Properties	BA-a	BA-mt	BA-35x
Tg (DSC)	168	209	238
Char yield (% at 800 °C)	30	31	28
Td at 5% wt. loss (°C)	315	350	350
Storage modulus at 28 °C (GPa)	1.39	1.78	1.63
Loss modulus at 28 °C (MPa)	15.7	35.8	25.9
Crosslink density (mol/cm^3)	1.1x10^{-3}	1.9x10^{-3}	2.6x10^{-3}

2.2 Epoxy Resin

The generalized structure for an epoxy resin is given in Figure 2.5. The epoxy, epoxide or oxirane group is a three-membered ring consisting of two carbon atoms and one oxygen atom. Figure 2.6 also summarizes the major types of commercial epoxy resin.

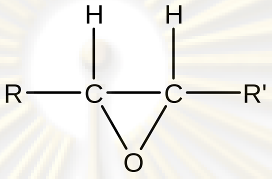


Figure 2.5 General structure of an epoxy resin [15].

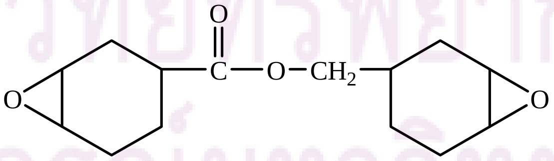
Three major types of epoxy resins include

1. Cycloaliphatic epoxy resins (R and R′ are part of a six-membered ring).

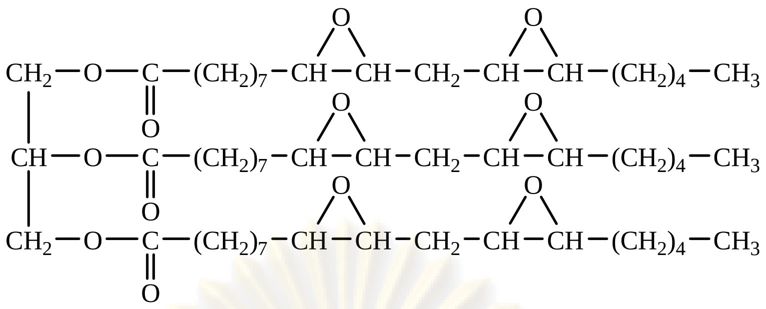
2. Epoxidized oils (R and R′ are fragments of an unsaturated fatty acid, such as oleic acid in soybean oil).

3. Glycidated resins (R is hydrogen and R′ can be a polyhydroxyphenol, polybasic acid, or polyamine). There are the epoxides used in most commercial application.

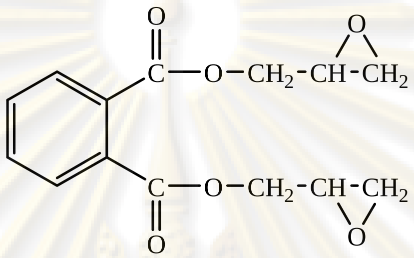
Figure 2.6 gives the structures of cycloaliphatic epoxy resin, epoxidized soybean oil, glycidated polybasic acid, aromatic polyamine (methylene dianiline), and bisphenol A, bisphenol-A based epoxy resin.



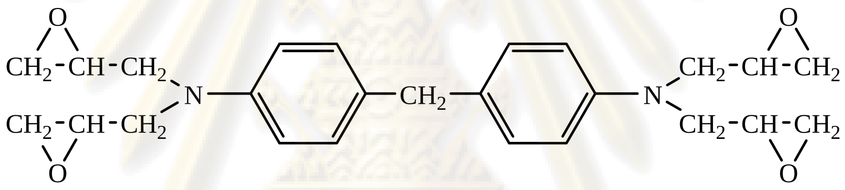
Cycloaliphatic Resin



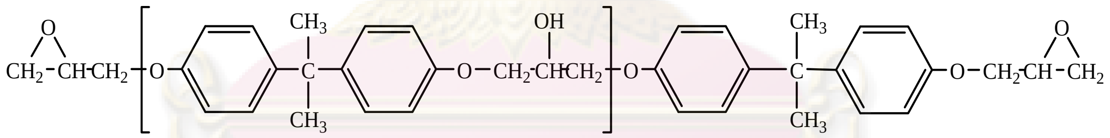
Epoxidized Soybean Oil [19]



Glycidated Polybasic Acid



Glycidated Polyamine



Glycidated Bisphenol A

Figure 2.6 Major types of commercial epoxy resins.

Generically epoxy resins can be characterized as a group of commercially available oligomeric materials which contain one or more epoxy (oxirane) groups per molecule. The value of epoxy resins is that they can be processed into a variety of useful products such as protective coating, adhesives, and structural components of almost any size and shape by reacting the epoxy groups with an appropriate curing agent. The products obtained from epoxy resins containing more than one epoxy group per molecule are called thermosetting polymers. Figure 2.7 exhibits contribution of chemical moieties in epoxy molecule on its properties.

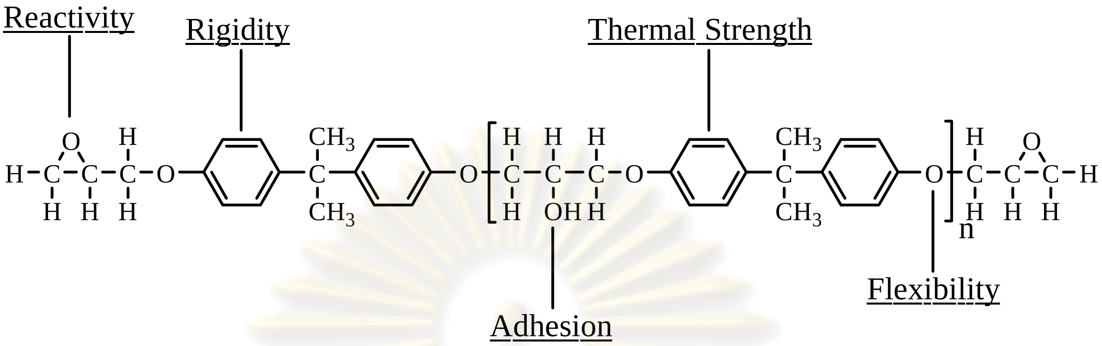


Figure 2.7 Sources of epoxy properties [20].

The advantages of epoxy resins are: [15]

1. Excellent adhesion to a variety of substrates and reinforcements.
2. Low shrinkage on cure.
3. No cure volatiles.
4. Outstanding mechanical and electrical properties.
5. Good chemical resistance and solvent resistance.
6. Thermal stability.
7. Good moisture resistance.
8. Good dimension stability and fatigue resistance.
9. Versatility i.e.
    - Many modes of cure.
    - Many resin types available.
    - Wide range of modifications possible.

The choice of resin and curing agent depends on the application and on handling characteristic (viscosity, pot life, gel time); curing temperature and time; use properties (mechanical, chemical, thermal and electrical); toxicological and environmental limits; as well as cost. A description of major epoxy curing agents is given in Table 2.3.

Table 2.3 Curing agents for epoxy resins [16].

Type	Advantages	Disadvantages	Applications
Aliphatic amines	low viscosity; ambient cure temperature; little color	short pot life; rapid heat evolution; critical mix ratio; moderately toxic; high moisture absorption	adhesives; small castings; electrical encapsulation; civil engineering
Aromatic amines	good elevated temperature performance; good chemical resistance; long pot life; low moisture absorption	incompatibility with epoxy resins; long cure cycles at high temperature; toxicity	high performance composites and coatings; adhesives; filament winding; electrical encapsulation
Polyamidoamines	low viscosity; ambient cure temperature; good mix ratios, mechanical properties, and pot life	poor performance at high temperature	construction adhesives; sealants; floorings; concrete bonding
Polyamides	good mix ratios, pot life, flexibility, toughness, and corrosion resistance; ambient cure temperature; low toxicity	low temperature performance; high viscosity; poor color	maintenance coatings; castings; trade sale paints; adhesives; marine coatings

Table 2.3 (Continued).

Type	Advantages	Disadvantages	Applications
Anhydrides	good mechanical and electrical properties; low shrinkage and viscosity; long pot life; little color	long cure cycles at high temperature	castings; potting; encapsulation; filament winding
Catalytic	high temperature resistance; very long pot lives	long cure cycles at high temperature; brittle	powder coatings; adhesives; electrical encapsulation
Dicyandiamide	good electrical properties; high temperature resistance; latent systems	incompatibility with epoxy resins; long cure cycles at high temperature	electrical laminates; powder coatings; single-package adhesives
polycarboxylic polyesters	good weatherability, corrosion resistance, and mechanical properties; low cost	poor chemical resistance	powder coatings
Isocyanates	fast cure at low temperature; good flexibility and solvent resistance	moisture-sensitive; toxicity	powder coating; maintenance coatings

Table 2.3 (Continued).

Type	Advantages	Disadvantages	Applications
phenol-formaldehyde, novolacs	good chemical resistance, electrical properties, shelf stability, and compatibility with epoxies; high temperature resistance	poor UV stability; high melting; high temperature cure	molding compounds; powder coatings
polysulfides and polymercaptans	rapid cure times; flexible systems	poor performance at high temperature; odorous	sealants; adhesives
melamine-formaldehyde	good color and hardness; stable one-component systems	high temperature cure; low compatibility with epoxy resins	stove paints; can coatings; finishes
urea-formadehyde	stable one-component systems; little color	high temperature cure	fast-bake enamels; stove primers; can and drum coatings; topcoats
resole phenolics	stable one-component systems; good chemical resistance	high temperature cure; brittle; poor weatherability	baked enamels; drum and pail coatings

In this investigation, epoxy resin, grade EPON Resin 828, is selected as a base resin to be alloyed with those three arylamine-based benzoxazine resins. EPON Resin 828 is an undiluted clear difunctional bisphenol A/epichlorohydrin derived liquid epoxy resin. When cross-linked or hardened with appropriate curing agents, very good mechanical, adhesive, dielectric and chemical resistance properties can be obtained. Because of this versatility, EPON Resin 828 has become a standard epoxy resin used in formulation, fabrication and fusion technology. The structure and the typical properties of EPON Resin 828 are shown in Figure 2.8 and summarized in Table 2.4, respectively.

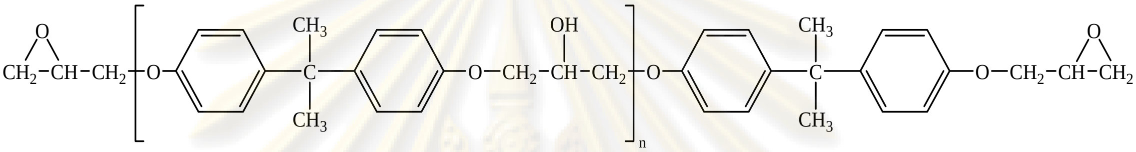


Figure 2.8 The structure of EPON Resin 828 [21].

Table 2.4 Typical properties of EPON Resin 828 [22].

Properties	
Approximate average molecular weight [15], g/mol	380
Epoxide equivalent weight (EEW)	185 -192
Viscosity, poise at 25°C	110 -150
Density, g/ml at 25°C	1.16
Flash point, °C	No flash at 249°C
Vapor pressure, mmHg at 77°C	0.03
Specific heat, cal/g/°C	0.5

End-use applications of bisphenol A epoxy resin:

- Fiber reinforced pipes, tanks and composites
- Tooling, casting and molding compounds
- Construction, electrical and aerospace adhesive
- High solids/low VOC maintenance and marine coatings
- Electrical encapsulations and laminates
- Chemical resistance tank linings, flooring and grouts
- Base resin for epoxy fusion technology

CHAPTER III

LITERATURE REVIEWS

The regioselectivity of aromatic amine-based benzoxazine polymerization was investigated by Ishida and Sanders, 2000 [23] through systematic manipulation of the monomer chemistry. The network structures of the cured materials are elucidated by FTIR as shown in Figure 3.1a and b. Figure 3.1a, for cured BA-mt spectra, shows the development of a band near 810 cm^{-1} which was assigned to the 3,4-dimethylaniline absorption. This spectroscopic evidence suggested that the pendant arylamine rings activated in the para position can undergo an aminomethylation reaction during the polymerization. To further support this phenomenon, one can examine the case of BA-35x as shown in Figure 3.1b, which the pendant arylamine ring is even further activated. The figure, for cured BA-35x, shows a prominent band near 847 cm^{-1} corresponding to the 1,2,3,5-tetrasubstituted arylamine ring. Furthermore, the actual network structure of the cured materials is expected, BA-a being similar to the phenolic Mannich bridge network as shown in Figure 3.2a, and BA-mt and BA-35x containing additional amounts of arylamine Mannich bridges (as can be seen in Figure 3.2b) and methylene linked structures. As a consequence, the additional arylamine Mannich bridges significantly resulted in a higher T_g in BA-mt, 209°C, and BA-35x, 243°C, than BA-a, 168°C.

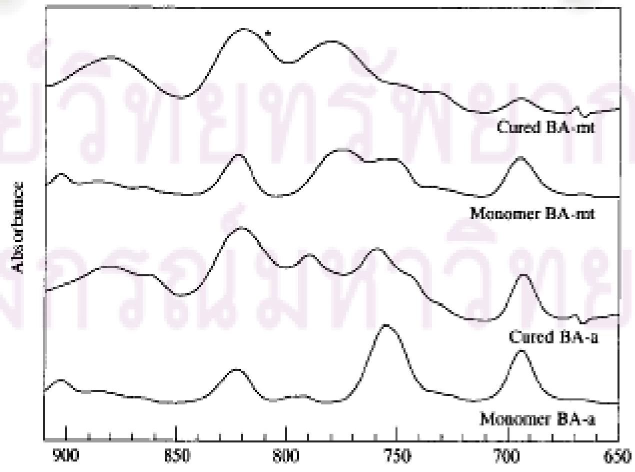


Figure 3.1a FTIR spectra comparison of cured BA-a and BA-mt.

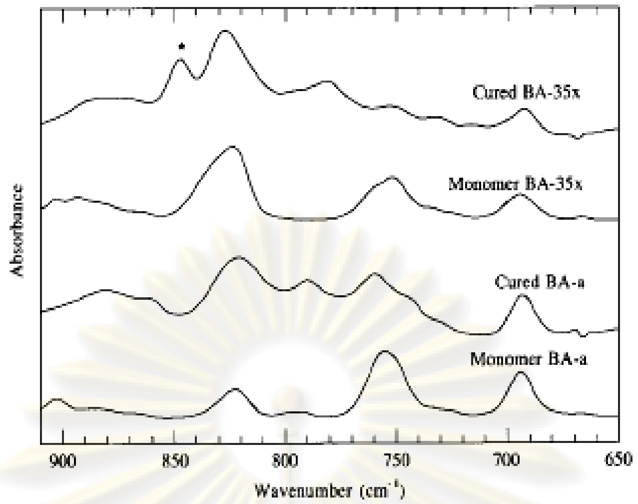


Figure 3.1b FTIR spectra comparison of cured BA-a and BA-35x.

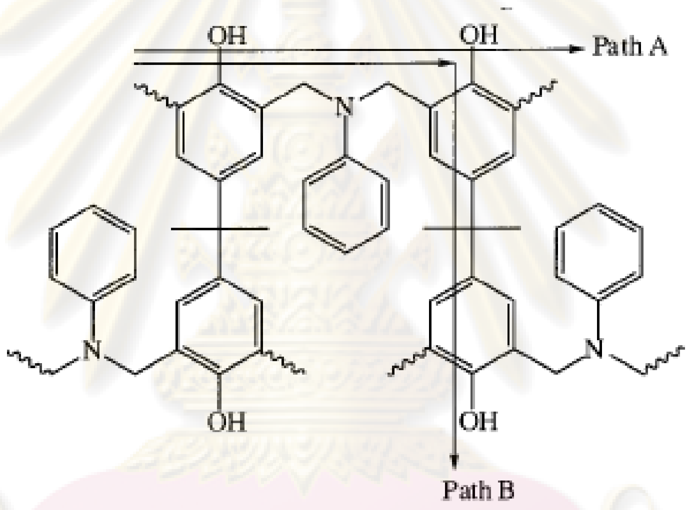


Figure 3.2a The phenolic Mannich bridge network formation.

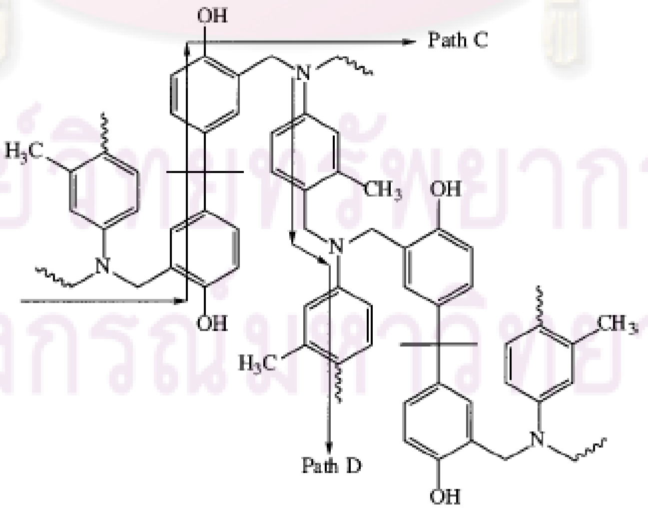


Figure 3.2b The arylamine Mannich bridge network formation.

The thermal and mechanical properties of polybenzoxazine thermoset networks containing varying amounts of phenolic Mannich bridges, arylamine Mannich bridges, and methylene bridges have been further investigated by Ishida and Sanders, 2000 [10]. In materials based on m-toluidine and 3,5-xylidine, the thermal degradation at 5% weight loss is delayed until around 350°C, however, with no significant effect on the final char yield. Materials with additional amounts of arylamine Mannich bridges and methylene bridges show improved mechanical properties, including higher crosslink densities. Correlations between the observed mechanical properties and network structures were established. The major properties of the neat arylamine-based polybenzoxazines (BA-a, BA-mt, and BA-35x) are shown in Table 2.2.

Mechanical characterization of benzoxazine and epoxy copolymer was investigated by Ishida and Allen, 1996 [24]. The benzoxazine resin was copolymerized with an epoxy resin in order to modify their mechanical performance. The addition of epoxy to the polybenzoxazine network greatly increases the crosslink density of the thermosetting matrix and strongly influences its mechanical properties. The copolymerization led to significant increases in the flexural strength, and flexural strain at break over those of the polybenzoxazine homopolymer, with only a minimal loss of stiffness. By understanding the structural changes by variation of epoxy content and their effect on material properties, the copolymer network can be tailored to specific performance requirements. Figure 3.3a and b show the flexural strength and the flexural strain at break of obtained copolymer showing enhanced flexural strength and flexural strain at break with an amount of the epoxy. The opposite trend, however, was observed in the case of their flexural modulus as shown in Figure 3.3c.

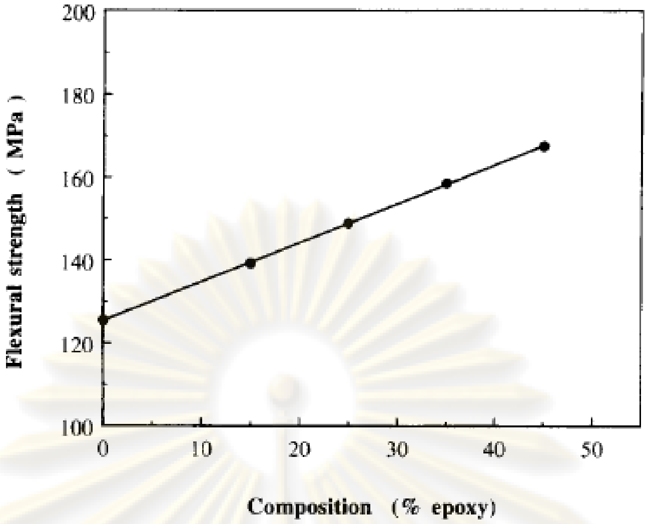


Figure 3.3a Flexural strength of polybenzoxazine and epoxy alloys.

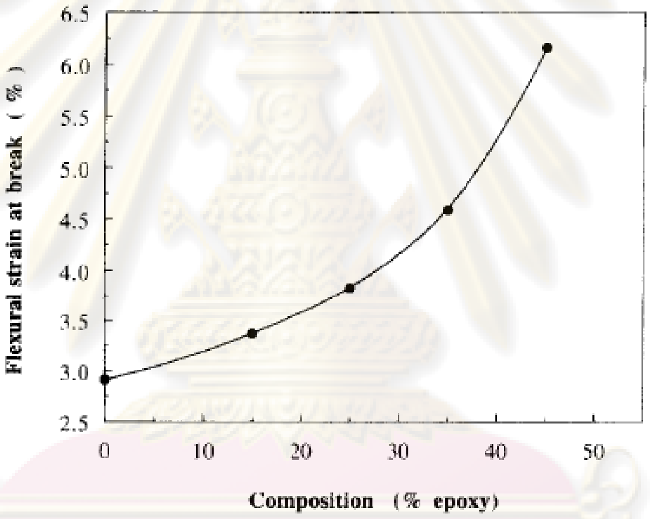


Figure 3.3b Flexural strain at break of polybenzoxazine and epoxy alloys.

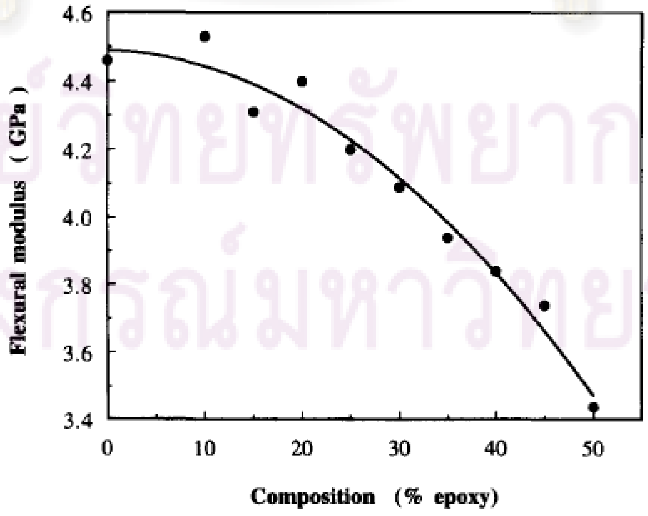


Figure 3.3c Flexural modulus of polybenzoxazine and epoxy alloys.

The Fourier transform mechanical spectroscopy technique (FTMS) was utilized as a powerful tool to study the sol-gel transition of covalent bonded polymeric network of benzoxazine resin mixtures by Rimdusit and Ishida, 2002 [25]. The gelation behaviors of low melt viscosity ternary systems of benzoxazine, epoxy, and phenolic resins were investigated and analyzed by the technique in order to study the effect of epoxy diluent on the rheological property development before and after the gel points. The processing window of ternary systems was observed to be widened with increasing the amount of epoxy resin as shown in Figure 3.4a. In addition, gel time as a function of temperature was also investigated. The gel time is obtained from the point where the loss tangents of different frequencies intersect as can be seen in Figure 3.4b. From the results, the gel time was decreased with increasing gel temperature. Moreover, the gel time of those benzoxazine resin mixtures can be well predicted by an Arrhenius equation, i.e. $t_{gel} = A\exp(\Delta E/T)$.

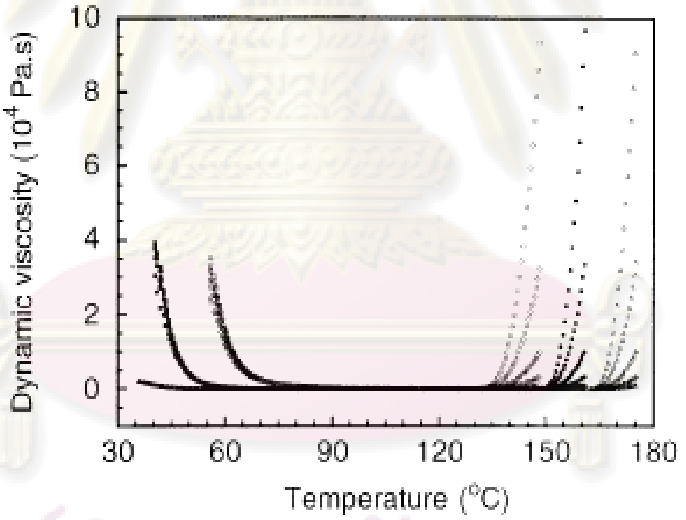


Figure 3.4a Processing windows of ternary systems:
(○) BEP 111, (●) BEP 121 and (Δ) BEP 131

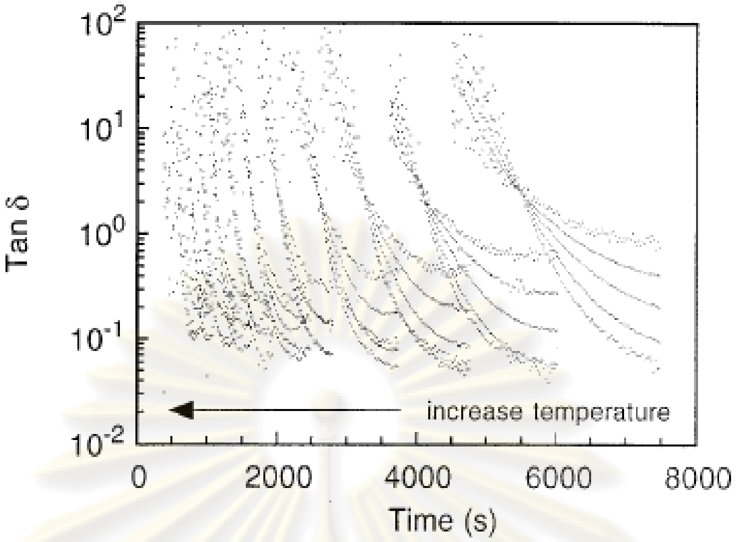


Figure 3.4b The effect of temperature on gel time.

The synergism in the glass-transition temperature (T_g) of binary systems based on benzoxazine, and epoxy resins and ternary systems based on benzoxazine, epoxy, and phenolic resins had been reported by Rimdusit and Ishida, 2000 [17]. The systems showed the maximum T_g of about 145°C in benzoxazine and epoxy at 70:30 mass ratio. The molecular rigidity from benzoxazine and the improved crosslink density from epoxy had been attributed to the observed synergistic behavior. Effect of the epoxy content on glass transition temperature of the binary and ternary systems in their work is shown in Figure 3.5.

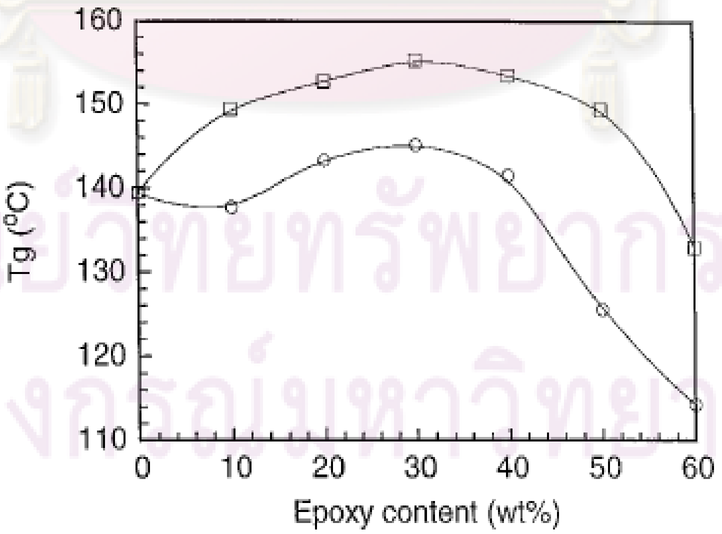


Figure 3.5 Effect of the epoxy content on glass transition temperature of binary (○) and ternary (□) systems.

The polymeric systems based on the ternary mixture of benzoxazine, epoxy, and phenolic novolac resins had also been examined by Rimdusit and Ishida, 2000 [12]. Low melt viscosity resins rendered void-free specimens with minimal processing steps. The material properties showed a wide range of desirable reliability and processability, which are highly dependent on the composition of the monomers in the mixture. A thermal stability at 5% weight loss up to 370°C can be obtained from these systems as shown in Figure 3.6a. The moduli at room temperature of the ternary systems decreased with increasing amount of the epoxy resin in the ternary mixture as shown in Figure 3.6b. This is due to the more flexibility or less stiffness of the bisphenol A based epoxy compared with the polybenzoxazine used in the experiment. On the other hand, the moduli in the rubbery plateau of the ternary systems increased with increasing amount of the epoxy resin. The greater plateau moduli of the specimens which had higher amount of epoxy diluent was attributed to higher crosslink density in the materials thus led to higher glass transition temperature of the ternary systems.

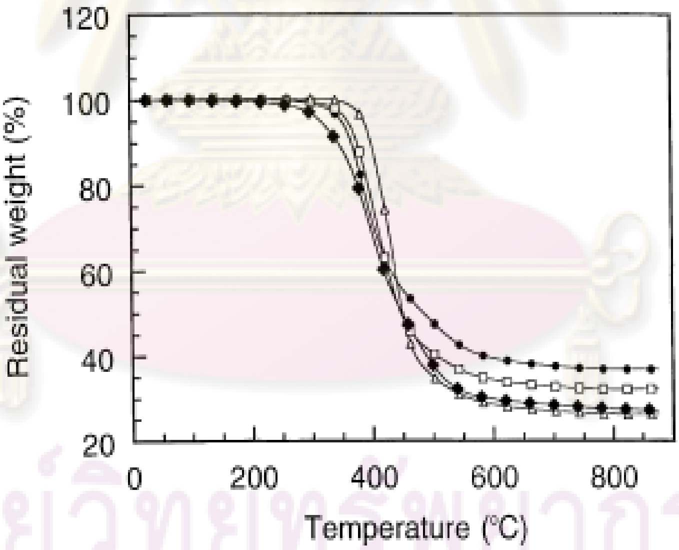


Figure 3.6a TGA thermogram of ternary systems:

(●) BEP 111, (□) BEP 121, (Δ) BEP 131, and (♦) BA-a

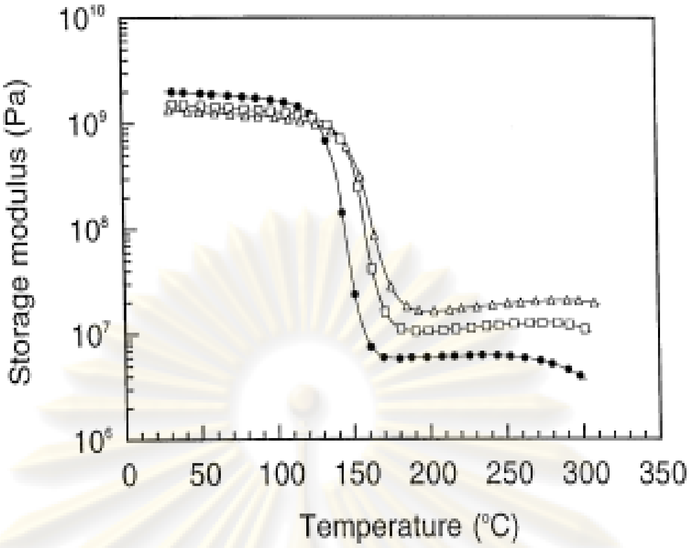


Figure 3.6b Storage moduli of ternary systems:

(●) BEP 111, (□) BEP 121, and (Δ) BEP 131

CHAPTER IV

EXPERIMENTAL

4.1 Raw Materials

Bisphenol-A, polycarbonate grade, was contributed by Thai Polycarbonate Co., Ltd. Para-formaldehyde ($\geq$ 95% purity) was purchased from Merck & Co. Inc. A series of arylamines i.e. aniline (99% purity), m-toluidine ($\geq$ 99% purity), 3,5-xylidine ($\geq$ 97% purity), from Fluka Chemicals Co. were used as-received. Bisphenol A Epoxy resin (EPON Resin 828) was from East Asiatic (Thailand) Public Co., Ltd. The resin is a colorless liquid at room temperature.

4.2 Preparation of Arylamine-based Benzoxazine Resins

Aniline-based benzoxazine resin abbreviated as BA-a was synthesized from bisphenol-A, para-formaldehyde, and aniline at a molar ratio of 1:4:2. The mixture was heated at about 110°C in an aluminum pan and was mixed rigorously for about 30 minutes to yield a light yellow solid monomer product. The same procedure was used to synthesize m-toluidine-based benzoxazine resin (BA-mt) and 3,5-xylidine-based benzoxazine resin (BA-35x).

4.3 Samples Preparation

Each type of benzoxazine monomer was mixed with epoxy resin at various mass fractions. The mixture was heated at about 90°C in an aluminum pan and was thoroughly mixed until a homogeneous resin mixture was obtained. The resin mixture can be kept at room temperature for further use. The molten resin was poured into an aluminum mold and was cured in an air-circulated oven. The specimens were, then, left to cool down to room temperature and were taken for material characterization. The same procedure was used to prepare BA-mt and BA-35x alloyed with the epoxy.

4.4 Sample Characterization

4.4.1 Chemorheology of arylamine-based benzoxazine resins and their mixtures with epoxy

Rheological and gelation behaviors of each resin and resin mixture were investigated using a Rheometer (Haake Rheo Stress 600, Thermo Electron Corp.) equipped with disposable parallel plate geometry. The measuring gap was set at 0.5 mm. The processing window was performed under an oscillatory shear mode at a frequency of 1 rad/s (0.159 Hz). The testing temperature was ramped at a heating rate of 2°C/min to a temperature beyond the gel point of each resin and the dynamic viscosity was recorded. For the gel point determination, frequency sweep in the range of 10-100 rad/s was performed isothermally as a function of time at 170, 180, 190, 200°C for BA-a and 150, 160, 170, 180°C for BA-mt and BA-35x. The gel point is obtained from the point where the loss tangents of different frequencies, i.e. 1.6, 2.8, 5.0, 9.0, and 15.9 Hz, intersect each other.

4.4.2 Differential Scanning Calorimetry (DSC)

Curing behaviors of each resin and its mixture with epoxy were studied using a differential scanning calorimeter (DSC) model 2910 from TA Instruments. Each specimen with a mass in a range of 3-5 mg was sealed in an aluminum pan with lid. The heating rate used was 10°C/min and the sample temperature was scanned from room temperature to 300°C under nitrogen purging. The purge nitrogen gas flow rate was maintained to be constant at 50 ml/min.

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

$$\alpha = 1 - \left(\frac{H_{rxn}}{H_0} \right) \tag{4.1}$$

where H_{rxn} = the heat of reaction of the partially cured specimen as determined from the DSC experiment, mW/mg.

H_o = the heat of reaction of the uncured resin, mW/mg.

4.4.3 Fourier Transform Infrared Spectroscopy (FTIR)

The chemical structure of each sample was analyzed by a Fourier transform infrared spectroscopy (FTIR). The FTIR measurement was carried out on a Spectrum GX FTIR spectrometer from Perkin Elmer instrument with an ATR accessory. All spectra were taken as a function of time with 32 scans at a resolution of 4 cm^{-1} and spectra range of 4000-650 cm^{-1}.

4.4.4 Density Measurement

The densities of benzoxazine resins alloyed with epoxy were determined by water displacement method according to ASTM D 792-00 (Method A). The dimension of each rectangular shape specimen is 10 × 50 × 2 mm^3. All measurements were performed at room temperature.

The density of the specimen was calculated by a following equation:

$$\rho = \left(\frac{A}{A-B}\right) \times \rho_o \tag{4.2}$$

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.

The measurement was run 5 times for each specimen and the average value of the sample volume was obtained.

4.4.5 Dynamic Mechanical Analysis (DMA)

A dynamic mechanical analyzer (NATZSH, model DMA242) was used to obtain a storage modulus (E′) and loss modulus (E″) of the polymeric specimens. The specimen, with a dimension of 10 × 50 × 2 mm^3, was tested using a 3-point bending mode at the frequency of 1 Hz and heating rate of 2^{o}C/min from room temperature to the temperature beyond the glass transition temperatures (T_g) of each specimen. The glass transition temperature was taken as the maximum point on the loss modulus or loss tangent curves.

4.4.6 Thermomechanical Analysis (TMA)

The coefficient of thermal expansion (CTE) was measured with a Perkin Elmer Instrument Technology SII Diamond thermal mechanical analyzer (TMA). The thickness of specimens was set about 2mm. During the TMA measurement, the specimen was heated from room temperature to the temperature beyond the glass transition temperature at a heating rate of 10°C/min. Generally thermal expansion of a material increases with an increase in its temperature and the CTEs were calculated from the slope of the thermogram. An abrupt change in slope of the expansion curve indicates a transition of the material from glassy to rubber state.

Coefficient of thermal expansion (CTE) of a specimen was calculated by a following relationship:

$$\varepsilon_l(T,\alpha)=\frac{(l-l_0)}{l}=\gamma^{CTE}(\alpha)\Delta T \qquad (4.3)$$

where ε_l = the thermal linear strain.
l = the final specimen length.
l_0 = the initial specimen length.
$\gamma^{CTE}(\alpha)$ = the coefficient of thermal expansion.
ΔT = the temperature variation.

4.4.7 Thermogravimetric Analysis (TGA)

Degradation temperature (T_d) and char yield of all polybenzoxazines and benzoxazine alloys at various mass fractions of epoxy resin were studied using a Perkin Elmer Instrument Technology SII Diamond TG/DTA thermogravimetric analyzer. A heating rate of 20°C/min from room temperature to 900°C under nitrogen atmosphere was used to acquire TGA thermograms. The purge nitrogen gas flow rate was maintained at 100 ml/min. The sample mass used was measured to be approximately 10-15 mg. Weight loss of the sample was measured as a function of temperature. The degradation temperature (Td) of polybenzoxazines and benzoxazine-epoxy polymer alloys was reported at their 5% weight loss. Char yield of the above specimens were also reported at 800°C.

4.4.8 Universal Testing Machine (Flexural Mode)

The flexural strength, flexural strain and the corresponding modulus of the polymers or polymer alloy were determined using a universal testing machine (model 5567) from Instron Co., Ltd. The test method was a three-point loading with the supporting span of 32 mm and tested at a crosshead speed 0.85 mm/min. A dimension of a specimen is 25 × 50 × 2 mm^3. Flexural properties were determined based on ASTM D790-03. The flexural strength, flexural strain and the modulus were calculated by the following equations:

$$E_B = \frac{L^3 m}{4bd^3} \qquad (4.4)$$

$$S = \frac{3PL}{2bd^2} \qquad (4.5)$$

Where E_B = Flexural modulus, GPa.

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.

4.4.9 Hardness Measurement (Shore D)

The Shore hardness is a measure of the resistance of a material to the penetration of a needle under a defined spring force. It is determined as a number from 0 to 100 on the scales A or D. The higher the number is the higher the hardness. The letter A is used for flexible typed specimen and the letter D is for a rigid type. In this research, the Shore D scale was used to determine a hardness value of those specimens because of a relatively rigid nature of all polybenzoxazines and their alloys. A dimension of each specimen was 25 × 50 × 2 mm^3 and the specimen was determined following ASTM D2240 using a Bareiss hardness tester, Germany, at room temperature. The measurement was evaluated 5 times at different position of each specimen and the average hardness value of the sample was obtained.

CHAPTER V

RESULTS AND DISCUSSION

5.1 Arylamine-based Benzoxazine Resins and Epoxy Resin Characterization

5.1.1 Chemorheological Properties

Several techniques have been employed as tools to determine the gel point of a material such as static and dynamic light scattering, dissolution and extraction by solvents of the sol fraction, infrared, Raman, and nuclear magnetic resonance spectroscopies, differential scanning calorimetry, dielectric measurement, and rheometry. Among these, rheological property measurement is found to be one of the most utilized and sensitive technique for the gel point determination [25]. In this research, chemorheological property development of the benzoxazine-epoxy systems, particularly in the vicinity of a gel point, will be examined. The effect of epoxy on the gelation behaviors of these systems will also be investigated using this rheometry technique. Figure 5.1 shows the plot of dynamic viscosity (Pa.s) as a function of temperature (^{o}C) of the three arylamine-based benzoxazine resins i.e. BA-a, BA-mt, and BA-35x. From the figure, the major thermal event on the left hand side or low temperature range is called the liquefying point which is the transition of solid to liquid and on the right hand side or high temperature range is called the gel point which is the transition of liquid to solid in other words the transition of monomer to polymer. At these points, the complex viscosity of resin rapidly approaches its minimum value. Furthermore, the temperature range from the liquefying point to the gel point is called processing window which is the range of the lowest viscosity useful for polymer compounding or processing. On the left hand side of Figure 5.1, for consistency, the temperature at the viscosity value of 500 Pa.s was used as a liquefying temperature of each resin. On the basis of this convention, the liquefying temperatures of BA-a, BA-mt, and BA-35x resins were determined to be approximately 76^{o}C, 78^{o}C, and 88^{o}C, respectively. On the right hand side of Figure 5.1, gel temperature of each resin mixture can also be determined. In this case, the maximum temperature at which the viscosity was rapidly increased above 500 Pa.s was used as gel temperature of each resin. Based on this convention, the gel temperatures of BA-a, BA-mt, and BA-35x were determined to be 187, 180, and 178°C, respectively. As a result, the liquefying point of BA-a exhibits the lowest value compared with those of BA-mt, and BA-35x whereas the gel point of BA-a showed the highest value among the three benzoxazine resins. Consequently, BA-a provided the widest processing window compared to BA-mt, and BA-35x which exhibited the narrowest one. To see the effect of epoxy on processing window of benzoxazine resins, Figure 5.2 presents the plot of dynamic viscosity (Pa.s) as a function of temperature (°C) exhibiting processing windows of BA-35x mixed with epoxy resin at various epoxy contents. From the figure we can see that, by using an epoxy as a diluent, the viscosity of the monomer mixture can be significantly lowered comparing at the same temperature. The room temperature appearance of the uncured resins ranged from hard solid in BA-35x/Epoxy at 100:0 mass ratio, to soft solid in BA-35x/Epoxy at 60:40 mass ratio. Based on the same convention, the liquefying temperature or transition of solid to liquid of the resin mixtures was observed to decrease from 88 to 55°C with an increasing amount of the epoxy resin from 0 to 40%wt in the resin mixture. This is due to the fact that the epoxy resin used is liquid at room temperature while the benzoxazine resin is solid at room temperature. An addition of liquid epoxy into the solid benzoxazine thus lowered the liquefying point of the resulting mixture. The gel temperatures of BA-35x/Epoxy mixture were systematically shifted to higher temperature from 178 to 206°C with the amount of the epoxy. The gel point or transition of liquid to solid of the resin mixtures increased with increasing amount of epoxy was likely to be due to the dilution effect of the epoxy. Therefore, the processing window of the mixtures was widened by the amount of the epoxy resin. In other words, the processing window of each benzoxazine resin can be partly controlled by adding appropriate amount of epoxy. However, all resins are low viscosity liquid within the temperature range of 100 to 175°C which provides sufficient processing window, particularly for the compounding process. The resin mixtures of BA-a, and BA-mt with epoxy also provided a similar result.

The knowledge of factors that control the transition point and the time for gelation to occur will lead to the ability to obtain likable products with appropriate processing conditions and methods. One important feature of thermosetting polymers is their gelation behavior, especially, the kinetics of gelation as well as gel time. Sol-gel transition or liquid-solid transition, known as the gel point, is one critical phenomenon that is significant, especially, for the material processing. The linear viscoelastic properties in a dynamic experiment are sensitive to the three-dimensional network formation and can be used to accurately investigate the gel point. Gel time of BA-35x mixed with epoxy resin at a representative mass ratio of 70:30, evaluated isothermally at 150, 160, 170 and 180°C, is shown in Figure 5.3. This figure displays the plot of tan δ at various frequencies, i.e., 1.6, 2.8, 5.0, 9.0, and 15.9 Hz, as a function of time (s). The gel time is obtained from the point where the loss tangent is frequency independent. Experimentally, it is the point where the loss tangents of different frequencies intersect each other [25]. From the figure, the gel times of the mixture expectedly decreased with increasing temperature. Figure 5.4 exhibits the plot of the gel time as a function of gel temperature (°C) or sol-gel diagram of BA-35x mixed with epoxy resin at a fixed composition of 70:30 determined from Figure 5.3. The graph shows an exponential decay behavior of the gel time with increasing gel temperature. This is due to the fact that increasing the processing temperature increases the rate of crosslinking of BA-35x/Epoxy systems. Consequently, at higher temperature, the systems reach their gel points more quickly and the gel times are shorter [26]. From the figure, the gel time of this resin mixture ranges from 15 min at gel temperature of 180°C to about 80 min at gel temperature of 150°C. An Arrhenius model is mostly used to predict the gelation behavior of crosslinked network [25]. The gelation of our resin mixtures was found to be well predicted by the Arrhenius equation as follow:

$$t_{gel} = A\exp(\Delta E/T) \tag{5.1}$$

or

$$\ln(t_{gel}) = \ln A + (\Delta E/T) \tag{5.2}$$

where A = constant

ΔE = activation energy with a unit in Kelvin

T = temperature in Kelvin

Consequently, the ΔE or activation energy for gelation can be determined from the slope of the plots of ln(t_{gel}) as a function of 1/T. Meanwhile, an A value can be also determined from the y-axis intercept of the graph. Figure 5.5 illustrates the plot of the ln(t_{gel}) as a function of $1/T*10^3$ (K^{-1}) of BA-35x mixed with epoxy resin at composition of 70:30 determined from Figure 5.4. From the figure, the Arrhenius plot of this gelation shows only single slope or activation energy signifying single thermal event in the gelation process of this binary system. In Figure 5.5, the value of A was determined to be 0.7012×10^{-7} and ΔE to be 10.563 K or equivalent to 87.8 J/mol. Meanwhile, the kinetic parameters of Arrhenius equation at the gel points of BA-a, and BA-mt mixed with epoxy resin at composition of 70:30 were determined to be A = 3.7214×10^{-7}, and 1.2387×10^{-7}, and ΔE = 10.169, and 10.289, or equivalent to 84.5, and 85.5 J/mol, respectively. Those values were also determined for other arylamine-based benzoxazine-epoxy resin mixtures from Figure 5.6. In Figure 5.6, the Arrhenius plots of the effect of types of arylamine-based benzoxazine resins on the gel time of their mixture with the epoxy resin at a fixed composition of 70:30 were compared. From the figure, the slopes of the three curves which are related to the activation energy values of the gelation of BA-a/Epoxy, BA-mt/Epoxy, and BA-35x/Epoxy mixtures were approximately the same. This implies the gelation process of these binary mixtures was controlled by the ring opening polymerization of the oxazine ring in both three monomers thus resulting in the similar ΔE values. This also suggested that the types of the arylamine-based benzoxazine resins used do not significantly affect the activation energies of the gelation process of the resin mixtures. The y-axis intercepts or the A values of the BA-35x/Epoxy system indicated the smallest value while that of the BA-a/Epoxy system exhibited the largest value. This A value is related to the initial temperature that the mixture can start the gelation process. Therefore, BA-35x/Epoxy system tended to require lowest temperature to be able to start the gelation while BA-a/Epoxy needed highest starting temperature for the gelation process.

5.1.2 Curing Characteristics

The ring opening polymerization of the neat arylamine-based benzoxazine resins and the benzoxazine-epoxy mixtures can be completed by thermal treatment alone and does not yield any by-product. The curing reaction can also take place either with or without a catalyst. The curing mechanisms of arylamine-based benzoxazine-epoxy mixtures can be analyzed by a differential scanning calorimeter. Figure 5.7-5.9 illustrates the plot of the DSC heat flow (mW/mg) as a function of temperature (^{o}C). The curing behaviors due to the ring opening polymerization of the neat arylamine-based benzoxazine resins are shown in Figure 5.7. From the figure, it can be observed that BA-a showed only one exothermic peak at 230^{o}C while BA-mt showed two overlapped exothermic peaks at 216^{o}C, and 235^{o}C, same as BA-35x which exhibited two overlapped exothermic peaks at 208^{o}C, and 240^{o}C. As a result, the developments of network structure in the substituted and unsubstituted arylamine-based benzoxazines are different. The curing mechanism in the first exothermic peak at lower temperature, i.e., 208^{o}C, of BA-35x resin was assigned to be the same as that of BA-a resin [27]. Jubsilp et al., 2006 [27] reported, the average activation energy value of reaction (1), or the first peak, for BA-35x resin is almost the same as the average activation energy of BA-a resin. This implies that the curing mechanism in the first stage of BA-35x resin is the same as that of BA-a resin. Meanwhile, the second shoulder exothermic peak at high temperature, i.e., at 240^{o}C, corresponds to the side reactions which generate the biphenolic methylene linkages and possible reaction to the para position of the arylamine ring called arylamine Mannich bridge and methylene linked structures [23, 27]. As a result, though the curing of the BA-35x can be initiated at lowest temperature i.e. 208^{o}C, it appears to be the most difficult to get fully cured due to its highest second exothermic reaction at 240^{o}C. Figure 5.8 exhibits effect of epoxy on curing behaviors of its mixture with BA-35x. From the figure, we can evidently see that the curing reaction of these binary systems can proceed without the need of a catalyst or a curing agent for the polymerization process. In the BA-35x/Epoxy system, we can observe the two exothermic peak of the curing reaction suggesting that the reaction of BA-35x with BA-35x itself and BA-35x with epoxy to form the network structure took place simultaneously at the same temperature range in the first exothermic peak at low temperature. This phenomenon is similar with the curing behavior of benzoxazine (BA-a) and epoxy binary mixture which was reported previously by Rimdusit and Ishida, 2000. In principle, the reactions between benzoxazine and epoxy were expected to comprise of at least two reactions; the first reaction is the exothermic curing peak among the benzoxazine monomers, while the second one is likely to be the reaction between the epoxide group on the epoxy with the phenolic hydroxyl group on the polybenzoxazine. The reaction between the epoxide groups with phenolic hydroxyl group on polybenzoxazine was expected to proceed after phenolic hydroxyl group from the ring opening of the benzoxazine monomer was produced [12, 17]. Meanwhile, the second shoulder exothermic peak was observed to be the same as our previously result. Furthermore, in Figure 5.8, the exothermic peaks of BA-35x was observed to systematically shift to higher temperature with an addition of epoxy resins. The positions of the exothermic peaks, curing temperatures, of BA-35x/Epoxy mixtures at 100:0, 90:10, 80:20, 70:30, and 60:40 mass ratios were determined to be 208, 215, 221, 227, and 235^{o}C, respectively. As a consequence, the degree of curing retardation was increased with the increasing amount of the epoxy in the binary mixtures. This indicates that BA-35x/Epoxy at composition 60:40 weight ratio was the most difficult to be thermal cured i.e. required higher temperature or longer time to be fully cured.

The curing condition of the benzoxazine and epoxy mixtures was determined from the disappearance of the area under the curve of the exothermic peak in DSC experiment. Figure 5.9 indicates the DSC thermogram of the BA-35x benzoxazine resin alloyed with epoxy resin at a mass ratio of 60:40 at various curing conditions. This composition was selected to represent all alloys for determining the fully cured condition as this ratio of the resin mixture required the most curing temperature for achieving a fully cured stage. From the figure, the heat of reaction determined from the area under the exothermic peak of the uncured BA-35x alloyed with epoxy resin, the top curve, was 302.1 J/g corresponding to the 0% conversion. The area under the curing peak tended to decrease with increasing the curing temperature or curing time. The heat of reaction was reduced to 234.4 J/g (22% conversion) after curing at 150^{o}C for 1 hour, and decreased to 75.9 J/g (75% conversion), 51.1 J/g (83% conversion), 14.0 J/g (95% conversion), 9.55 J/g (97% conversion), and 4.82 J/g (98% conversion) after further curing at 170°C for 1 hour, 190°C for 1 hour, 200°C for 1 hour, 200°C for 2 hours, and 200°C for 3 hours, respectively. After final cure at 200°C for 4 hours, the exothermic heat of reaction was completely disappeared (100% conversion) which corresponds to the fully cured stage of the alloys. The degree of conversion of each sample was determined according to the following relationship:

$$\%\ \text{conversion} = \left(1 - \frac{H_{rxn}}{H_o}\right) \times 100 \qquad (5.3)$$

where H_{rxn} = the heat of reaction of the partially cured specimen.

H_o = the heat of reaction of the uncured resin.

Both H_{rxn} and H_o values are directly determined from DSC experiments. As a consequence, the curing temperature at 150°C for 1 hour, 170°C for 1 hour, 190°C for 1 hour and 200°C for 4 hours was chosen as an optimum curing condition of all benzoxazine-epoxy polymer alloys.

5.1.3 Fourier Transform Infrared Spectroscopy Investigation

In this research, arylamine-based benzoxazine resins were mixed with epoxy resin at various compositions. The chemical structures of arylamine-based benzoxazine resins, epoxy resin and their network formation reactions were studied by FTIR spectroscopic technique. The important functional groups of the benzoxazine monomers are the oxazine ring and the tri-substituted benzene ring in the benzoxazine ring structure whereas that of the epoxy is its epoxide ring. These functional groups were used to characterize the presence of the monomer in the polymerization reaction. The FTIR spectra of arylamine-based benzoxazine monomers and the epoxy resin are shown in Figure 5.10. In Figure 5.10 (a, b, c), the absorption bands appeared at 941 and 1496 cm^{-1} were assigned to the oxazine ring [23] and the tri-substituted benzene ring [28] in the benzoxazine ring structure, respectively while the absorption bands at 757 (a), 775 (b) and 833 cm^{-1} (c) were assigned to those of mono-substituted benzene in BA-a, meta-substituted benzene in BA-mt, and 1,3,5-trisubstituted benzene in BA-35x, respectively [23]. Finally, the absorption band situated at 913 cm^{-1} was assigned to the epoxide ring in epoxy resin [24, 28, 29] as shown in Figure 5.10 (d).

Figures 5.11a - 5.11c display the FTIR spectra of benzoxazine monomers and the fully cured polybenzoxazines of all three types of the benzoxazine resins. As the curing process proceeded upon heat treatment, an infinitely three dimensional network was formed. According to the polymerization mechanism reported [24, 30], the oxazine ring is opened by the breakage of a C-O bond of the oxazine ring. Then the benzoxazine molecule transformed from a ring structure to a network structure. During this process, the tri-substituted benzene ring, backbone of benzoxazine ring, became tetra-substituted benzene ring with the characteristic absorption band appeared at 1477cm^{-1} [24]. It also led to the formation of a phenolic Mannich base polybenzoxazine structure. The network structure of a fully cured BA-a was composed of the phenolic Mannich bridge network whereas those of BA-mt and BA-35x composed of additional amounts of arylamine Mannich bridge and methylene linked structures [28]. Figures 5.11a – 5.11c (b) show the absorption bands of the neat arylamine-based benzoxazine monomers. These absorptions disappeared after the thermal treatment at 150°C/1 hour, 170°C/1 hour, 190°C/1 hour, 200°C/4 hours as shown in Figures 5.11a – 5.11c (a) and a broad intensive IR absorption band observed at 3400 cm^{-1} was assigned to the phenolic hydroxyl group [31]. These phenomena confirmed that benzoxazine monomers were thermally polymerized through its ring-opening reaction to yield polybenzoxazine network. In addition, from Figure 5.11b (a), BA-mt-typed polybenzoxazine shows the additional absorption band at 810 cm^{-1} which was assigned to the 3,4-dimethylaniline while BA-35x illustrates the new absorption band at 847 cm^{-1} and was assigned to the 1,3,4,5-tetrasubstituted arylamine ring as shown in Figure 5.11c (a). The development of these absorption bands is consistent with those reported by Ishida and Sander, 2000 [28].

The infra-red spectrum of arylamine-based benzoxazine monomers alloyed with epoxy resin at 60:40 weight ratios was also monitored by FTIR spectroscopy as shown in Figures 5.12a – 5.12c. Figures 5.12a – 5.12c (b) illustrate the absorption bands at 941 cm^{-1} assigned to the oxazine ring in benzoxazine structure and

913 cm^{-1} assigned to the epoxide ring of epoxy resin. After being fully cured, both bands were disappeared as clearly scan in Figures 5.12a - 5.12c (a). It was realized that the benzoxazine and epoxy rings opened, and the crosslinking reaction proceeded quantitatively without the use of curing accelerators. The epoxy appears to be reacting with the phenolic hydroxyl groups as soon as the ring opening polymerization makes them available. Thus, the epoxy appears to be completely consumed at the later stage of cure.

5.2 Characterization of Arylamine-based Polybenzoxazines and Epoxy Alloys

5.2.1 Density Measurement

In this study, the density measurement based on water displacement principle of all specimens was used to investigate the presence of void in polymeric alloys. The density of benzoxazine-epoxy alloy at room temperature was calculated using equation 4.2. Figure 5.13 exhibits the density of all three types polybenzoxazines alloyed with epoxy at various weight ratios. From the figure, the density of BA-35x was determined to be about 1.126 g/cm^3 which was the lowest density value among the three polybenzoxazines. The density of BA-a and BA-mt were calculated to be about 1.191 g/cm^3 and 1.156 g/cm^3 respectively. Moreover, an additional of the epoxy into the polybenzoxazines caused systematic variation in the alloy densities. In the BA-a system, the density of the polymer alloys trended to decrease from 1.191 g/cm^3 of the neat BA-a to about 1.184 g/cm^3 with increasing the epoxy resin contents from 0 to 40%wt. The density of the epoxy used equals to 1.160 g/cm^3 [11]. The density of the alloys seems to follow a simple rule of mixture. On the other hand, the density of the polymer alloys from the BA-mt and BA-35x systems increased with increasing the mass fraction of the epoxy as the property followed the rule of mixture as discussed above. In addition, for mass ratio of epoxy above 40 wt%, the density of the polymer alloys was unlikely to be in line with a simple rule of mixture because the amount of epoxy resin may exceed its stoichiometric amount for infinite network formation. At this point, some unreacted epoxy resin may exist in the polymer alloy network. The density of the obtained network system thus needed to consider that of the unreacted epoxy resin as well.

5.2.2 Dynamic Mechanical Properties

Dynamic mechanical analysis (DMA) is useful to investigate thermomechanical properties of polymeric materials, especially the transitions and relaxations of the materials. Knowledge of the transitions and relaxations of the materials will lead to an understanding of how materials behave at different temperatures and to an identification of a suitable service temperature. The change in molecular mobility of the specimen when temperature changed was sensed by dynamic mechanical analysis. Figure 5.14 and 5.16 shows the dynamic mechanical behaviors of the three types of the neat polybenzoxazines. Figure 5.14 displays the plot of the loss modulus (MPa) as a function of temperature (^{o}C) of the neat arylamine-based polybenzoxazines and the glass transition temperature or T_g was taken at the maximum point on the loss modulus curves. From the figure, the T_gs of the three types of the neat polybenzoxazines were found to be 172, 210 and 241^{o}C for BA-a, BA-mt and BA-35x, respectively. As a result, BA-35x indicates the highest T_g among the three polybenzoxazines. The greater T_g of BA-mt or BA-35x comparing with BA-a can be explained by the development of increasing amounts of various phenolic Mannich bridge, arylamine Mannich bridge, and methylene linkages and the enhancement of significant amounts of additional crosslinks via those linkages that would increase the T_g of the network substantially [23]. The glass transition temperatures of the three types of polybenzoxazines and epoxy alloyed at various compositions were shown in Figure 5.15. From the figure, the T_gs of BA-35x alloyed with the epoxy resin rendered the highest values though those values tended to decrease from 241^{o}C of the neat BA-35x to 223^{o}C with increasing the epoxy resin contents from 0 to 40% by weight. On the other hand, the synergy in T_g was observed in the BA-a and BA-mt alloyed with the epoxy. The T_g maxima of BA-a/Epoxy and BA-mt/Epoxy were found at about 80:20 mass ratio with the T_g values of 182 and 213^{o}C, respectively. The additional crosslinks of epoxy in the benzoxazine matrix have the effect on increasing the glass transition temperature of the alloy material over the pure polybenzoxazine thus the observed synergy in T_g. While the T_gs lower than the pure polybenzoxazine were likely to be due to the fact that the stoichiometric ratio of components is approached, unreacted or small molecular weight epoxy molecules may remain in the network formed and may interfere with network formation or act as a plasticizer [17].

Figure 5.16 illustrates a plot of storage modulus (MPa), a material stiffness, as a function of temperature (^{o}C) of the three types of the neat polybenzoxazines. From the figure, the highest storage modulus at room temperature was observed in BA-a which was found to be 5.9 GPa. For BA-mt and BA-35x those values were determined to be 5.3 and 5.0 GPa. This is possibly due to the effect of side methyl group on the arylamine ring. From the chemical structure of the three types of the neat polybenzoxazines, BA-a does not contain any methyl group on the arylamine ring, therefore, provides the highest storage modulus at room temperature. On the other hand, BA-mt contains one methyl group at meta position of the arylamine ring and BA-35x contains 2 groups. The presence of the more methyl groups thus caused the lowering of the storage modulus at room temperature. Kojio et al., 2004 reported the effect of side methyl and dimethyl groups of soft segment component in polyurethane elastomers [32]. The Young's modulus (tensile mode) was observed to decrease with an increase in methyl group content which is in good agreement with our polybenzoxazine systems. The addition of methyl group into each phenyl of the monomer substituent's, in the ortho, meta, or para position, to influence various polymer properties was reported by Velickovic et al., 1991 [33]. From their report, in the case of substitution in the ortho position, the methyl-group seemed to restrict strongly the free rotation of the phenyl ring, In this particular case a dipole/dipole interaction between the ester group dipole and the dipole introduced with the methyl group contributed further towards the reduced segmental mobility of the substituent groups as a whole. In the case of meta and para substitution the dipole/dipole interactions were much weaker. The introduction of a methyl group in any of these two positions increased the bulkiness of the substituent. In both cases, the free volume was increased without creating strong steric hindrance. In general, free volume could be related to the chemical structure. The greater the number of methyl side group in the repeating unit, the lower the density and the bigger the free volume as reported by Espeso et al., 2006 [34]. Finally, the plot of the storage modulus at room temperature of benzoxazine resin alloyed with epoxy resin of all three binary systems as a function of epoxy contents (%wt) is shown in Figure 5.17. From the figure, the storage modulus at room temperature of all three binary systems was found to decrease systematically from 5.9 GPa of the neat BA-a, 5.3 GPa of the neat BA-mt and 5.0 GPa of the neat BA-35x to 4.8, 4.4 and 3.8 GPa with increasing the amount of the epoxy resin from 0 to 40%wt. This is due to the more flexibility or less stiffness of the epoxy compared to the polybenzoxazines used. The less stiff due to the presence of the soft segments, ether linkage, in its molecular structure as can be seen in Figure 2.7. The effect of the epoxy resin mass fraction on the storage modulus at room temperature of the ternary systems (benzoxazine/epoxy/phenolic) was reported previously by Rimdusit and Ishida, 2000. In their case, the storage modulus at room temperature of the polymer alloys also decreased with increasing amount of the epoxy resin [12].

5.2.3 Thermal Expansion Properties

Figure 5.18 shows the plot of coefficient of thermal expansion (ppm/^{o}C) as a function of epoxy content (%wt) of the arylamine-based polybenzoxazines alloyed with epoxy resin. The coefficient of thermal expansion (CTE) of the neat arylamine-based polybenzoxazines was calculated from the slope based on the thermal expansion curve of each specimen of the plot of the probe position as a function of temperature. The coefficient of thermal expansion in the glassy state was taken from the same temperature range of 30^{o}C to 120^{o}C. From Figure 5.18, the CTE of BA-35x was determined to be 47.3 ppm/^{o}C which was the lowest CTE value among the three polybenzoxazines. For those of BA-mt and BA-a were found to be 49.5 ppm/^{o}C and 57.9 ppm/^{o}C, respectively. This is due to the presence of meta-methyl in arylamine rings may increase the free volume of the polymers; therefore resulted in the lowering of their CTE in BA-mt and BA-35x comparing with BA-a. The longer chain length between two reactive OH tail-end groups, caused an increase in free volume of the cured resin. The steric hindrance of methyl substituent to cause a decrease in the CTE of redistributed-poly(phenylene oxide)/epoxy than that of 4,4'-diamino-diphenylmethane/bisphenol-A-epoxy, was reported by Hann-Jang Hwang, 2008 [35]. The effect of epoxy on the coefficient of thermal expansion of the three types of polybenzoxazines alloyed with epoxy resin was also shown in this figure. From the figure, the coefficient of thermal expansion of polybenzoxazine-epoxy alloys of all three binary systems from BA-35x, BA-mt, and BA-a, were increased from 47.3, 49.5 and 57.9 ppm/°C to 63.9, 68.6 and 70.3 ppm/°C, respectively with increasing amount of the epoxy from 0 to 40%wt. Typical epoxy resins have CTEs value in the range of 100-150 ppm/°C. As a result, the increase in the epoxy fraction in the alloys caused the loosing in their CTE with an epoxy fraction.

5.2.4 Thermal Degradation and Thermal Stability Properties

Thermogravimetric analyzer (TGA) is a technique which a change in sample mass is monitored as a function of temperature or time. Degradation temperature (T_d) is one of the key parameters that needed to be considered for high temperature applications of materials. In this study, degradation temperatures of the polymer alloys were defined as the temperature at 5% weight loss and the char yields were obtained at 800°C under nitrogen atmosphere for each polymer. The TGA thermograms of the neat arylamine-based polybenzoxazines are shown in Figure 5.19 which clearly revealed that only one major process occurred during the thermal degradation. The degradation temperature of BA-a was determined to be about 329°C whereas those of BA-mt and BA-35x possessed the degradation temperatures of similar value of 358°C. In BA-mt and BA-35x, the polymerized network structure was not a pure phenolic Mannich bridge network (as seen in Figure 3.2 (a)) but contained additional structures, like those found in an arylamine Mannich bridge network (as seen in Figure 3.2 (b)) and various methylene bridges. An anchoring of the pendent rings in the BA-mt and BA-35x through reaction at the para position should not significantly increase the thermal stability of the Mannich bridge unless the phenolic moiety contributed significantly to the degradation mechanism of the phenolic Mannich bridge structure. The arylamine Mannich bridge structures that comprised the main chain were not ortho to a phenolic moiety, they could degrade at a higher temperature and, hence, delay the onset of weight loss. However, the more rigid network created by the methylene linkages created kinetic barriers to weight loss as well. This explanation was reported in detail by Ishida and Sanders, 2000 [10]. Furthermore, the char yields at 800°C of the three types of the neat polybenzoxazines rendered about the same value of 30%. Hemvichian and Ishida [36], 2002 reported that the char yield of BA–35x was almost the same as that of BA-a since BA-35x has similar chemical functionalities to BA-a, without any additional reactive functional groups. Increased char yield due to the higher crosslinking density in BA-35x than BA-a was offset by the evaporating methyl groups, resulting in a very similar char yield.

Figure 5.20 shows the plot of T_d (^{o}C) as a function of the arylamine-based polybenzoxazine alloyed with epoxy resin at various compositions. The T_d's of BA-a/Epoxy polymer alloys were found to increase from 329^{o}C for the neat BA-a to 350^{o}C for the alloy with epoxy content of 40wt%. Meanwhile, the T_d's of BA-mt/Epoxy and BA-35x/Epoxy were found to maintain at about 360^{o}C with increasing amount of the epoxy. However, the char yields of all three benzoxazine/epoxy binary systems were found to decrease with increasing amount of the epoxy as shown in Figure 5.21. This is due to the fact that polybenzoxazines are known to possess higher char yield than the epoxy [12].

5.2.5 Flexural Properties

The flexural properties of polybenzoxazines alloyed with epoxy resin at various epoxy contents are shown in Figure 5.22 – 5.24. The specimens for flexural analysis were loaded until failure such that both flexural stress and strain at breakage could be measured for the polybenzoxazine-epoxy alloys. Flexural strength and strain represent an ability of materials to absorb maximum force at rupture. This ability concerns with storing and dissipating forces in polymers in the form of movement, rotation and vibration of molecule, which is transformed to heat, deformation or sound, etc [24]. Figure 5.22 exhibits the plot of the flexural strength (MPa) as a function of the epoxy content (% by weight) of polybenzoxazines-epoxy alloys at various compositions. The flexural strength of a thermosetting resin is influenced by a number of interrelated parameters including T_g, molecular weight between crosslinks, free volume, chemical structure, network regularity and perfection, and many other contributing factors [24]. From the figure, it can be observed that the flexural strength of the BA-a was found to be about 141.4 MPa which provided the highest value among the three arylamine-based polybenzoxazines. Those of BA-mt and BA-35x were determined to be about 128.7 and 112.2 MPa, respectively. This is also possibly due to the effect of side methyl groups on the arylamine ring in BA-mt and BA-35x. From the chemical structure of the three types of the neat polybenzoxazines, BA-a does not contain methyl group on the arylamine ring thus renders the highest flexural strength. On the other hand, BA-mt and BA-35x contain one and two methyl groups in the arylamine ring respectively therefore provide the lowest flexural strength. Moreover, increasing the mass fraction of the epoxy resin from 0 to 40% in the benzoxazine-epoxy alloys caused an increase in flexural strength of the three binary systems from 141.4, 128.7 and 112.2 MPa to 181.9, 161.4 and 154.7 MPa in BA-a/Epoxy, BA-mt/Epoxy, and BA-35x/Epoxy, respectively. The increase in crosslink density and in T_g up to certain amount of the epoxy caused the strengthening of the alloy system. Also, it was suggested by Ishida and Allen, 1996 that the benzoxazine homopolymer and copolymers with low concentrations of epoxy may contain clusters of branched chains or at best may be characterized as a loosely crosslinked network. The addition of epoxy molecules allows the clusters to be joined, the network tightened, and the perfection of the network improved with a subsequent increase in flexural strength [24].

Figure 5.23 exhibits the plot of the flexural strain at break (%) of the arylamine-based polybenzoxazines alloyed with epoxy resin as a function of epoxy contents (% by weight). From the figure, the flexural strain at break of BA-a, BA-mt and BA-35x was observed to be about 2.4, 2.5 and 2.8%, respectively. BA-35x shows the highest strain value among of three types of polybenzoxazines as a result of the most quantity of the side methyl group on the arylamine ring in this system causing some flexibility in the polymer. From the result, BA-a exhibits a more brittle failure at a higher strain than BA-mt and BA-35x. The effect of epoxy on the flexural strain at break of polybenzoxazine can also be seen in this figure. The flexural strain at break of arylamine-based polybenzoxazines alloyed with epoxy resin was also observed to increase from 2.4, 2.5 and 2.8% to 4.0, 4.9 and 5.4% for BA-a, BA-mt and BA-35x systems, respectively, with increasing the amount of the epoxy resin from 0 to 40%wt.

Generally, intermolecular packing, free volume, molecular architecture, and molecular weight between crosslinks influence the large-strain glassy state properties [2]. The extensibility of a crosslinked polymer in its glassy state is constrained largely by its available free volume. A higher free volume decreases chain interactions and enhances the ability of molecular chain segments to flow under load by such means as rotational configurational changes. These effects on free volume may be at least partially responsible for the improved strain behavior observed in the alloys. The ability of chain segments to reach their fully extended state is also dependent on the intramolecular flexibility of the segments as well as their intermolecular packing constraints. Thus, the addition of the more flexible epoxy segments to the polybenzoxazine matrix should also contribute to the increased strain at breakage for the alloys [24].

Finally, the plot of flexural modulus (GPa) of arylamine-based polybenzoxazines alloyed with epoxy resin as a function of epoxy contents (% by weight) is shown in Figure 5.24. The flexural modulus shows a behavior nearly identical to that of the storage modulus at room temperature from DMA thermograms. From the figure, the flexural modulus of the BA-a was found to be about 6.1 GPa which is the highest value among the three polybenzoxazines. For BA-mt and BA-35x, those values were found to be about 5.4 and 4.7 GPa, respectively. For the alloys with epoxy, the flexural modulus of all alloys decreased from 6.1, 5.4 and 4.7 GPa to 4.9, 4.1 and 3.9 GPa for BA-a, BA-mt and BA-35x systems, respectively, with increasing the amount of the epoxy resin from 0 to 40%wt. The phenomenon was due to the basic principle that the addition of the more flexible or less stiff epoxy into the more rigid polybenzoxazine can cause the softening of the resulting polymer alloys. These results are consistent with those of DMA.

5.2.6 Hardness (Shore D) Measurement

Figure 5.25 illustrates hardness of polybenzoxazines alloyed with epoxy resin at various epoxy contents. From the figure, the hardness of the neat BA-a polybenzoxazine exhibits the highest value among the three types of the neat polybenzoxazines with the value of 89.2 shore D. For those of BA-mt and BA-35x were found to be 88.6 and 88.4 shore D, respectively. The hardness of BA-35x and BA-mt were lower than BA-a due to the effect of side methyl group on the arylamine ring causing an increase in their free volume. Kojio et al., 2004 reported [32] the effect of side methyl and dimethyl groups of soft segment component on polyurethane elastomers was investigated, the hardness decreased with an increase in methyl group content. The effect of epoxy on hardness property of polybenzoxazines is shown in the figure. The hardness of the polybenzoxazine-epoxy alloys for the three types of polybenzoxazines (BA-a, BA-mt and BA-35x) were observed to decrease slightly from 89.2, 88.6 and 88.4 shore D to 87.8, 87.2 and 86.6 shore D, respectively, with increasing the amount of the epoxy resin from 0 to 40%wt. This is due to the lower hardness of the epoxy compared with the polybenzoxazine. The bisphenol A based epoxy possessed a hardness value is 84 shore D [37].

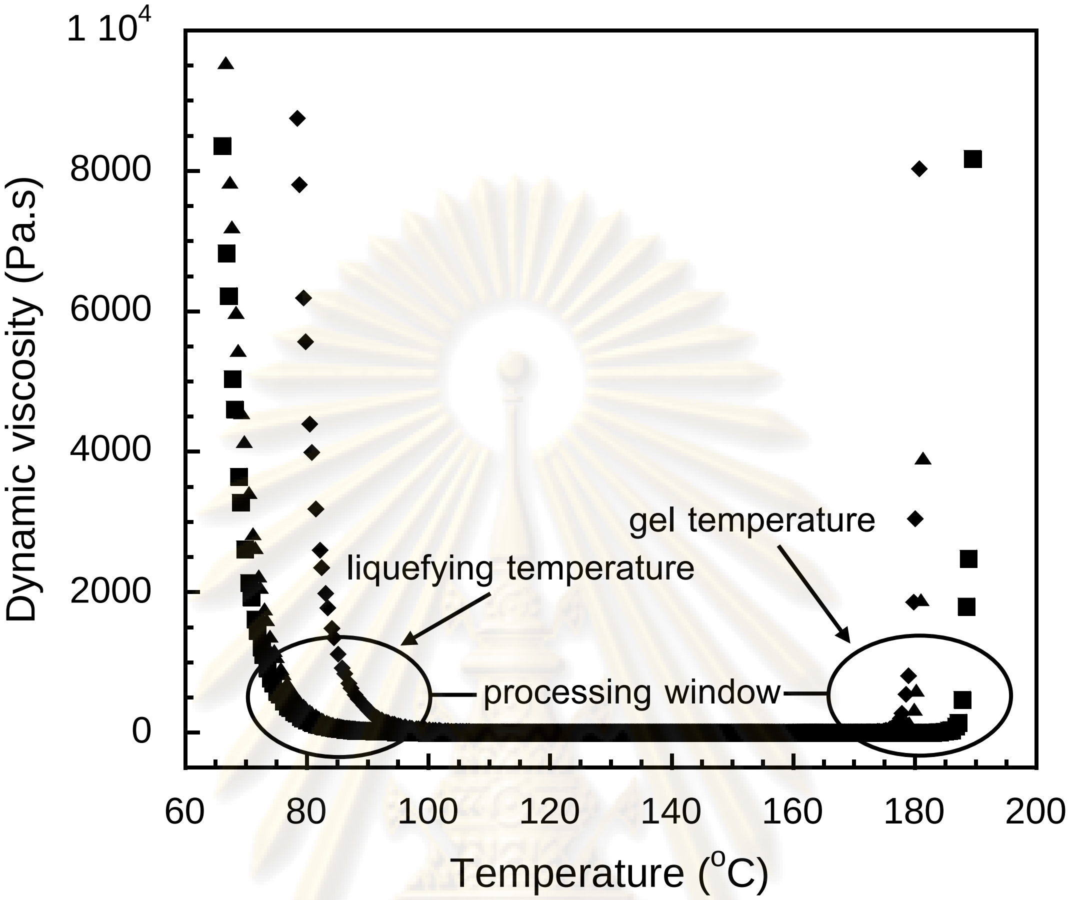


Figure 5.1 Processing window of the neat arylamine-based benzoxazine resins: (■) BA-a, (▲) BA-mt, and (♦) BA-35x.

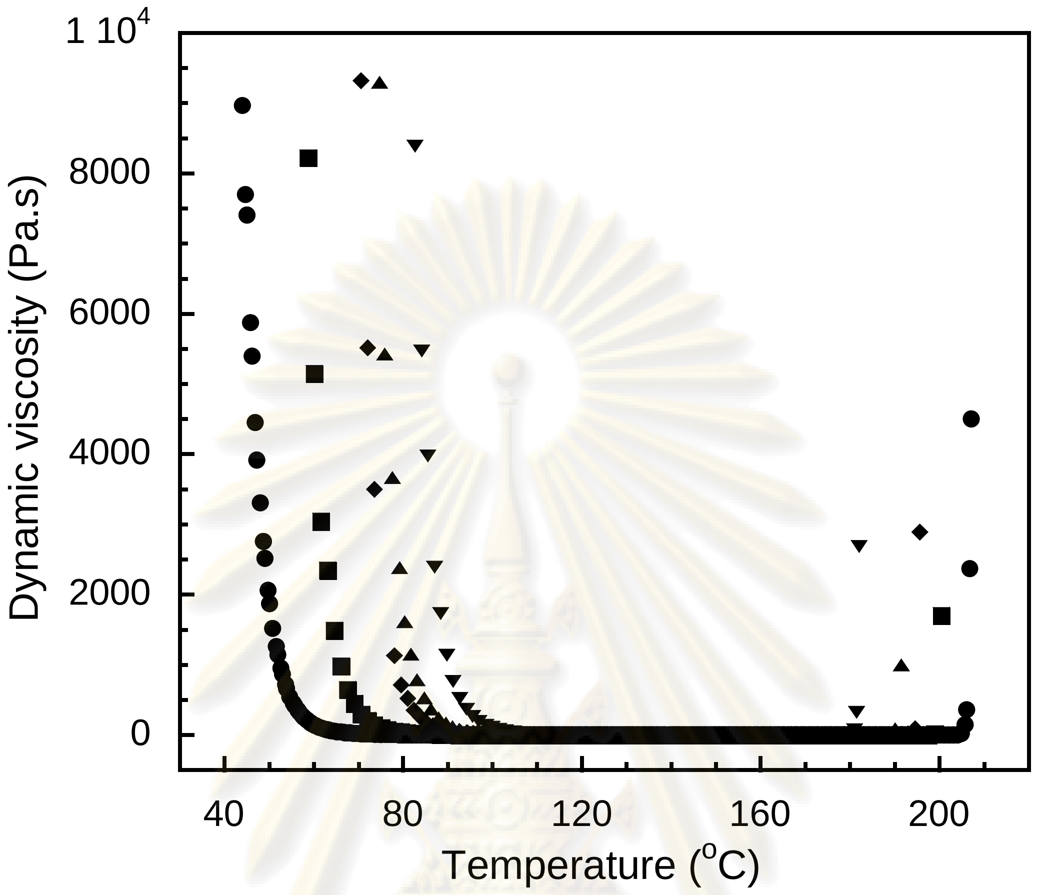


Figure 5.2 Processing window of BA-35x mixed with epoxy resin at various compositions: (●) 60:40, (■) 70:30, (♦) 80:20, (▲) 90:10, and (▼) neat BA-35x.

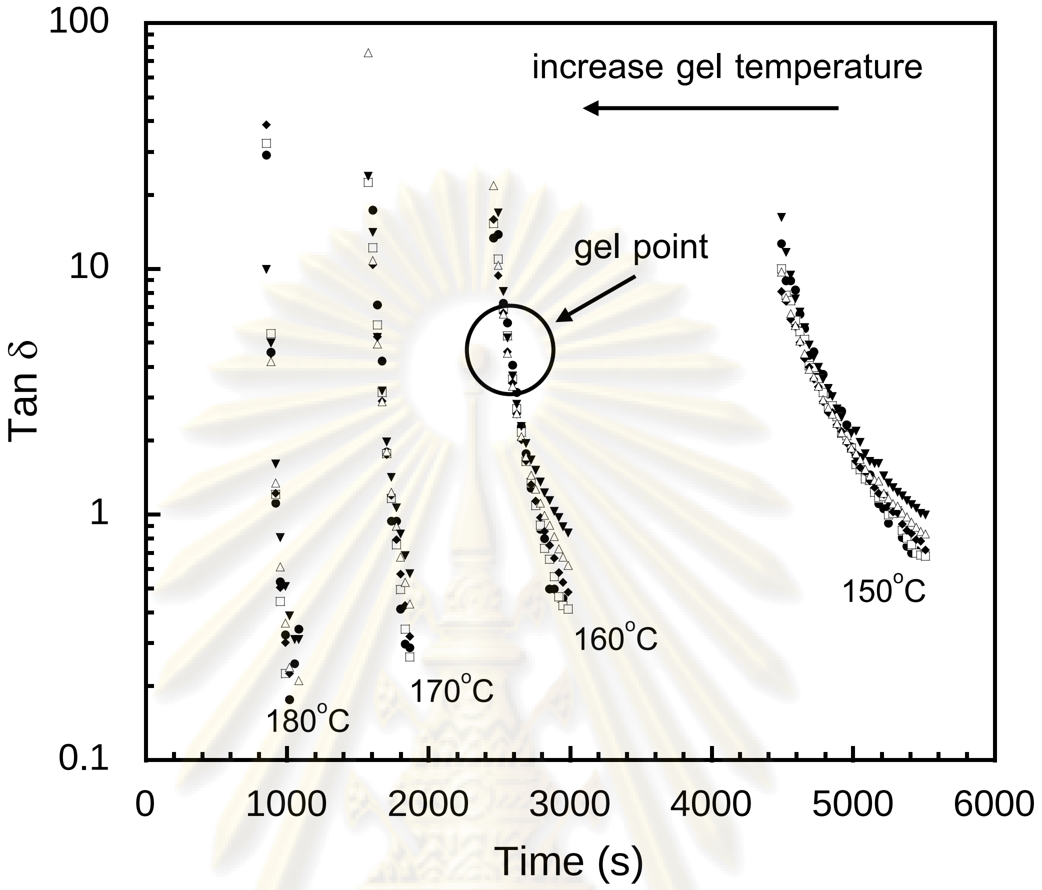


Figure 5.3 Effect of gel temperature on the gel time of BA-35x mixed with epoxy resin at composition 70:30: (●) 1.6Hz, (□) 2.8Hz, (♦) 5.0Hz, (Δ) 9.0Hz, and (▼) 15.9Hz.

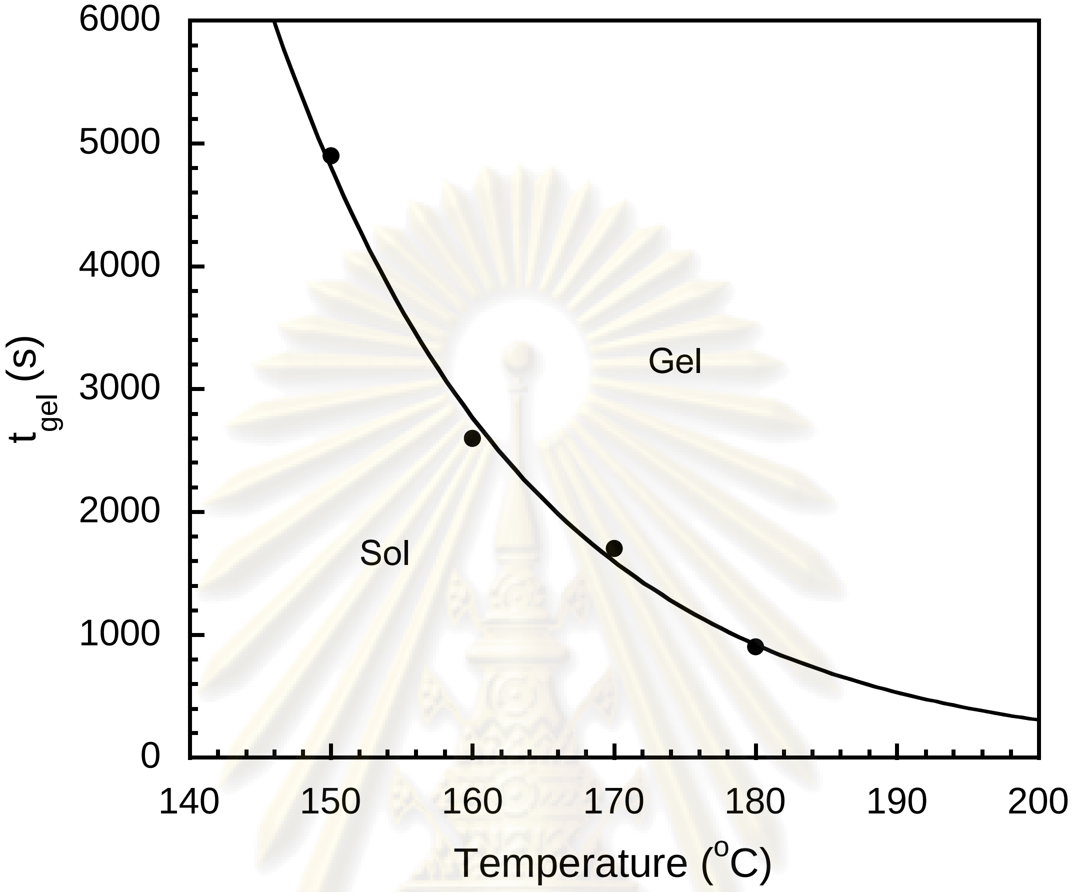


Figure 5.4 Gelation behavior of BA-35x mixed with epoxy resin at composition of 70:30 revealing the gel time as a function of gel temperature.

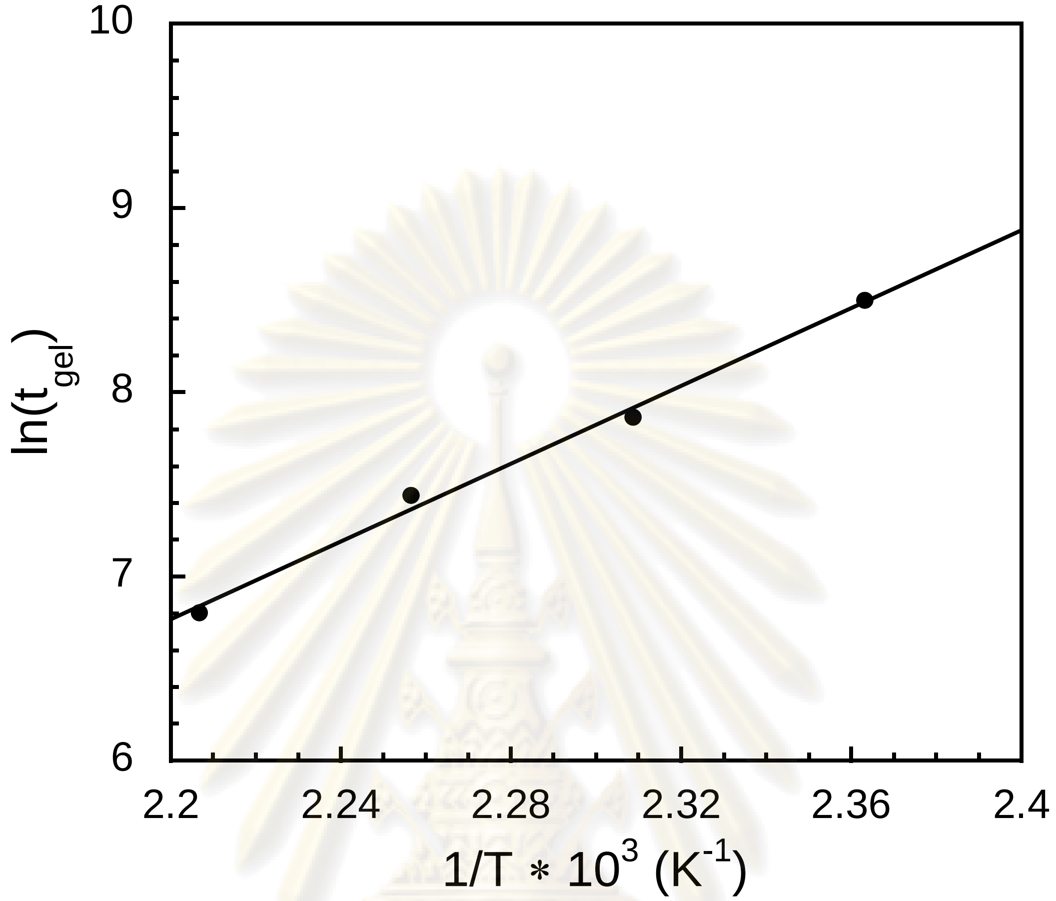


Figure 5.5 The Arrhenius plot of the gelation behavior of BA-35x mixed with epoxy resin at composition of 70:30.

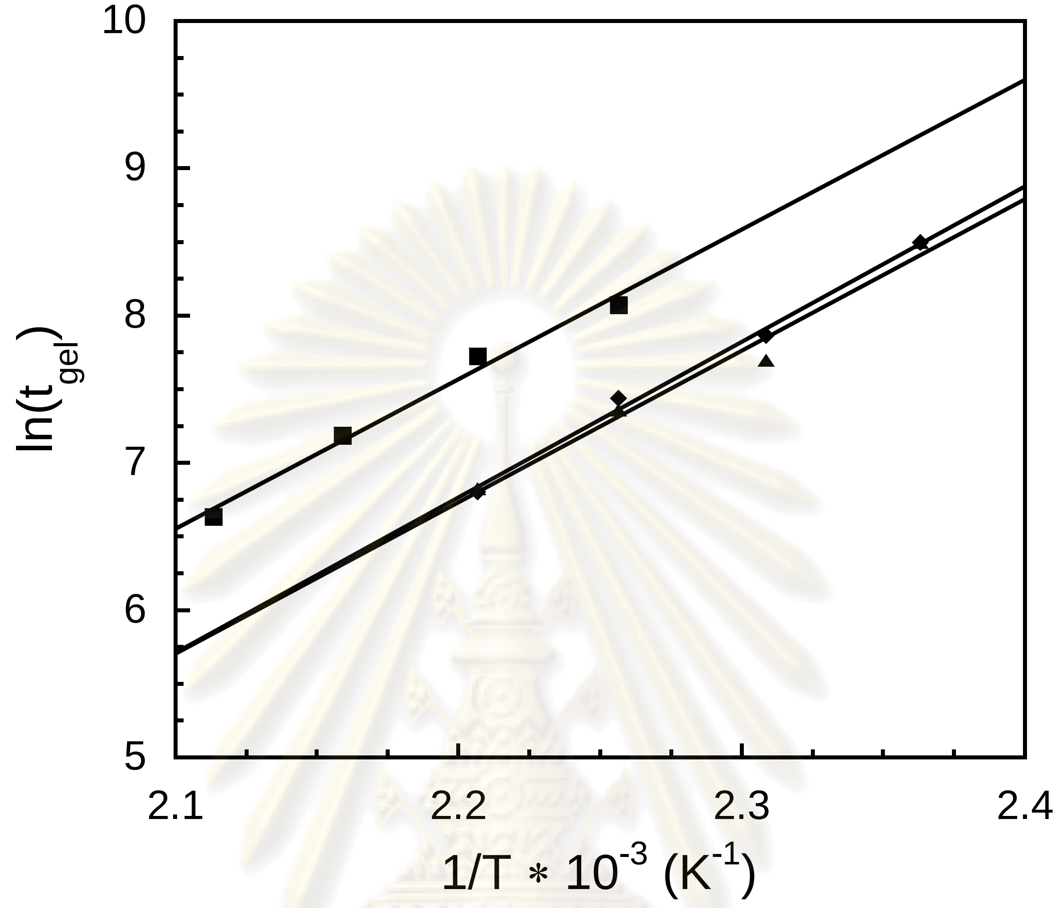


Figure 5.6 The Arrhenius plot of the gelation behavior of arylamine-based benzoxazine resins mixed with epoxy resin at composition of 70:30: (■) BA-a/Epoxy, (▲) BA-mt/Epoxy, and (♦) BA-35x/Epoxy.

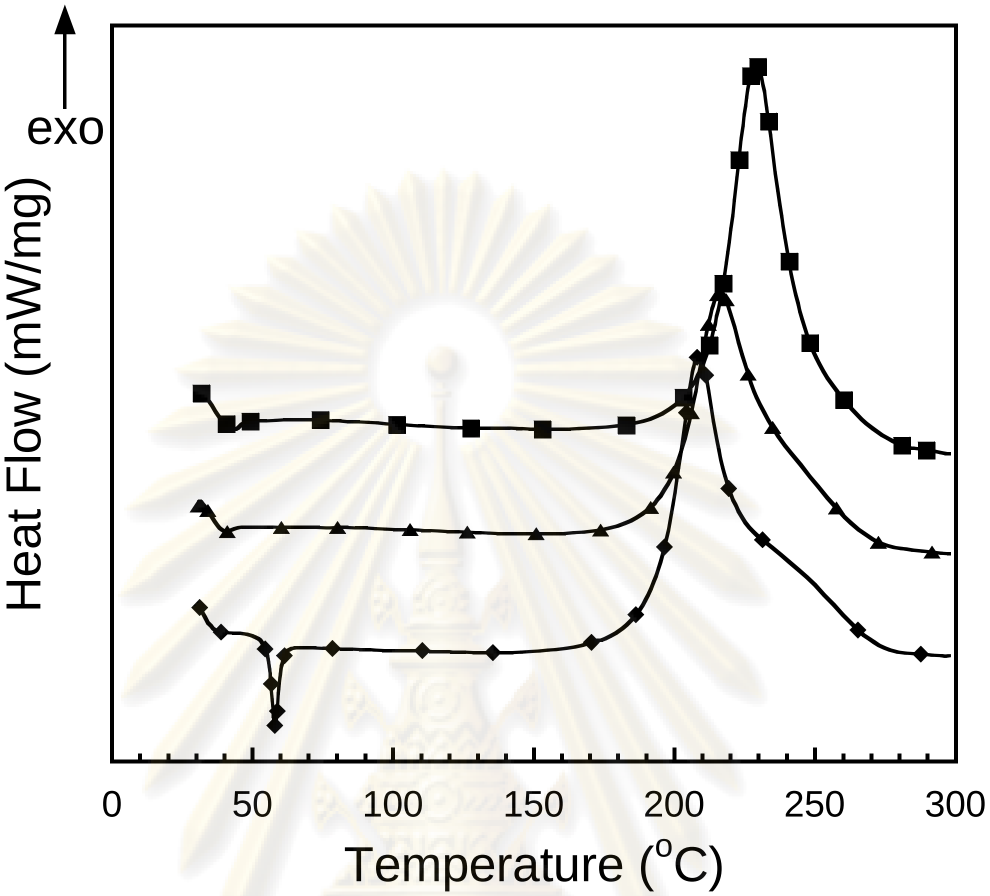


Figure 5.7 DSC thermograms of the neat arylamine-based benzoxazine resins: (■) BA-a, (▲) BA-mt, and (♦) BA-35x.

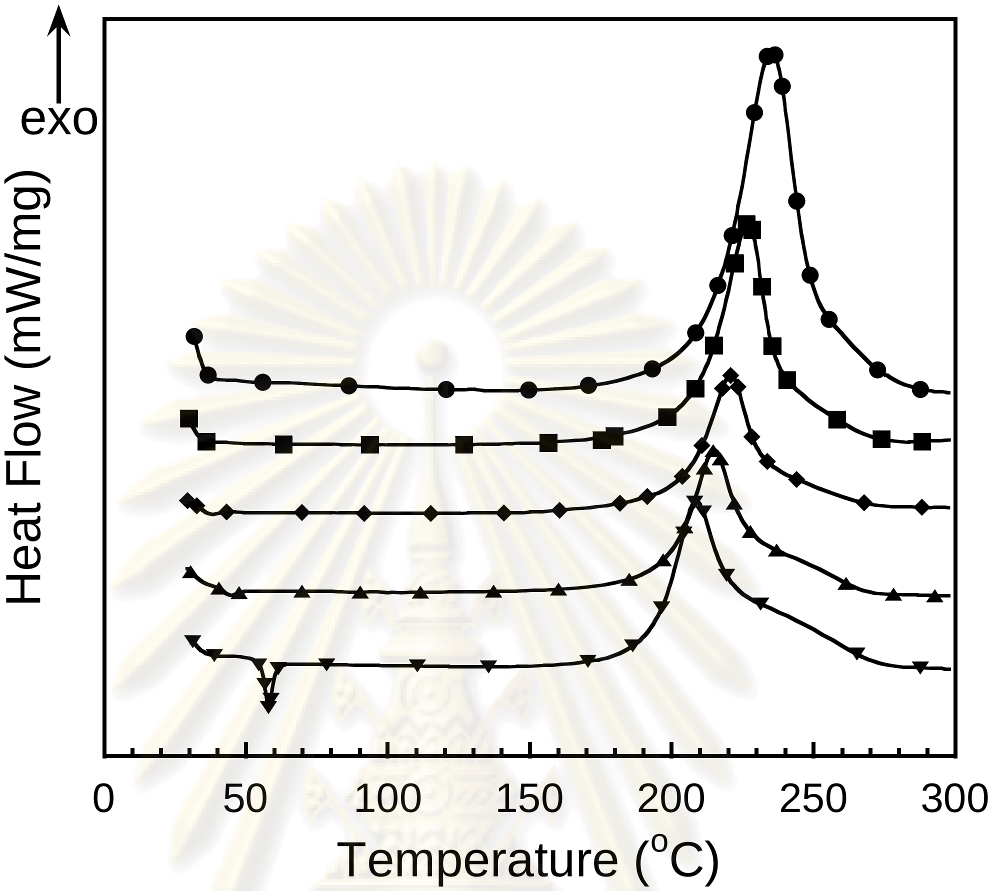


Figure 5.8 Curing behaviors of BA-35x mixed with epoxy resin at various compositions: (●) 60:40, (■) 70:30, (♦) 80:20, (▲) 90:10, and (▼) neat BA-35x.

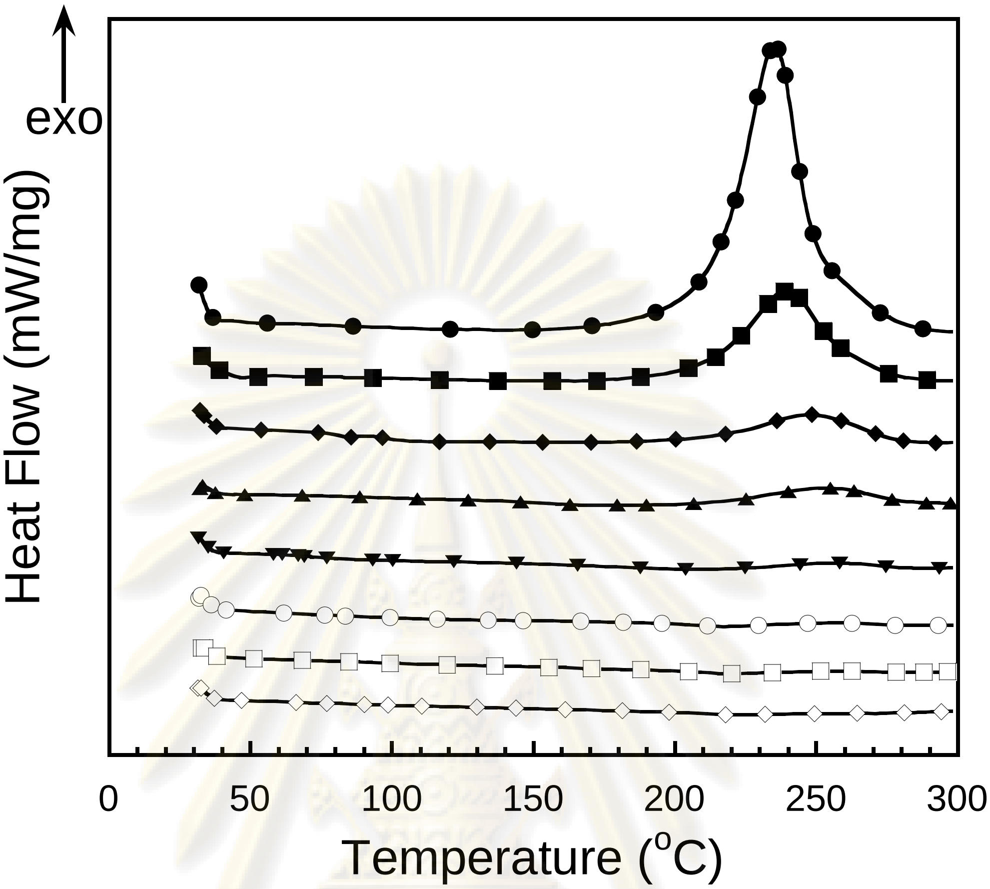


Figure 5.9 DSC thermograms of the BA-35x mixed with epoxy resin at a mass ratio of 60:40 at various curing conditions: (●) uncured, (■) 150°C/1hr, (♦) 150°C/1hr + 170°C/1hr, (▲) 150°C/1hr + 170°C/1hr + 190°C/1hr, (▼) 150°C/1hr + 170°C/1hr + 190°C/1hr + 200°C/1hr, (○) 150°C/1hr + 170°C/1hr + 190°C/1hr + 200°C/1hr 200°C/2hrs, (□) 150°C/1hr + 170°C/1hr + 190°C/1hr + 200°C/1hr 200°C/2hrs + 200°C/3hrs, and (◊) 150°C/1hr + 170°C/1hr + 190°C/1hr + 200°C/1hr 200°C/2hrs + 200°C/3hrs + 200°C/4hrs.

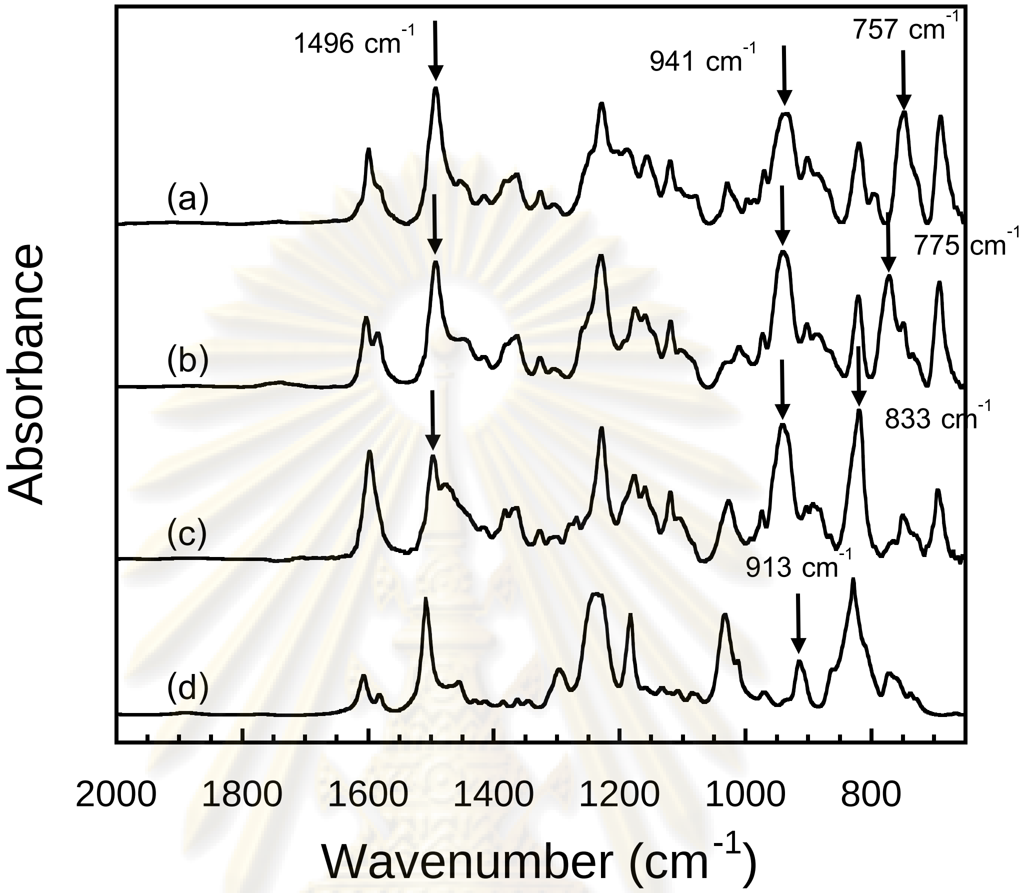


Figure 5.10 FTIR spectra of the neat arylamine-based benzoxazine monomers and epoxy resin: (a) BA-a, (b) BA-mt, (c) BA-35x, and (d) Epoxy resin.

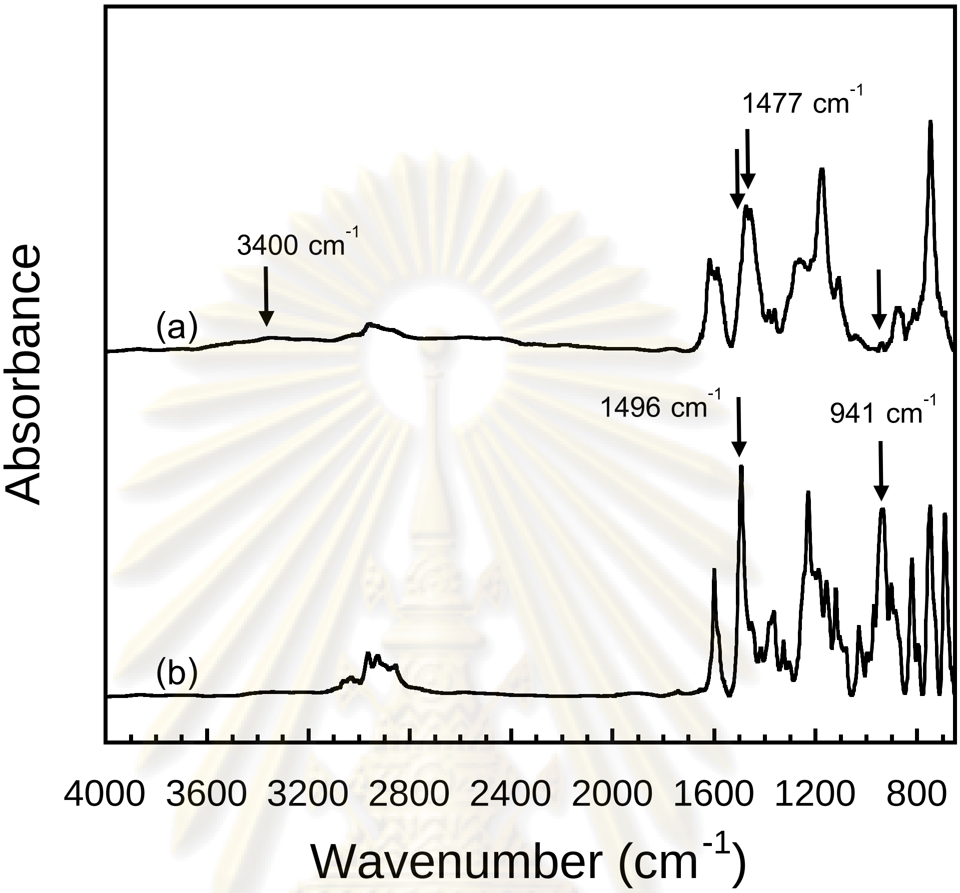


Figure 5.11a FTIR spectra of the neat BA-a formation:

(a) polymer and (b) monomer.

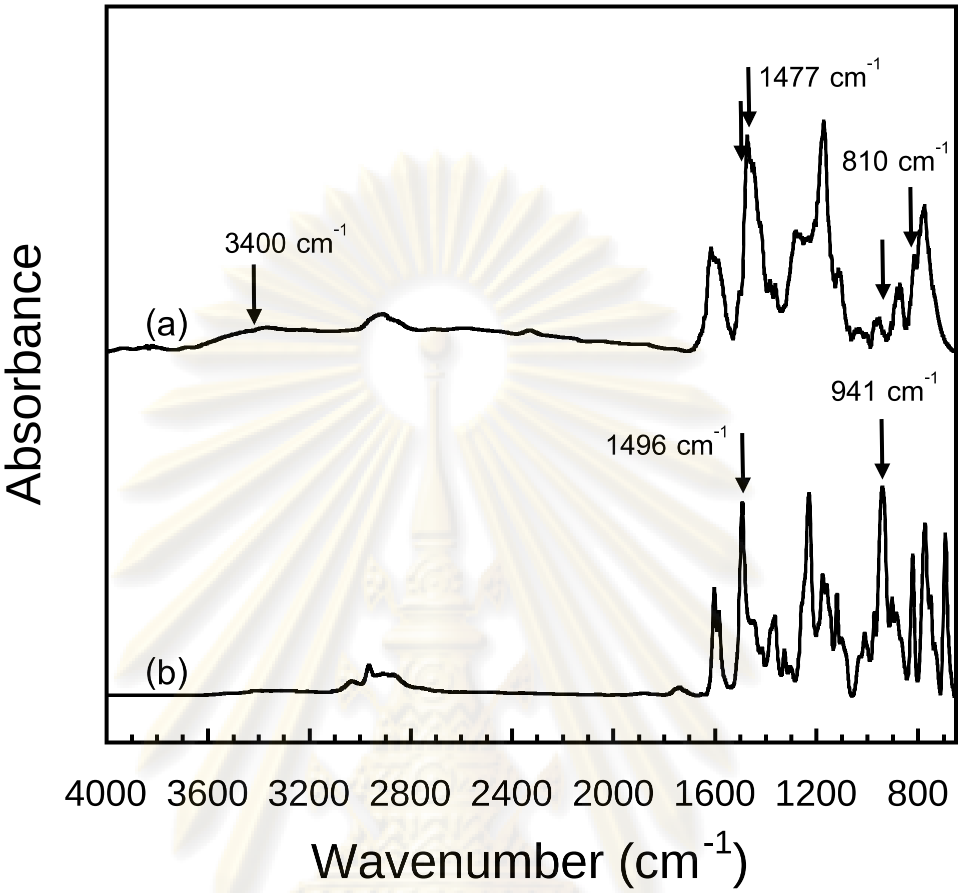


Figure 5.11b FTIR spectra of the neat BA-mt formation:

(a) polymer and (b) monomer.

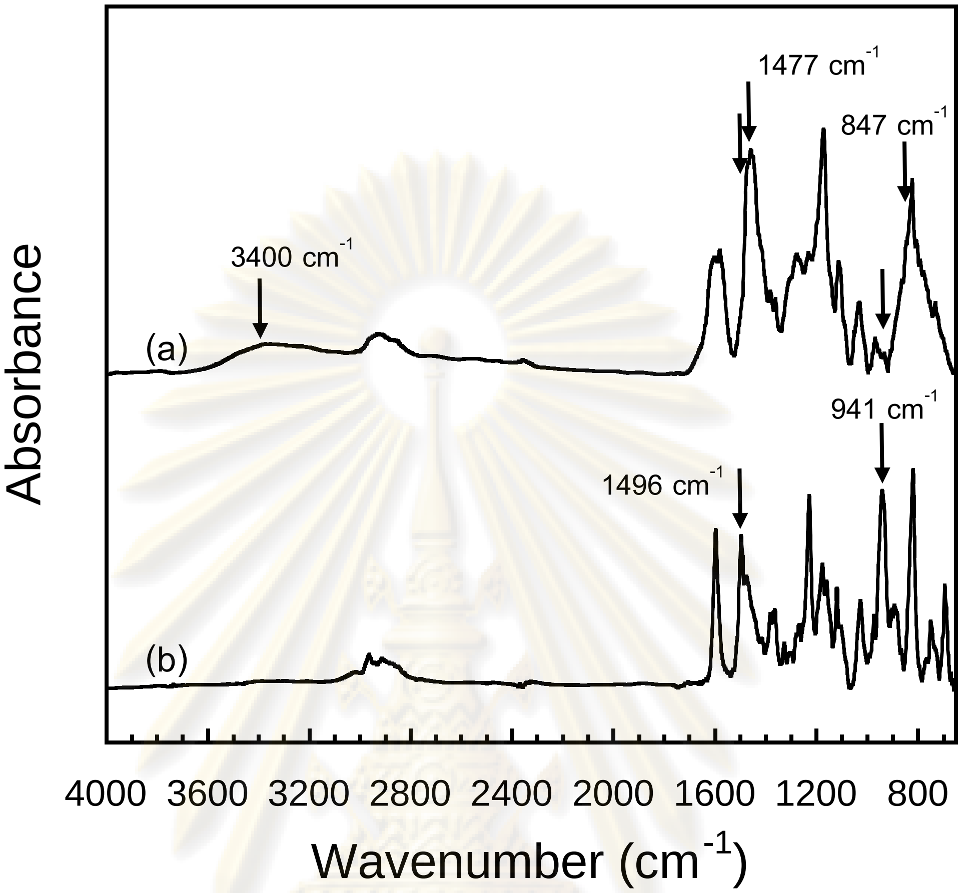


Figure 5.11c FTIR spectra of the neat BA-35x formation:

(a) polymer and (b) monomer.

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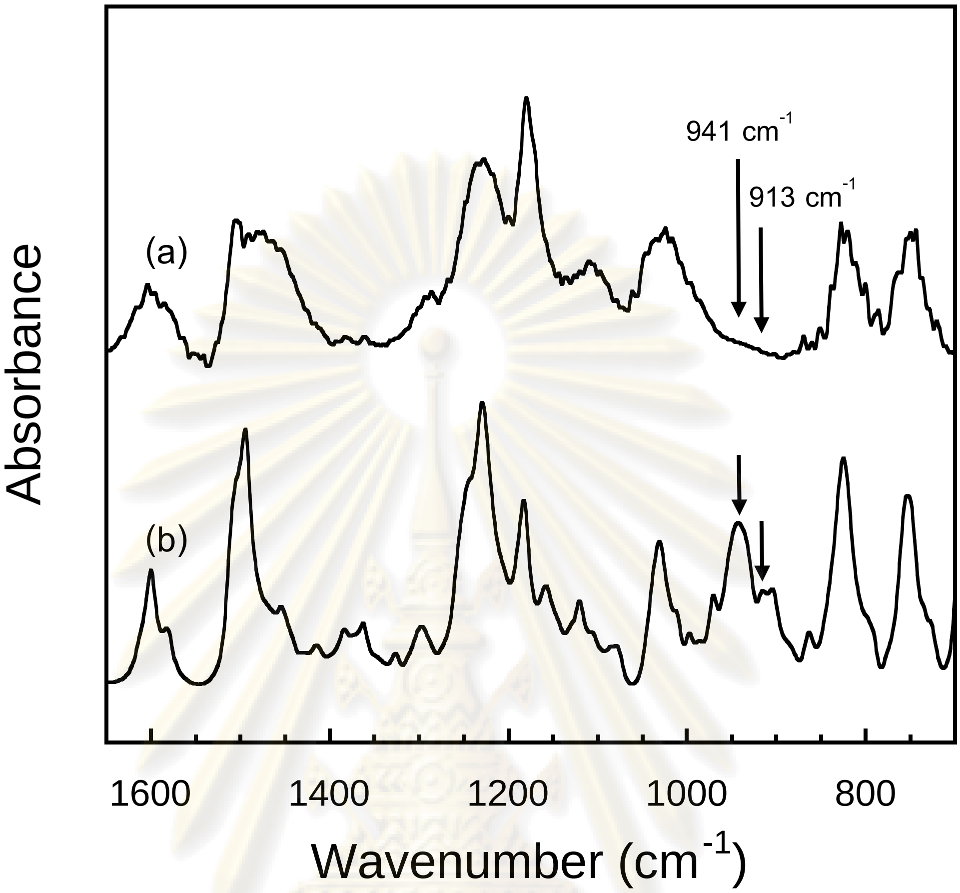

Figure 5.12a FTIR spectra of BA-a/Epoxy alloy at 60:40 mass ratio: (a) BA-a/Epoxy polymer and (b) BA-a/Epoxy monomer.

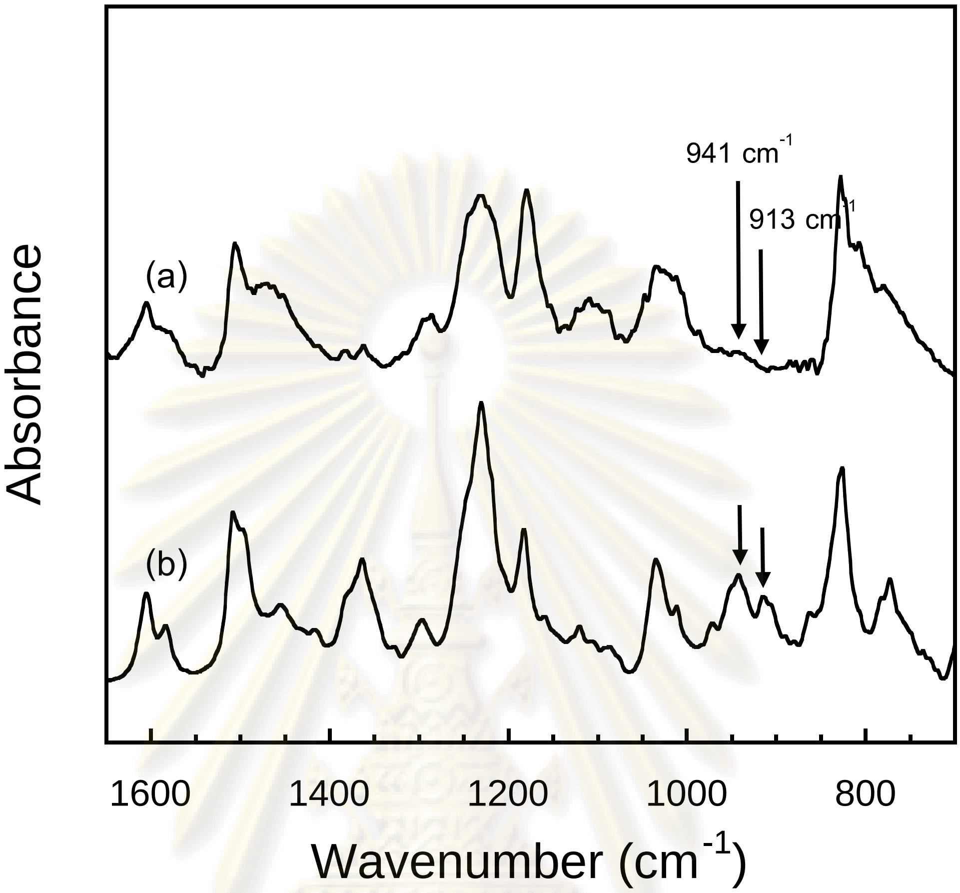

Figure 5.12b FTIR spectra of BA-mt/Epoxy alloy at 60:40 mass ratio: (a) BA-mt/Epoxy polymer and (b) BA-mt/Epoxy monomer.

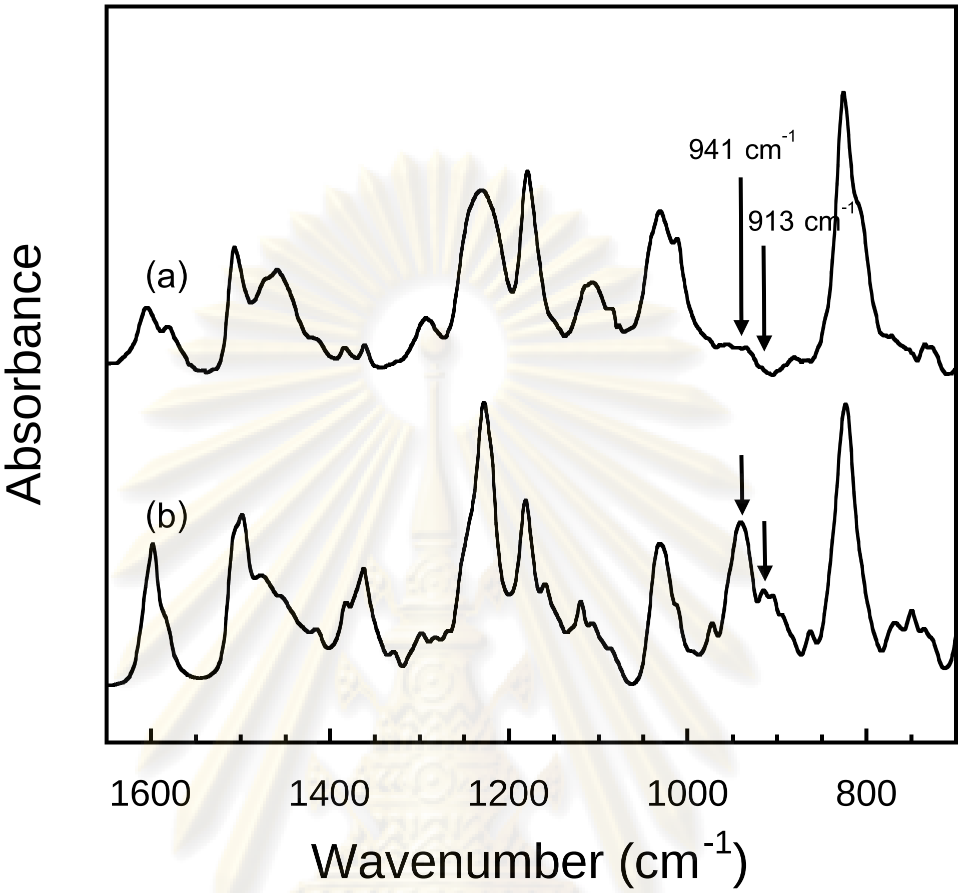

Figure 5.12c FTIR spectra of BA-35x/Epoxy alloy at 60:40 mass ratio: (a) BA-35x/Epoxy polymer and (b) BA-35x/Epoxy monomer.

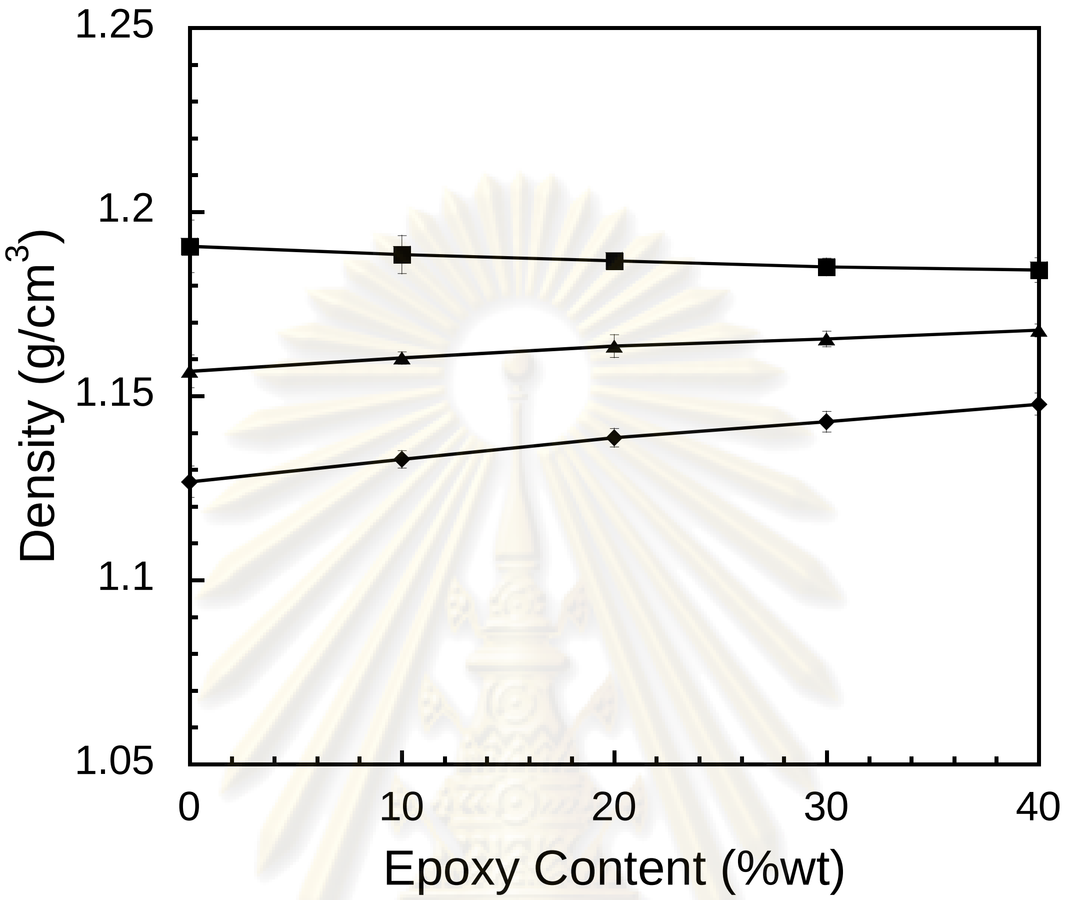

Figure 5.13 Density of arylamine-based polybenzoxazines alloyed with epoxy resin at various compositions: (■) BA-a/Epoxy, (▲) BA-mt/Epoxy, and (♦) BA-35x/Epoxy.

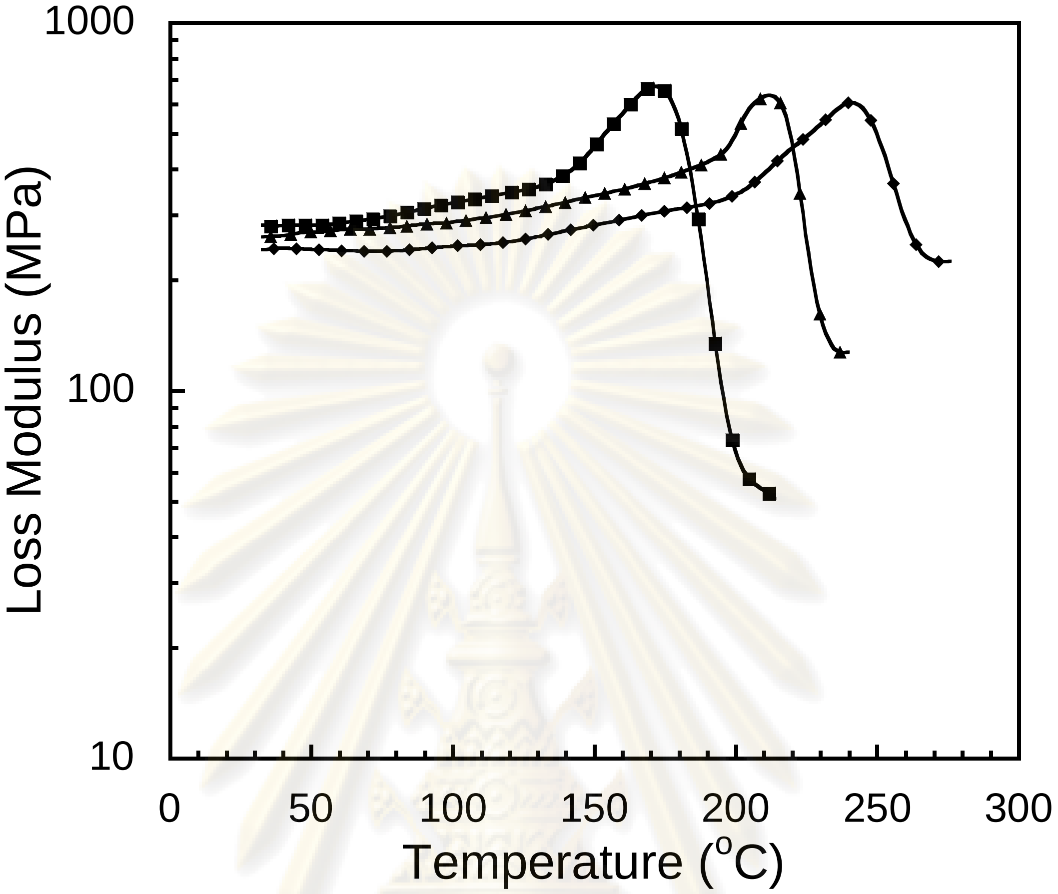

Figure 5.14 Loss modulus of the neat arylamine-based polybenzoxazines:

(■) BA-a, (▲) BA-mt, and (♦) BA-35x.

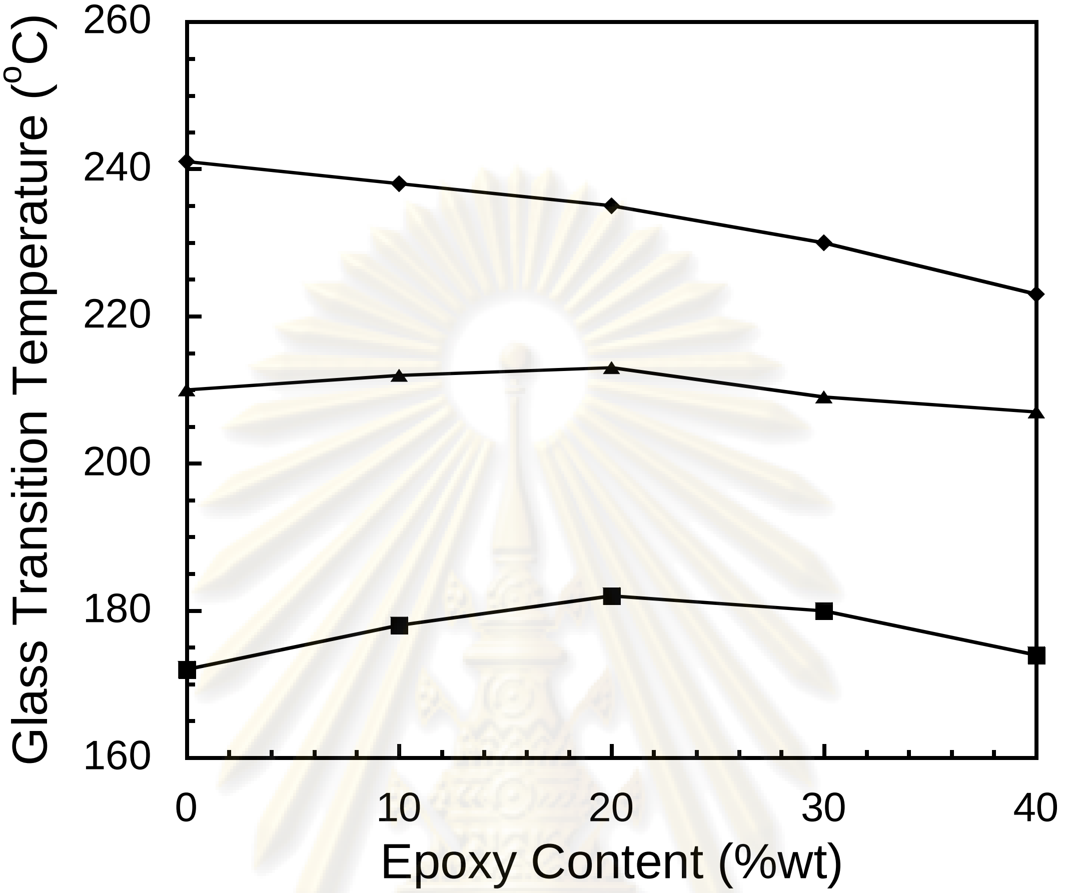

Figure 5.15 Glass transition temperature of arylamine-based polybenzoxazines alloyed with epoxy resin at various compositions: (■) BA-a/Epoxy, (▲) BA-mt/Epoxy, and (♦) BA-35x/Epoxy.

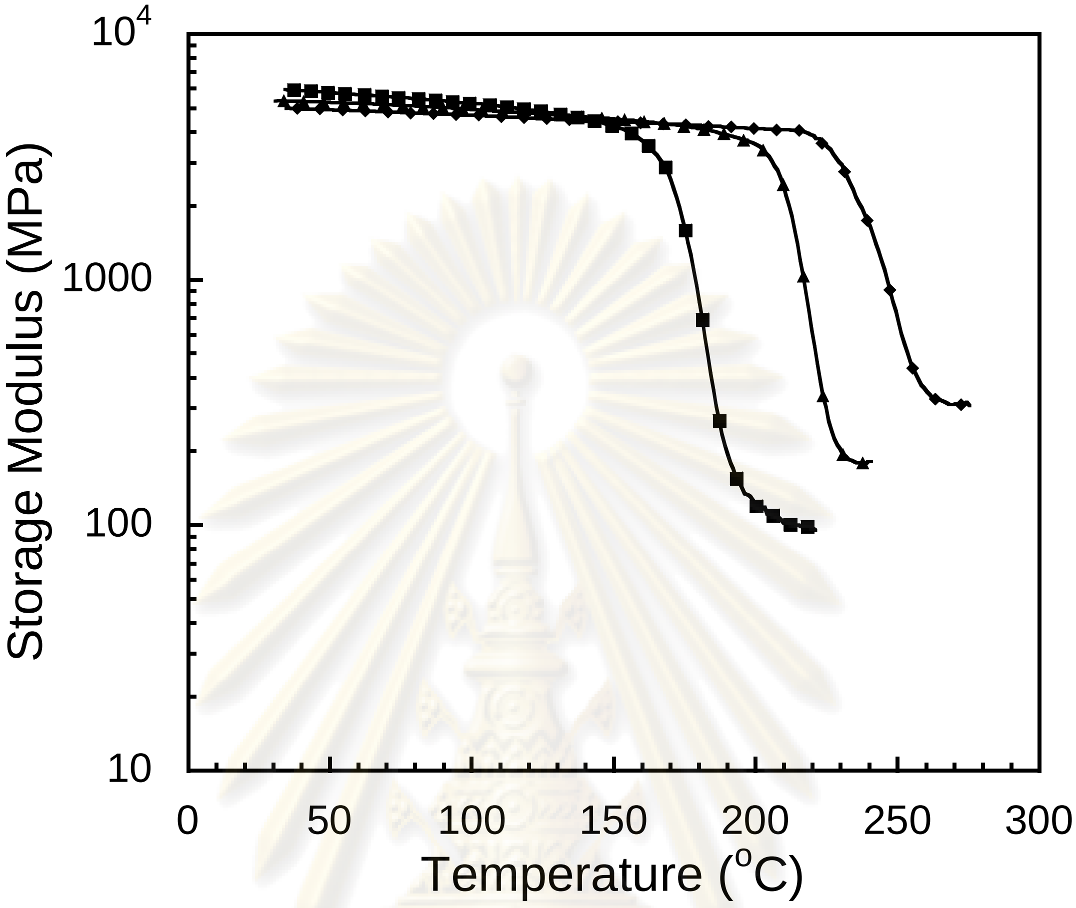

Figure 5.16 Storage modulus of the neat arylamine-based polybenzoxazines: (■) BA-a, (▲) BA-mt, and (♦) BA-35x.

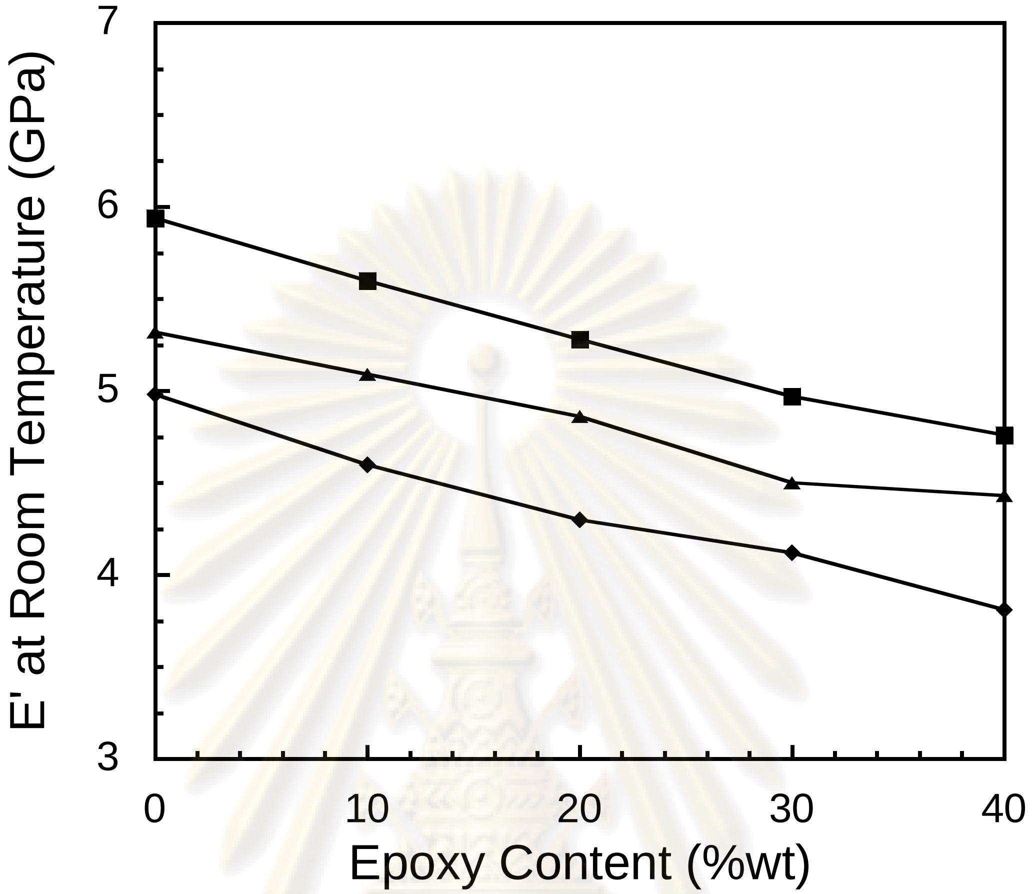

Figure 5.17 Storage modulus at room temperature of arylamine-based polybenzoxazines alloyed with epoxy resin at various compositions: (■) BA-a/Epoxy, (▲) BA-mt/Epoxy, and (♦) BA-35x/Epoxy.

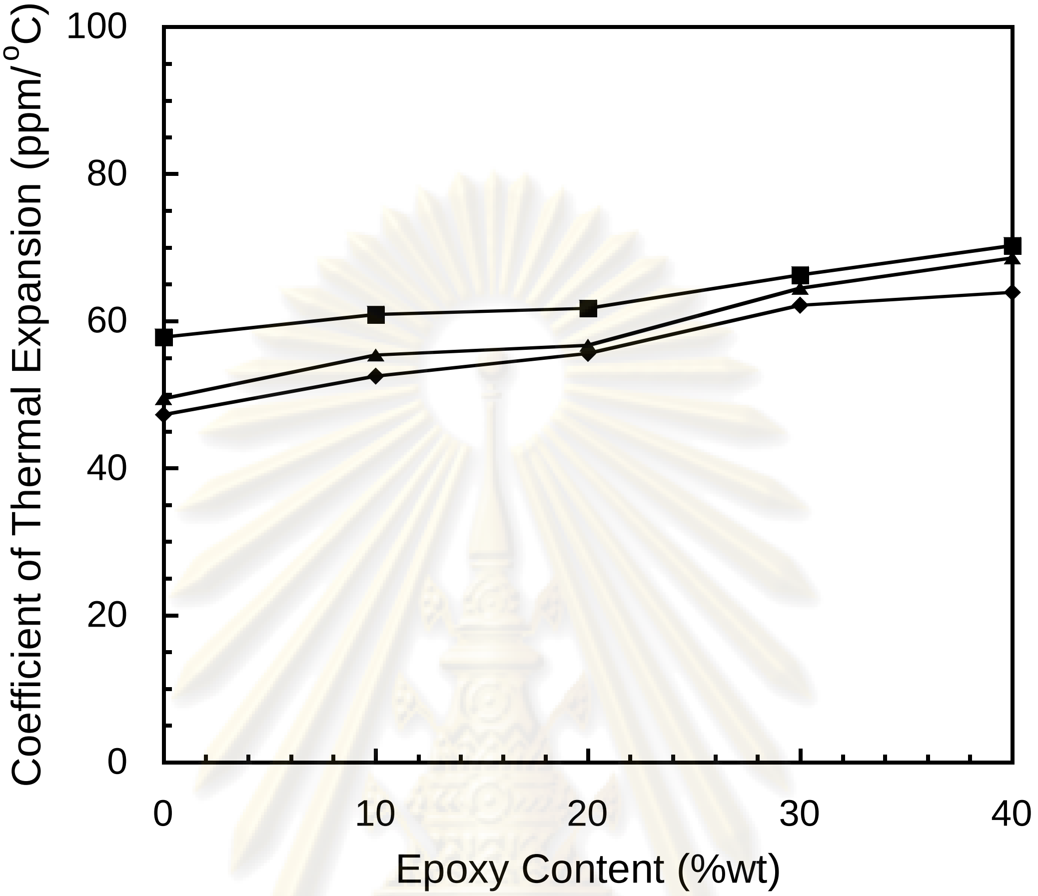

Figure 5.18 Coefficient of thermal expansion of arylamine-based polybenzoxazines alloyed with epoxy resin at various compositions: (■) BA-a/Epoxy, (▲) BA-mt/Epoxy, and (♦) BA-35x/Epoxy.

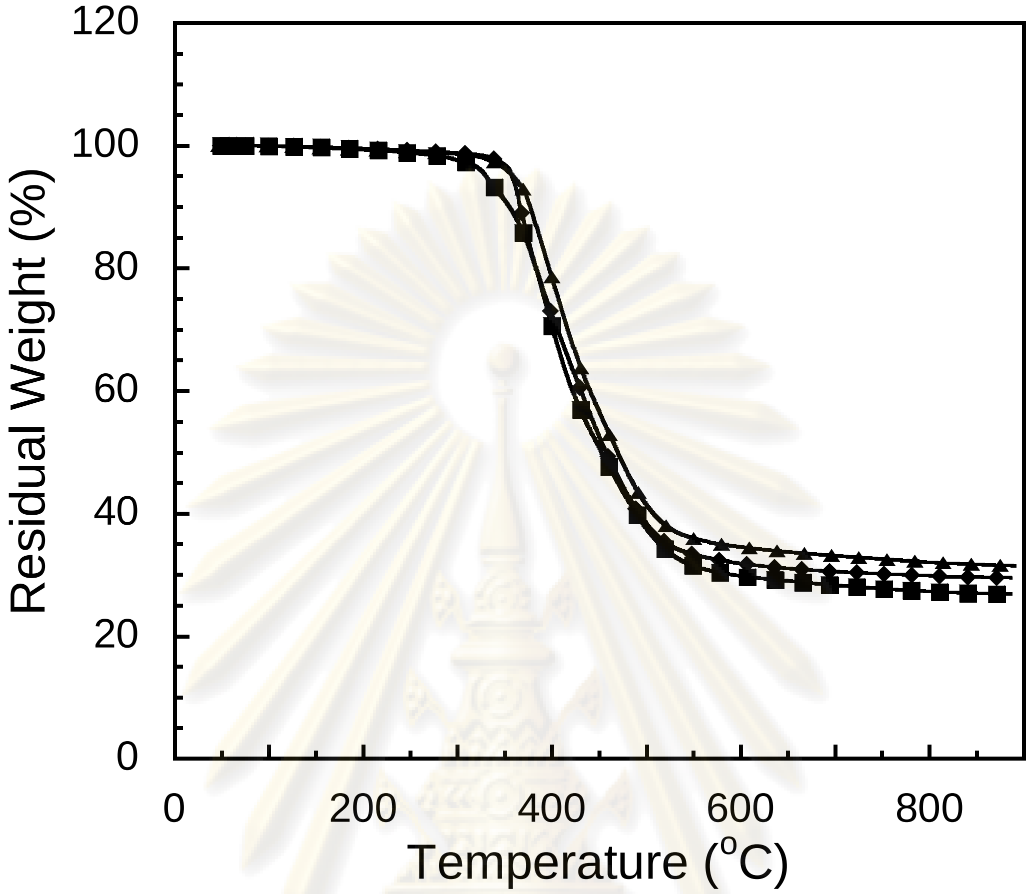

Figure 5.19 TGA thermograms of the neat arylamine-based polybenzoxazines: (■) BA-a, (▲) BA-mt, and (♦) BA-35x.

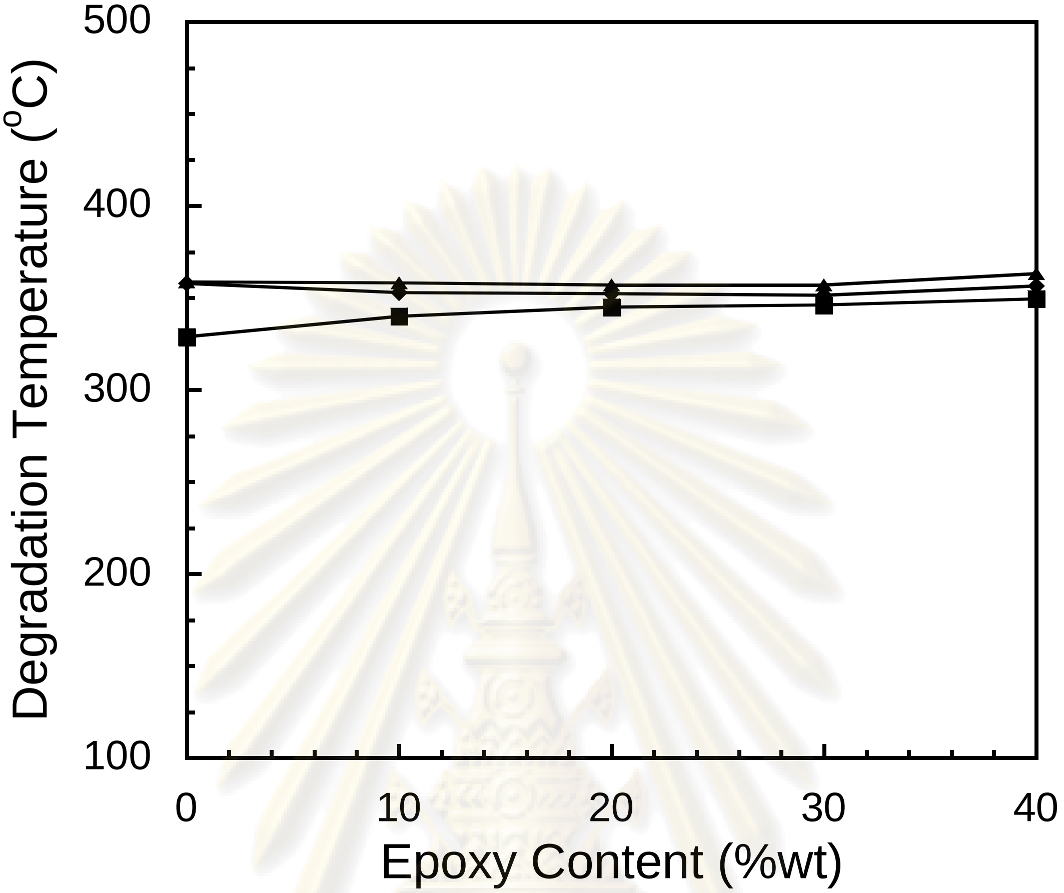

Figure 5.20 Degradation temperature of arylamine-based polybenzoxazines alloyed with epoxy resin at various compositions: (■) BA-a/Epoxy, (▲) BA-mt/Epoxy, and (♦) BA-35x/Epoxy.

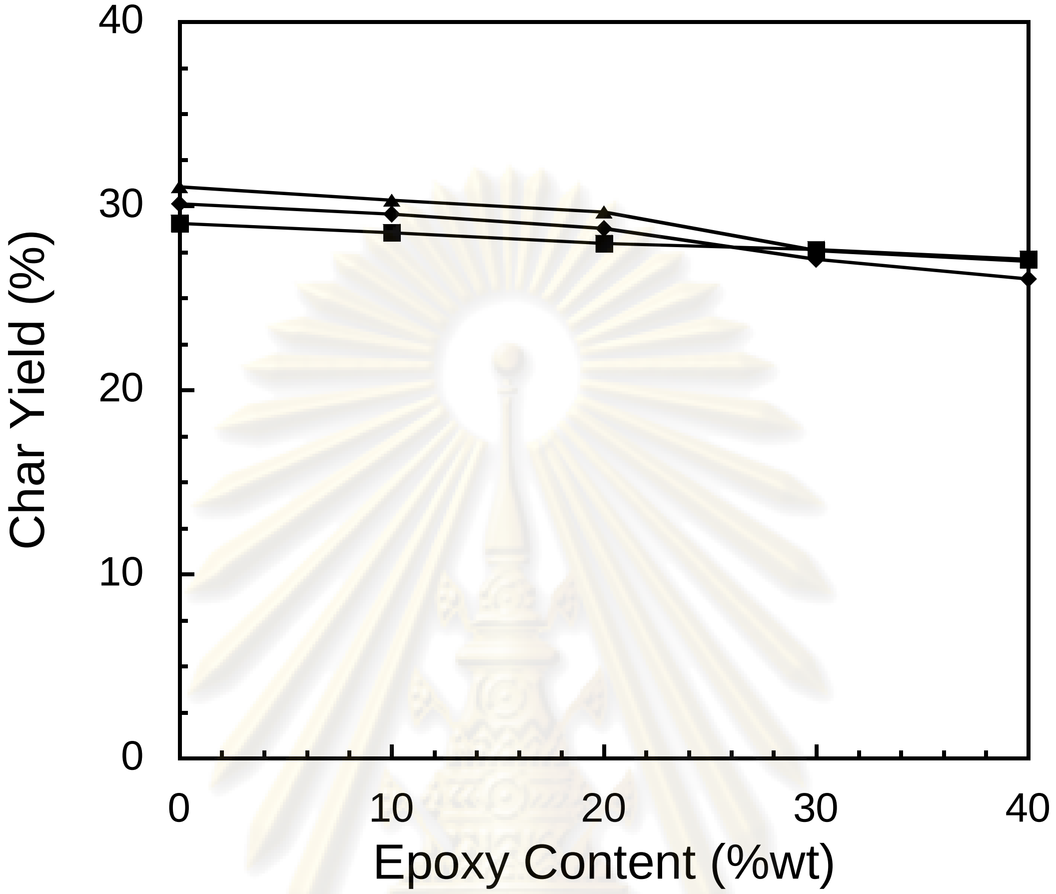

Figure 5.21 Char yield of arylamine-based polybenzoxazines alloyed with epoxy resin at various compositions: (■) BA-a/Epoxy, (▲) BA-mt/Epoxy, and (♦) BA-35x/Epoxy.

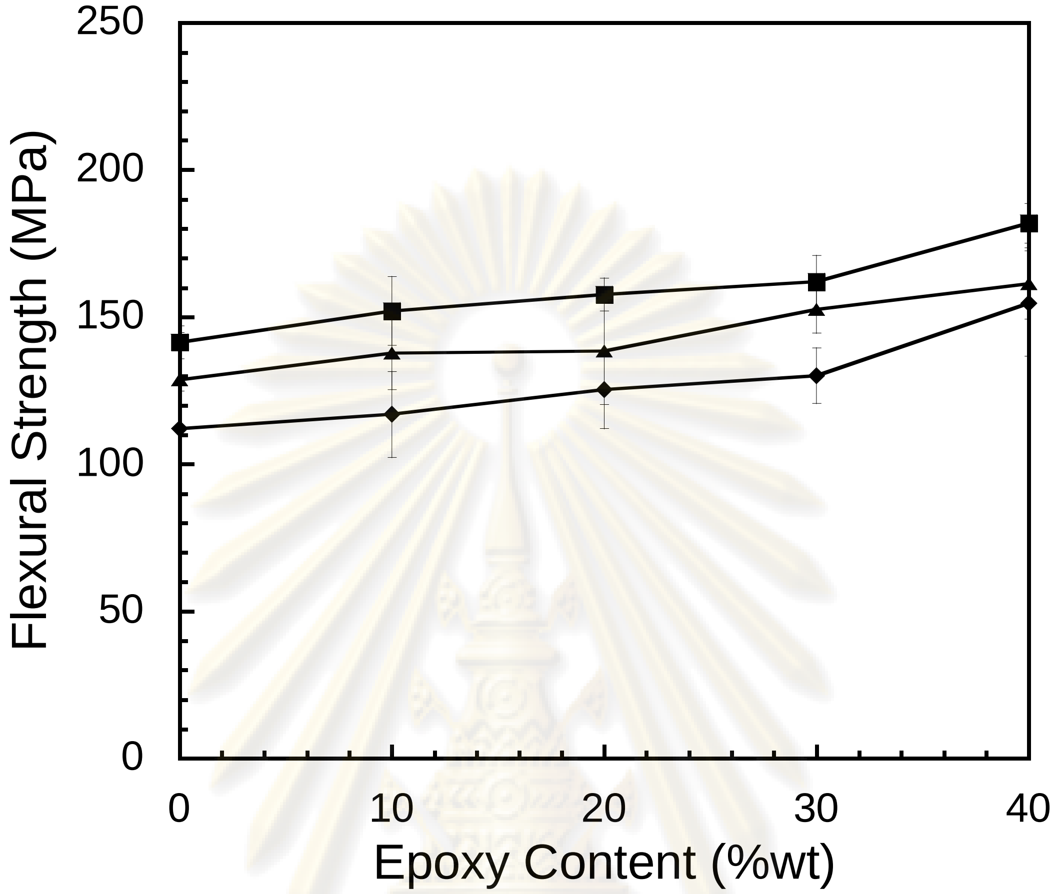

Figure 5.22 Flexural strength of arylamine-based polybenzoxazine/epoxy at various compositions: (■) BA-a/Epoxy, (▲) BA-mt/Epoxy, and (♦) BA-35x/Epoxy.

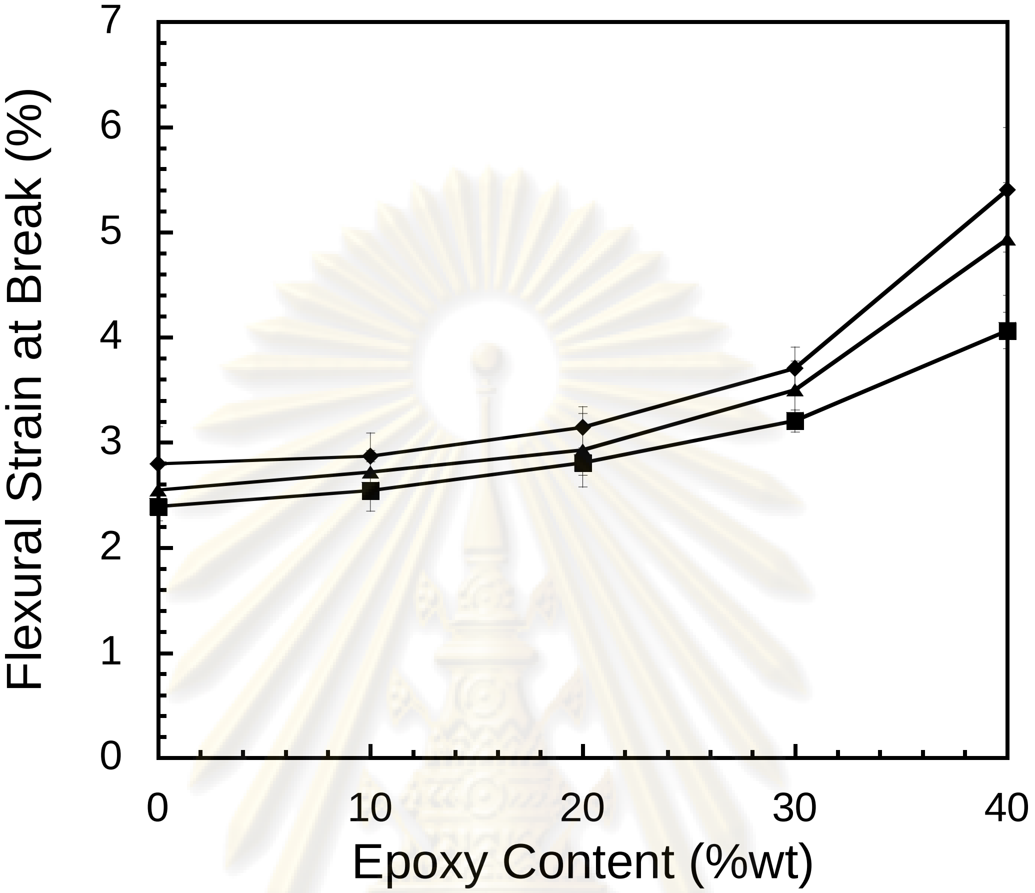

Figure 5.23 Flexural strain at break of arylamine-based polybenzoxazine/epoxy at various compositions: (■) BA-a/Epoxy, (▲) BA-mt/Epoxy, and (♦) BA-35x/Epoxy.

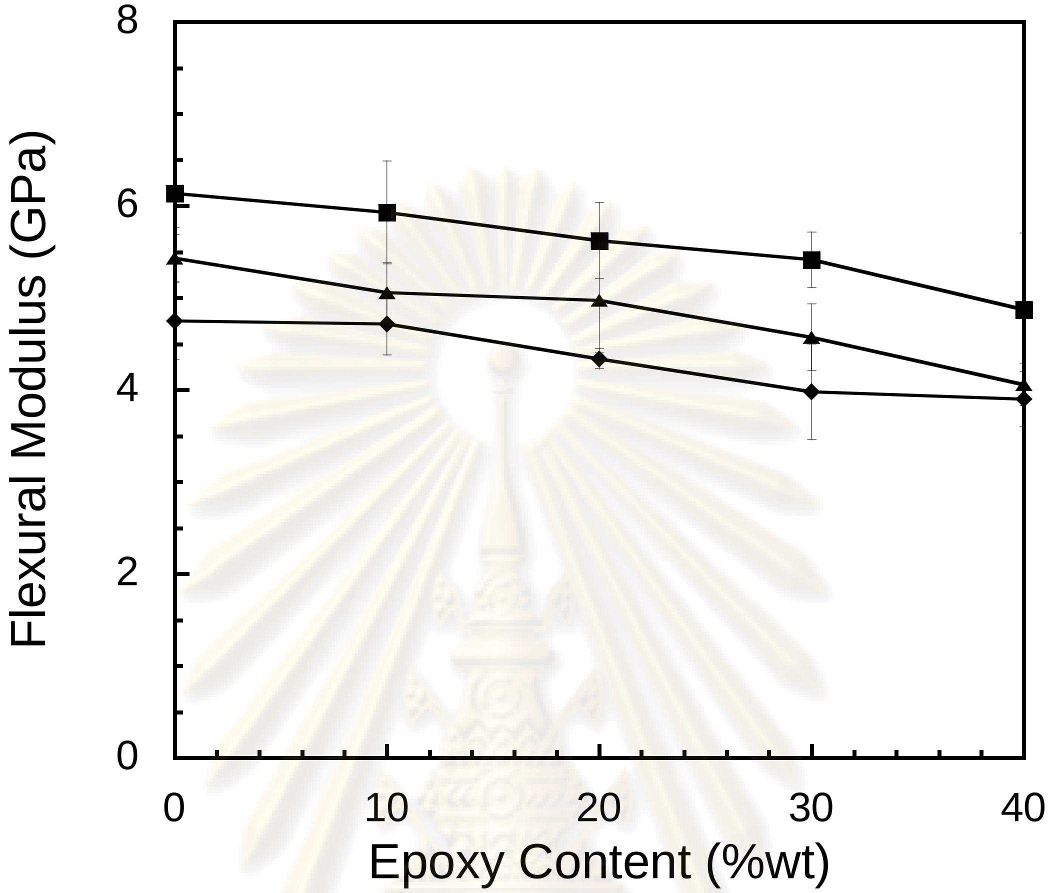

Figure 5.24 Flexural modulus of arylamine-based polybenzoxazine/epoxy at various compositions: (■) BA-a/Epoxy, (▲) BA-mt/Epoxy, and (♦) BA-35x/Epoxy.

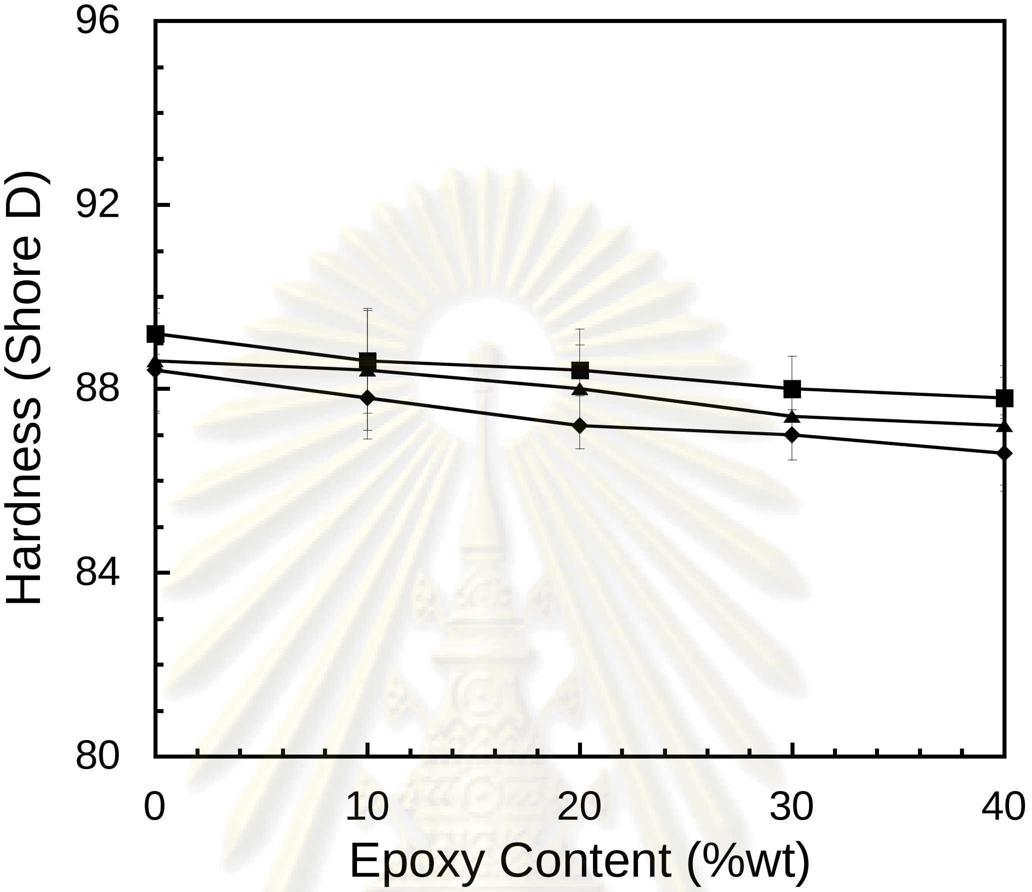

Figure 5.25 Hardness (shore D) of arylamine-based polybenzoxazine/epoxy at various compositions: (■) BA-a/Epoxy, (▲) BA-mt/Epoxy, and (♦) BA-35x/Epoxy.

CHAPTER VI

CONCLUSIONS

Effects of addition of epoxy resin into various arylamine-based benzoxazine resins, i.e. aniline, m-toluidine, and 3,5-xylidine systems, which designated as BA-a, BA-mt, and BA-35x, respectively, have been investigated. BA-a provided the widest processing window compared to BA-mt, and BA-35x which exhibited the narrowest one. Processing windows of BA-a, BA-mt, and BA-mt were found to be widened with the amount of the epoxy resin. Gel points of benzoxazine-epoxy resin mixtures can be well predicted by an Arrhenius equation e.g. the gel time of BA-35x alloyed with epoxy resin at composition 70:30 mass ratio can be estimated by $t_{gel}=0.7012\times10^{-7}\exp(10.563/T)$. Consequently, at higher temperature, the systems reached their gel points more quickly and the gel times were shorter.

The DSC experiment, a heat treatment at 150°C for 1 hour, 170°C for 1 hour, 190°C for 1 hour and 200°C for 4 hours was chosen as an optimum curing condition of all benzoxazine-epoxy polymer alloys due to the complete disappearance of an exotherm under their curing peak. From DMA experiment, T_g values obtained from the peaks of loss moduli of BA-a and BA-mt alloyed with epoxy resin were found to show a synergistic behavior with the maximum T_g's at the benzoxazine-epoxy composition of 80:20 mass ratio. However, in the BA-35x and epoxy binary mixture, the decreasing trend in T_g with an addition of epoxy resin was observed.

The coefficient of thermal expansion (CTE) of BA-35x was determined to be 47.3 ppm/°C which was the lowest CTE value among the three polybenzoxazines. The CTE of polybenzoxazine-epoxy alloys of all three binary systems from BA-35x, BA-mt, and BA-a, were increased with increasing amount of the epoxy due to the presence of the lower CTE epoxy fraction. Furthermore, in benzoxazine-epoxy polymer alloys based on m-toluidine, the degradation temperature at 5% weight loss (T_d) was found to show the highest among the three polybenzoxazine-epoxy alloys.

Lastly, flexural strength and flexural strain-at-break of all three binary systems were found to increase with increasing amount of the epoxy, meanwhile, the flexural modulus of all alloys was found to decrease with increasing the amount of the epoxy following the additivity rule. Whereas the Shore D hardness of the neat BA-a polybenzoxazine exhibited the highest value among the three types of polybenzoxazines.

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APPENDICES

APPENDIX A

Arylamine-based Benzoxazine Resins and Epoxy Resin Characterization

Appendix A-1 Liquefying and gel temperature at 500 Pa.s of arylamine-based benzoxazine resins mixed with epoxy resin.

Benzoxazine:Epoxy	BA-a		BA-mt		BA-35x	
	Liquefying (^{o}C)	Gel (^{o}C)	Liquefying (^{o}C)	Gel (^{o}C)	Liquefying (^{o}C)	Gel (^{o}C)
100:0	76	187	78	180	88	178
90:10	70	196	72	189	85	190
80:20	64	206	64	190	81	195
70:30	60	210	60	194	68	200
60:40	48	212	51	201	55	206

Appendix A-2 The kinetic parameter of Arrhenius equation at the gel points of arylamine-based benzoxazine resins mixed with epoxy resin at composition of 70:30.

Benzoxazine:Epoxy (70:30)	A	ΔE
BA-a/Epoxy	3.7214×10^{-7}	10.169
BA-mt/Epoxy	1.2387×10^{-7}	10.289
BA-35x/Epoxy	0.7012×10^{-7}	10.563

Appendix A-3 Curing temperature of the neat arylamine-based benzoxazine resins.

Benzoxazine resin	Curing temperature (°C)	
	Major	Minor
BA-a	230	-
BA-mt	216	235
BA-35x	208	240

Appendix A-4 The major of the curing temperatures of BA-35x/Epoxy mixtures.

BA-35x/Epoxy	Major of the curing temperature (°C)
100:0	208
90:10	215
80:20	221
70:30	227
60:40	235

APPENDIX B

Characterization of Arylamine-based Polybenzoxazine and Epoxy Alloys

Appendix B-1 The density of arylamine-based polybenzoxazine and epoxy alloys.

Benzoxazine:Epoxy	Density (g/cm^3)		
	BA-a	BA-mt	BA-35x
100:0	1.191	1.157	1.127
90:10	1.189	1.160	1.133
80:20	1.187	1.164	1.139
70:30	1.185	1.166	1.143
60:40	1.184	1.168	1.148

Appendix B-2 Glass transition temperature (T_g) and storage modulus at room temperature (E') of arylamine-based polybenzoxazine and epoxy alloys.

Benzoxazine:Epoxy	BA-a		BA-mt		BA-35x	
	T_g (°C)	E'(GPa)	T_g (°C)	E'(GPa)	T_g (°C)	E'(GPa)
100:0	172	5.94	210	5.32	241	4.98
90:10	178	5.60	212	5.09	238	4.60
80:20	182	5.28	213	4.86	235	4.30
70:30	180	4.97	209	4.50	230	4.12
60:40	174	4.76	207	4.43	223	3.81

Appendix B-3 Coefficient of thermal expansion of arylamine-based polybenzoxazine and epoxy alloys.

Benzoxazine:Epoxy	Coefficient of thermal expansion (ppm/°C)		
	BA-a	BA-mt	BA-35x
100:0	57.87	49.49	47.28
90:10	60.88	55.39	52.54
80:20	61.77	56.71	55.59
70:30	66.29	64.49	62.16
60:40	70.29	68.56	63.90

Appendix B-4 Degradation temperatures (T_d) at 5% weight loss and residue weights (char yield) at 800°C of arylamine-based polybenzoxazine and epoxy alloys.

Benzoxazine:Epoxy	BA-a		BA-mt		BA-35x	
	T_d(°C)	Char(%)	T_d(°C)	Char(%)	T_d(°C)	Char(%)
100:0	329	29.0	359	31.0	358	30.1
90:10	340	28.6	358	30.3	353	29.6
80:20	345	28.0	357	29.7	352	28.8
70:30	346	27.6	357	27.6	352	27.1
60:40	350	27.1	363	27.0	357	26.1

Appendix B-5 Flexural strength of arylamine-based polybenzoxazine and epoxy alloys.

Benzoxazine:Epoxy	Flexural strength (MPa)		
	BA-a	BA-mt	BA-35x
100:0	141	129	112
90:10	152	137	117
80:20	158	139	125
70:30	162	153	130
60:40	182	161	155

Appendix B-6 Flexural strain at break of arylamine-based polybenzoxazine and epoxy alloys.

Benzoxazine:Epoxy	Flexural strain at break (%)		
	BA-a	BA-mt	BA-35x
100:0	2.39	2.55	2.80
90:10	2.54	2.72	2.87
80:20	2.80	2.93	3.14
70:30	3.21	3.50	3.71
60:40	4.06	4.93	5.40

Appendix B-7 Flexural modulus of arylamine-based polybenzoxazine and epoxy alloys.

Benzoxazine:Epoxy	Flexural modulus (GPa)		
	BA-a	BA-mt	BA-35x
100:0	6.13	5.43	4.75
90:10	5.93	5.06	4.72
80:20	5.62	4.97	4.34
70:30	5.42	4.57	3.98
60:40	4.87	4.06	3.90

Appendix B-8 Hardness (shore D) of arylamine-based polybenzoxazine and epoxy alloys.

Benzoxazine:Epoxy	Hardness (shore D)		
	BA-a	BA-mt	BA-35x
100:0	89.2	88.6	88.4
90:10	88.6	88.4	87.8
80:20	88.4	88.0	87.2
70:30	88.0	87.4	87.0
60:40	87.8	87.2	86.6

VITAE

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