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รายงานการวิจัย

ผลของสารหน่วงการติดไฟชนิดไตรฟีนิลฟอสเฟตที่มีต่อสมบัติของพอลิเบนซอกซาซีน

EFFECT OF TRIPHENYLPHOSPHATE FLAME RETARDANT ON
PROPERTIES OF POLYBENZOXAZINES

คณะผู้วิจัย

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บทคัดย่อ

เพื่อเพิ่มความสามารถในการทนการติดไฟของพอลิเบนซอซซาลีน สารประกอบที่ไม่มีธาตุฮาโลเจนประเภทที่มีฟอสฟอรัสเป็นองค์ประกอบจะถูกนำมาทดสอบประสิทธิภาพในการหน่วงการติดไฟ งานวิจัยนี้พอลิเบนซอซซาลีนที่มีสมบัติทนการติดไฟ ถูกเตรียมโดยการผสมสารหน่วงการติดไฟประเภทที่มีฟอสฟอรัสเป็นองค์ประกอบลงในเบนซอซซาลีนเรซินที่มีกลุ่มของแอริลเอมีนที่แตกต่างกันเป็นองค์ประกอบ สมบัติทางด้านการทนไฟ ความร้อนและทางกลถูกทำการทดสอบ อัตราส่วนโดยน้ำหนักของเบนซอซซาลีนจะถูกทำการปรับเปลี่ยนเพื่อมีองค์ประกอบของธาตุฟอสฟอรัสที่แตกต่างกัน จากผล DSC แสดงให้เห็นว่า TPP ทำให้อุณหภูมิเริ่มต้นและอุณหภูมิ ณ จุดสูงสุดของพีคการคายความร้อนของการเกิดการเชื่อมโยงของเบนซอซซาลีนเรซินลดลง จากผลของ TGA อุณหภูมิการสลายตัวทางความร้อนของมวลที่สูญเสียไป 5% ของพอลิเบนซอซซาลีนมีค่าลดลงพอลิเบนซอซซาลีนทุกชนิดมีปริมาณเถ้าสูงขึ้นเมื่อปริมาณของ TPP เพิ่มมากขึ้น ซึ่งนับเป็นอีกตัวแปรหนึ่งที่บ่งบอกได้ว่าพอลิเบนซอซซาลีนจะสามารถทนการติดไฟได้มากขึ้น การทนการติดไฟของเทอร์โมเซตเหล่านี้สามารถตรวจสอบได้โดย limiting oxygen index (LOI) และมาตรฐานการทดสอบ UL-94 เมาในแนวตั้ง การเติม TPP 10% โดยน้ำหนัก ค่า LOI จะเพิ่มขึ้นจาก 23.5, 23, 22 เป็น 26, 25, 24 สำหรับ BA-a, BA-mt และ BA35x ตามลำดับ นอกจากนี้พบว่าความสามารถในการติดไฟเรียงตามลำดับ คือ BA-a < BA-mt < BA-35x วัสดุจะสามารถผ่านการทนการติดไฟระดับสูงสุด คือ V-0 เมื่อมีการเติม TPP ที่ ร้อยละ 2 โดยน้ำหนักสำหรับ BA-mt และ ร้อยละ 5 โดยน้ำหนัก สำหรับ BA-a และ BA-35x ซึ่ง TPP เป็นสาเหตุที่ทำให้เกิดการเพิ่มขึ้นของการทนการติดไฟของพอลิเบนซอซซาลีนทั้งสามชนิดถึงแม้ว่าจะมีการเติม TPP ในปริมาณน้อย นอกจากนั้นยังพบว่าความแข็งแรงและมอดูลัสภายใต้แรงดัดโค้งของพอลิเบนซอซซาลีนลดลงเมื่อมีการเติม TPP สุดท้ายยังเห็นได้ว่าค่าอุณหภูมิการเปลี่ยนสถานะคล้ายแก้วของ BA-a, BA-mt และ BA-35x ลดลงเมื่อเติม TPP มากขึ้นทั้งนี้อาจเป็นผลของความเป็นสารเสริมสภาพพลาสติกของ TPP

ABSTRACT

To enhance flame retardancy of polybenzoxazines, non-halogenated phosphorus compound has been evaluated for its potential flame retardant. In this research, the resulting flame retardated polybenzoxazines were prepared by mixing phosphorus flame retardant with three types of arylamine-based benzoxazine resins. Their fire resistance, thermal, and mechanical properties were investigated. The weight ratios of benzoxazine resins/TPP were varied to different phosphorus content. DSC results indicated that, in the presence of TPP, the onset and maximum temperature of the exothermic peak due to the ring opening polymerization of benzoxazine resins shifted to lower temperature. From TGA results, The degradation temperatures at 5% weight loss of polybenzoxazines were reduced. All polybenzoxazines possessed relatively high char yield, which increased as the TPP content increased. This implied that their flame retardancy could be enhanced. The flame-retardancy of these thermosets was evaluated by limiting oxygen index (LOI) and UL-94 vertical tests. Upon adding 10 wt% of TPP, LOI increased from 23.5, 23, 22 to 26, 25, 24 for BA-a, BA-mt, and BA35x, respectively. Furthermore, the flammability was found to be in an order of BA-a < BA-mt < BA-35x. The maximum flame retardancy of V-0 class specimens were obtained when adding TPP at 2 wt% for BA-mt and 5 wt% for BA-a and BA-35x. That is TPP contributes to the enhancement of flame retardancy of polybenzoxazines even at a relatively low amount of the TPP. Additionally, it was found that flexural strength and flexural modulus of those polybenzoxazines decreased with an addition of TPP. Finally, the reduction of T_g of BA-a, BA-mt, and BA-35x with increasing of TPP were also observed possibly from the plasticizing effect of the TPP additive.

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CHAPTER I

INTRODUCTION

1.1 General Introduction

Phenolic resins are a large family of polymers, consisting of a wide variety of structures based on the reaction products of phenols with formaldehyde. The traditional phenolic polymers have advantages including heat resistance, flame retardance, dielectric insulation properties thus they are employed in a wide range of applications. Nevertheless, they also have disadvantages. For example, they are brittle; and use acid or base catalysts upon curing; they release by-products during curing which sometimes affect the properties of materials because of voids formation problem [1, 2].

Benzoxazines, a new type of phenolic resins, were developed to overcome the shortcomings of traditional phenolic while retaining their benefits. Benzoxazine resins can be easily synthesized from phenol, formaldehyde and amine by employing solution or solventless methods [3]. The polymerization of benzoxazine resins proceeds via ring-opening of oxazine rings by thermal cure. In addition, they do not require catalysts for polymerization and do not produce by-product upon curing. Polybenzoxazines exhibit the characteristics that found in traditional phenolic such as heat resistance, flame retardance, and good electrical insulation property. Besides, they also exhibit lots of unique characteristics including low melt viscosity, dimensional stability, excellent mechanical properties, as well as low water absorption [4]. Because of these properties, they become one important class of thermosetting resins in various applications such as electronic, aerospace, aircraft and adhesives.

Notwithstanding, there have been attempts to enhance the performance of polybenzoxazines. Those approaches for improving their performance can be classified into several ways: (i) synthesis of benzoxazine monomers with additional functionality, (ii) incorporation of benzoxazine in polymer chain, and (iii) benzoxazine based composites or alloys. According to Ishida and Sanders., 2000 [5], thermal properties of

polybenzoxazines can be improved by varying amine groups. In their work, a series of benzoxazine resins was synthesized from bisphenol A, paraformaldehyde and various types of arylamine groups e.g. aniline, m-toluidine, 3,5-xylydine. The glass transition temperature (T_g) of 3,5-xylydine based benzoxazine as high as 243°C was obtained which was higher than m-toluidine and aniline based benzoxazines i.e. about 209°C and 168°C, respectively.

Although benzoxazines have high flame retardant properties, it is not enough for some applications, in which a UL-94 V-0 grade and high LOI value is required [6]. To improve the flame retardance, halogenated compounds are widely included into the formulation as flame retardants. However, these compounds produce environment problems because toxic combustion products are released during combustion. Because of concern about environment, non-halogenated based flame retardants become increasingly popular to replace halogenated flame retardants. Among non-halogenated based flame retardants, phosphorus containing compounds are frequently used as flame retardants owing to their low generation of smoke and toxic gases. They work very effectively in condensed phase by formation of char which is difficult to ignite. Char inhibits gaseous products from diffusing to the pyrolysis zone and protects the polymer surface from heat and air [7, 8]. Generally, phosphorus compounds are found to be significantly more effective in oxygen or nitrogen groups containing polymers. It is thus important to have oxygen or nitrogen atoms in the polymer chain. If the polymer cannot contribute to charring because of the absence of suitable reactive groups, a highly charring co-additive has to be introduced in combination with the phosphorus compound [9].

From the work of Sponton, M. et al [10], they reported that incorporating phosphorus can improve fire resistant properties. In their research, copolymerisation of aniline based benzoxazine (BA-a) with different phosphorus content by varying molar ratios of phosphorus containing glycidyls (Gly-P) were prepared. It was observed that the presence of phosphorus significantly increased the LOI values of the resulting polymers even when the phosphorus content was only 1.7%. Therefore, incorporation of phosphorus compound into benzoxazine resins was believed to increase the char yield and thus fire resistance of polybenzoxazines.

In this study, triphenyl phosphate flame retardant (TPP) will be incorporated in the aniline based benzoxazine (BA-a), m-toluidine based benzoxazine (BA-mt), and 3,5-xylylidine based benzoxazine (BA-35x). The samples will also be characterized by DSC, DMA, FTIR, flexural test, TGA, LOI test, UL-94 test.

1.2 Objectives

1. To study effects of types of arylamines on the obtained flammability of the obtained polybenzoxazines (BA-a, BA-mt, BA-35x).
2. To find suitable amount of triphenylphosphate flame retardant in benzoxazine resins to achieve UL94 V-0.
3. To examine mechanical and thermal properties of the resulting flame retarded polybenzoxazines.

1.3 Scopes of Research

1. Synthesize benzoxazine resins from different arylamines (aniline, m-toluidine, 3,5-xylylidine) by a solventless method.
2. Combine triphenylphosphate flame retardant with benzoxazine resins at various contents of the flame retardant at 0, 2, 5, 8, 10% by weight.
3. Study functional groups by Fourier Transform Infrared Spectroscopy (FTIR).
4. Find curing condition by Differential Scanning Calorimeter (DSC).
5. Examine fire resistant properties.
 - Underwriter's Laboratory Flammability Vertical Test (UL94).
 - Limiting Oxygen Index (LOI).
6. Investigate thermal and mechanical properties.
 - Differential Scanning Calorimeter (DSC).
 - Dynamic Mechanical Analyzer (DMA).
 - Thermal Gravimetric Analyzer (TGA).
 - Universal Testing Machine (INSTRON: Flexural Test).

CHAPTER II

THEORY

2.1 Benzoxazine Resins

Benzoxazine resins are a new type of phenolic resins that are obtained from reaction of phenols, formaldehyde and amines. Polybenzoxazine overcomes many shortcomings of traditional phenolic resins i.e. use of acid or base catalyst and release of condensation by-products while retaining good thermal properties and flame retardancy of phenolic resins [10].

The chemistry of benzoxazine offers a wide range of molecular design flexibility by using appropriate starting materials. Various types of benzoxazine resins can be synthesized using various phenols and amines with different substitution groups attached. These substituting groups can provide additional polymerizable sites and also affect the curing process and properties. [3]. Benzoxazine resins can be classified in 2 major categories as shown in Figure 2.1 and 2.2, respectively.

(1) Monofunctional benzoxazine monomer.

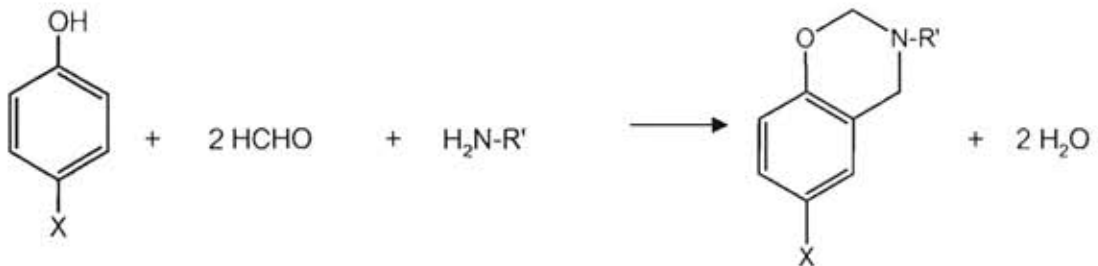


Figure 2.1 Synthesis of monofunctional benzoxazine monomer [11].

Where X and R' are substitution group

R' includes a group such as CH₃, C₂H₅, and benzene

(2) Bifunctional benzoxazine monomer.

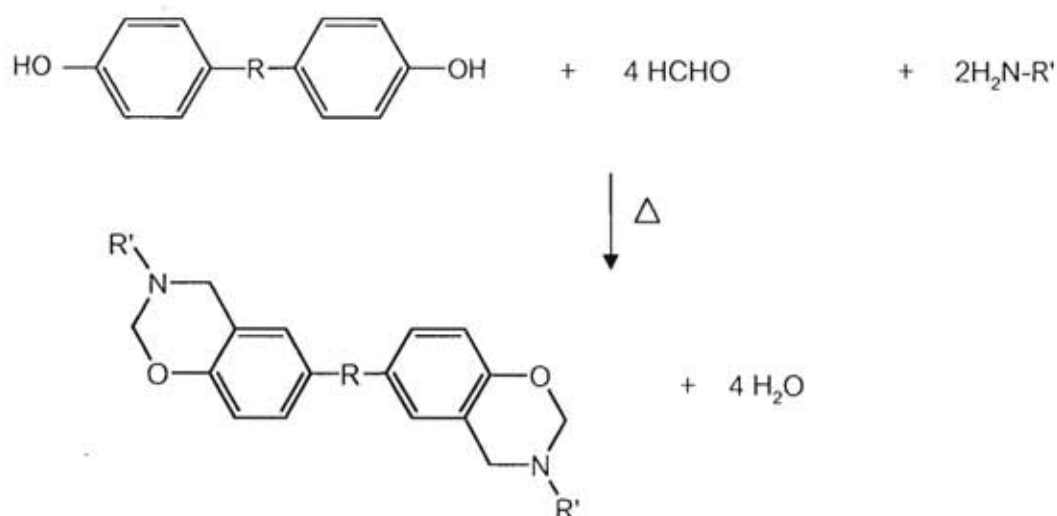


Figure 2.2 Synthesis of bifunctional benzoxazine monomer [11].

Where R' is substitution groups such as CH₃, C₂H₅, and benzene

R is a group such as O, CH₂, C(CH₃)₂, C(CF₃)₂, S, S=O, SO₂.

Benzoxazine resins can be self-polymerized by heating which induces ring-opening reaction to form a phenolic structure as characterized by a Mannich-based bridge (-CH₂-NR-CH₂-) [12] and without using any catalyst. The resins generates no by-products, or volatiles, during crosslinking reaction and thus offers an excellent dimensional stability for the final product. The ring opening mechanism occurs by breaking of a C-O bond of the oxazine ring at temperature in the range between 160°C and 220°C as shown in Figure 2.3 [13].

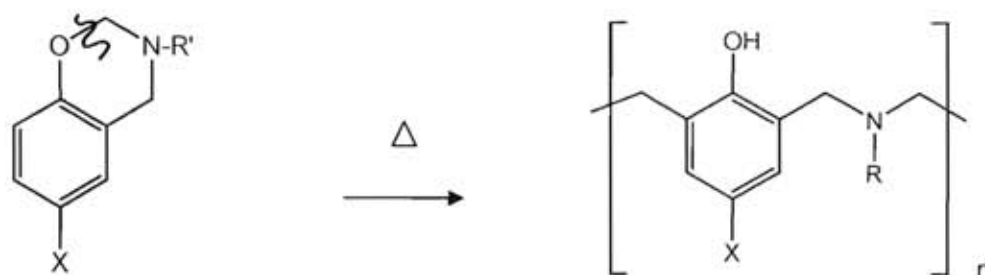


Figure 2.3 Polymerization of monofunctional benzoxazine monomer.

Polybenzoxazines offer good thermal stability which is possibly due to the stabilization of the Mannich bridges by the very strong intramolecular hydrogen bonding between the phenolic OH groups and the nitrogen atom of the Mannich bridge [11]. In addition, polybenzoxazines exhibit other outstanding performances including:

- Dimensional stability due to near-zero volumetric shrinkage upon cure.
- Low water absorption
- Low dielectric constant
- High temperature resistance
- Flame retardance

In this research, a series of benzoxazine resins are synthesized from varying types of arylamines as shown in Figure 2.4. Benzoxazine resins are synthesized from bisphenol A, paraformaldehyde and three types of amines.

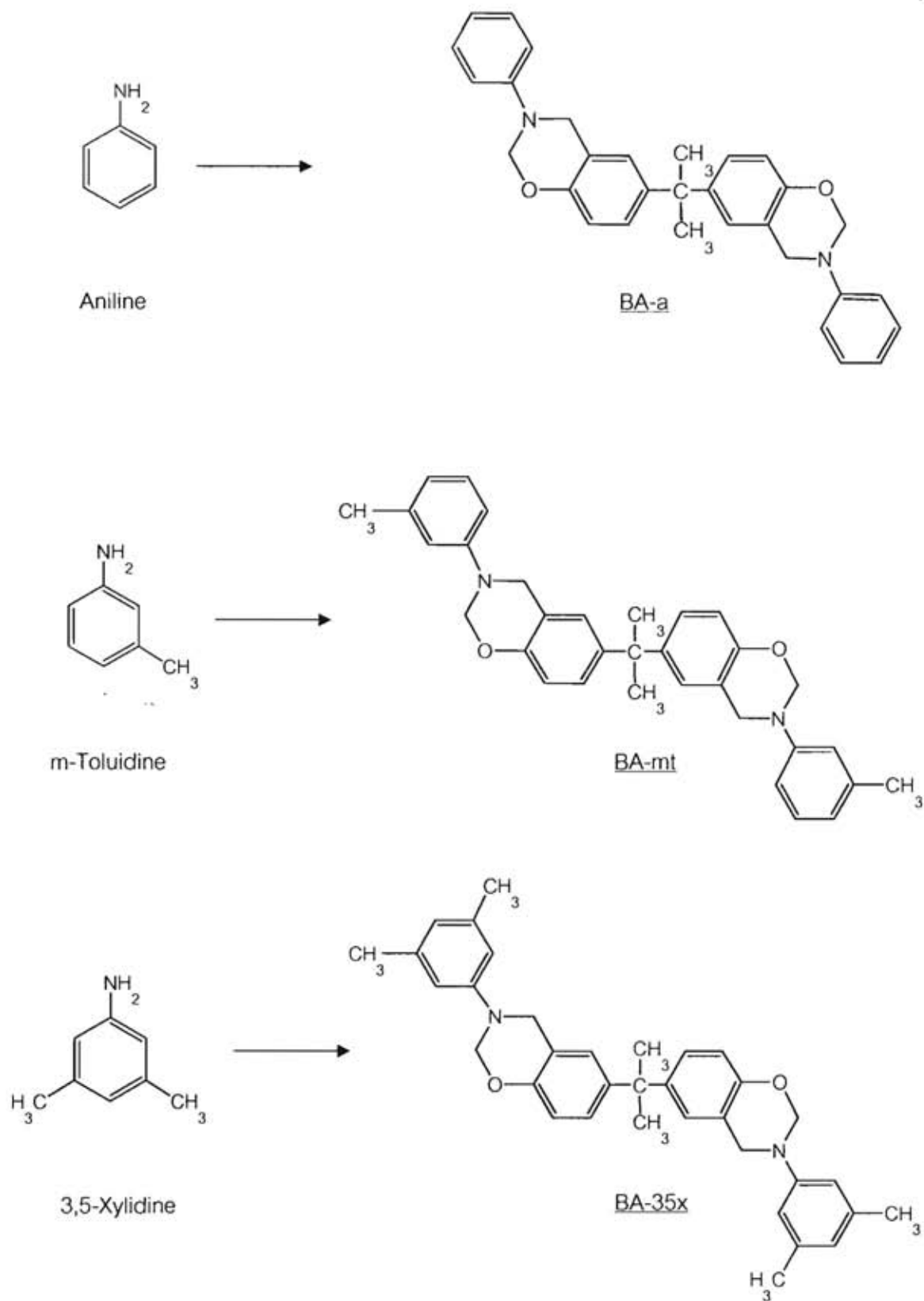


Figure 2.4 A series of benzoxazine resins from varying types of amines [12].

Table 2.1 Properties of three types of arylamines -based benzoxazine resins [11].

Properties	BA-a	BA-mt	BA-35x
T_g , DSC ($^{\circ}\text{C}$)	170	210	245
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)	1.1×10^{-3}	1.9×10^{-3}	2.6×10^{-3}
Temperature 5% Weight Loss ($^{\circ}\text{C}$)	315	350	350
Char yield (% at 800°C)	30	31	28

2.2 Combustion of Polymer

The fire triangle, depicted in Figure 2.5, illustrates the three components required for the fire: fuel, air and heat are necessary. These three components combined together in the proper ratio lead to fuel ignition and combustion.

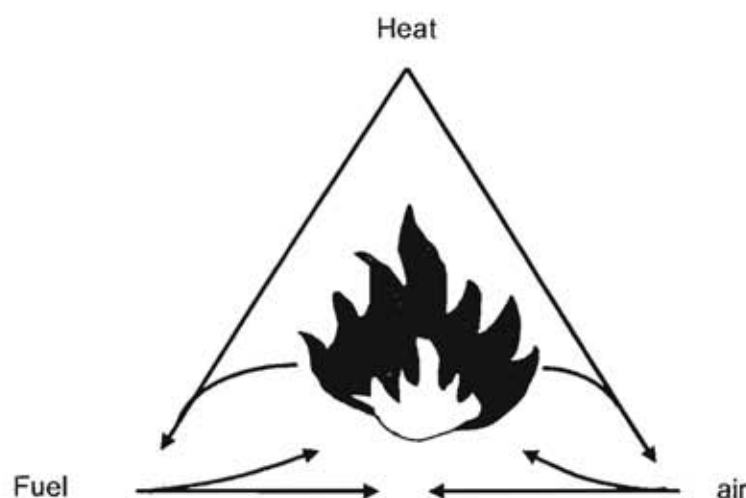


Figure 2.5 Fire triangle - three components required for a fire [16].

As illustrated in Figure 2.6, combustion is initiated by heating a plastic material to its decomposition point. Decomposition is an endothermic process which breaks the chemical bonds. The volatile fraction of the resulting polymer fragments diffuses into the

air and creates a combustible gaseous mixture. This gaseous mixture ignites when the auto-ignition temperature (defined as the temperature at which the activation energy of the combustion reaction is attained) is reached, liberating heat. Some of the heat is transferred back to the surface of the polymer (fuel), maintaining the flow of flammable volatile degradation products [9, 14].

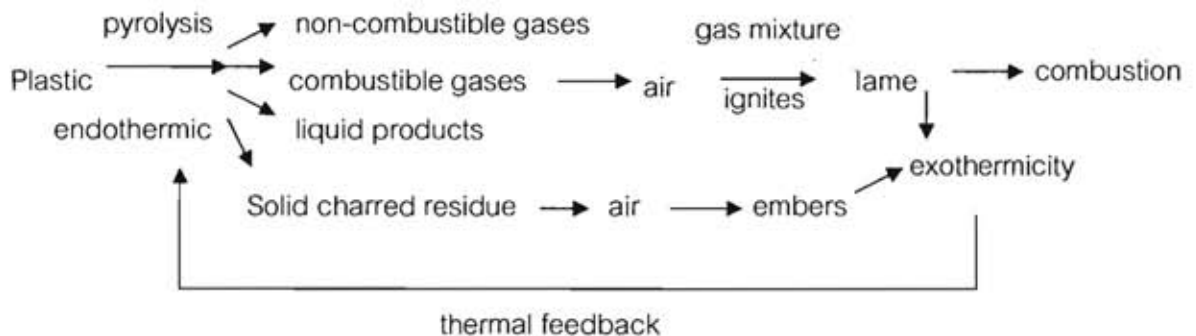
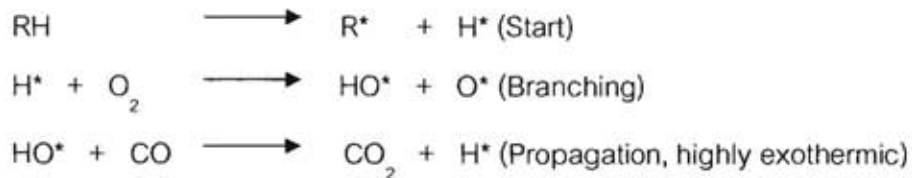


Figure 2.6 Combustion process [14].

2.3 Flame Retardants

Flame retardants are chemicals which are added to combustible materials to increase resistance to ignition, reduce flame spread, suppress smoke formation, and prevent a polymer from dripping. The primary goal is to delay the ignition and burning of materials and allow people more time to escape the affected area. A secondary consideration is to limit property damage. Flame retardants work by interfering with one or more of three components of fire, either physically or chemically [15].

2.3.1 Mode of Action

A flame retardant should inhibit or even suppress the combustion process. Depending on their nature, flame retardants can act chemically and/or physically in the solid, liquid or gas phase. The various ways in which flame retardants are described below [9, 14].

- **Physical Action** There are several ways in which the combustion process can be retarded by physical action:

By Cooling: The additive can degrade endothermally which cools the substrate to a temperature below that required for sustaining the combustion temperature.

By Formation of Protective Layer: the condensed combustion layer can be shielded from the gaseous phase with a solid or gaseous protective layer. The condensed phase is thus cool, smaller quantities of pyrolysis gases are evolved, the oxygen necessary to the combustion process is excluded and heat transfer is impeded.

By Dilution: The inert gases are generated by the additives (which evolve as inert gases on decomposition) dilutes the fuel in the solid and gaseous phase so that the lower ignition limit of the gas mixture is not reached.

- **Chemical Action** The most significant chemical reactions interfering with the combustion process take place in the solid and gas phases:

Reaction in Gas Phase: The radical mechanism of combustion which takes place in gas phase is interrupted by flame retardant. The exothermic reactions are stopped, The system cools down and the supply of flammable gases is reduced and eventually completely suppressed. (e.g. Halogenated flame retardants)

Reaction in Solid Phase: Flame retardants can cause a layer of carbon (charring) on the polymer's surface. This occurs, for example, through the dehydrating action of the flame retardant generating double bonds in the polymer. These processes form a carbonaceous layer via cyclizing and crosslinking processes cycle. (e.g. phosphorus compounds)

2.3.2 Types of Flame Retardants

A distinction is made between reactive and additive flame retardants. Reactive flame retardants are reactive components chemically built into a polymer molecule. Additive flame retardants are incorporated into the polymer either prior to, during or (most frequently) following polymerization [15].

There are three four main families of flame-retardant chemicals:

- Halogenated-containing flame retardants
- Phosphorus-containing flame retardants
- Nitrogen-containing flame retardants
- Inorganic flame retardants

In addition, there are several other types of flame retardant used in smaller quantities which are suitable for certain types of plastic such as silicon -containing flame retardants and stannates.

- Halogenated-containing Flame Retardants

The effectiveness of halogen-containing flame retardants increases in the order $F \ll Cl < Br < I$. Bromine and chlorine compounds are the only halogen compounds having commercial significance as flame-retardant chemicals. Fluorine compounds cannot become effective as a radical interceptor in the gas phase because of the C-F bond is too strong. Iodine compounds, although effective, are expensive and too unstable to be useful. The brominated flame retardants are much more numerous than the chlorinated types because of its weaker bonding to carbon enable it to interfere at a more favourable point in the combustion process [14, 16].

Halogen-containing flame retardants act by interfering with radical chain mechanism taking place in the gas phase. The exothermic processes, which occur in the flame, are thus stopped, the system cools down, the supply of flammable gases is reduced and eventually completely suppressed. The high-reactive radicals HO^* and H^*

can react in the gas phase with other radicals, such as halogenated radicals X^* resulted from flame retardant degradation as shown in Figure 2.7. Less reactive radicals which decrease the kinetics of the combustion are created.

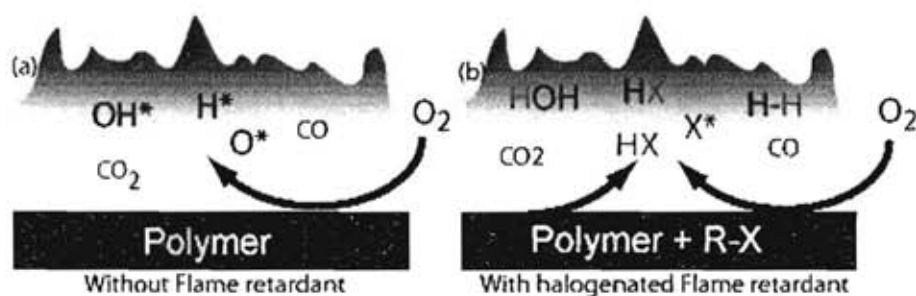
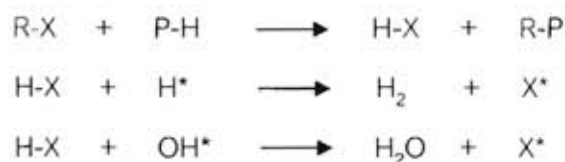


Figure 2.7 Mechanism of action of halogenated flame retardants [16].

- Phosphorus-containing Flame Retardants

Phosphorus-containing flame retardants are effective in thermoset resins and mainly influence the reactions taking place in the condensed phase/or vapor phase or sometimes in both phases.

The most important phosphorus-containing flame retardants are:

- Phosphate esters
- Phosphonates and phosphinates
- Red phosphorus and ammonium polyphosphate

In the condensed phase, the phosphorus-based flame retardants are particularly effective in oxygen- or nitrogen-containing polymers. With most of them, thermal decomposition leads to the production of phosphoric acid, which condenses readily to produce pyrophosphate structures and liberate water. The water released dilutes the

oxidizing gas phase. In addition, phosphoric acid and pyrophosphoric acid can act as dehydrating agents, altering the thermal degradation of the polymer, and promoting the formation of char. This char (carbonized layer) isolates and protects the polymer from the flames and:

- limits the volatilization of fuel and prevents the formation of new free radicals;
- limits oxygen diffusion, which reduces combustion;
- insulates the polymer underneath from the heat.

Phosphorus-based flame retardants can also volatilize into the gas phase, to form active radicals (PO_2^* , PO^* and HPO^*), and act with H^* and OH^* radicals which terminates the highly active flame propagating radicals (H^* and OH^*). Volatile phosphorated compounds are among the most effective combustion inhibitors since phosphorus-based radicals are, on average, five times more effective than bromine and 10 times more effective than chlorine radicals [9].

In this research, we use arylphosphate as flame retardant. Structure and properties of arylphosphate are shown in Figure 2.8 and Table 2.2, respectively.

Triphenylphosphate (TPP)

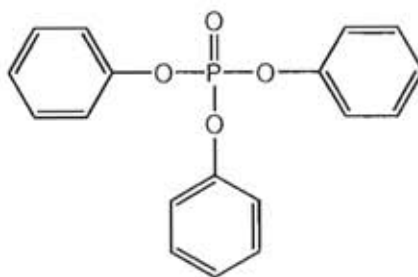


Figure 2.8 Structure of triphenylphosphate flame retardant.

Table 2.2 Properties of triphenylphosphate flame retardant [17].

Properties	TPP
Chemical name	Triphenyl Phosphate
Appearance	Solid
Phosphorus content (%)	9.5
Density at 25°C (g/cm ³)	-
Viscosity at 25°C (mPa.s)	Melting point 49°C

Triphenylphosphate is used as;

- Flame-retardant in many plastics and reins especially in phenolic resin for the manufacture of electrical and automobile parts.
 - Non-flammable plasticizer or additive in cellulose for photographic films, polyester and polyurethane.
 - Non-combustible substitute for camphor in celluloid for fireproof.
 - Plasticizer in lacquers and varnishes, vinyl automotive upholstery and in cellulose acetate articles.
- **Nitrogen-containing Flame Retardants**

Melamine, melamine cyanurate, other melamine salts and guanidine compounds are currently the most used group of nitrogen-containing flame retardants. Nitrogen based compounds work differently and have an effect both in the gas phase (by releasing non flammable nitrogen, which dilutes the oxygen content) and condensed phase, especially when combined with phosphorus compounds, helping the formation of a more stable, cross-linked char.

- Inorganic Flame Retardants

Aluminum hydroxide

Currently this is the most widely used flame retardant. It is low cost and easy to incorporate in plastics. Aluminum hydroxide starts to break down in the temperature range of 180 to 200°C. Conversion to aluminum oxide takes place in an endothermic reaction. The flame retardant mechanism is based on the release of water which cools and dilutes the flame zone.

Magnesium hydroxide

Magnesium hydroxide acts in a similar way as aluminum hydroxide, but magnesium hydroxide has a higher decomposition temperature of 300°C.

Zinc borate

Boron containing compounds act through the endothermic, stepwise release of water and by the formation of a glassy coating protecting the substrate.

2.4. Flammability Testing

2.4.1 UL94

The UL94 series of flammability tests find widespread use in industry, particularly with regard to the testing of parts and materials used in electrical and electronics applications. The set of UL94 tests has been approved by the "Underwriters Laboratories" as tests of the flammability of plastic materials for parts in devices and appliances. The most common tests are the UL94HB test and UL94V tests. In terms of practice and usage, the most commonly used test is UL94 V for measuring the ignitability and flame-spread of vertical bulk materials exposed to a small flame. The Vertical Burning Test (UL 94V-0, UL 94V-1, UL 94V-2) is used mainly for encapsulants and the Horizontal Burning Test (UL 94HB) for coatings. The UL 94V-0 is the most flame retardant vertical burn rating.

UL94V is a more stringent flammability test than the UL94HB test. This vertical burn test has three performance categories. V-0 is the most severe requirement, while V2 is the least severe. Passing the UL 94V test with a V-0 rating requires efficient flame retardant performance, either from an inherently flame retardant material or from an additive package. The standard specifies that five specimens must be tested. The specimen is classified as V0, V1 or V2 according to the criteria listed in Table 2.3 [9, 18].

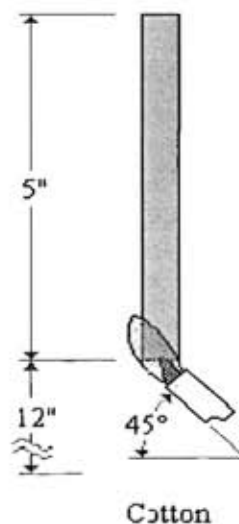


Figure 2.9 Vertical flame test [19].

Table 2.3 Classification of material for the UL94V flammability test [19].

Vertical Ratings	Requirements
V-0	<ul style="list-style-type: none"> • Specimens must not burn with flaming combustion for more than 10 seconds after either test flame application.
	<ul style="list-style-type: none"> • Total flaming combustion time must not exceed 50 seconds for each set of 5 specimens.
	<ul style="list-style-type: none"> • Specimens must not burn with flaming or glowing combustion up to the specimen holding clamp.
	<ul style="list-style-type: none"> • Specimens must not drip flaming particles that ignite the cotton.
	<ul style="list-style-type: none"> • No specimen can have glowing combustion remain for longer than 30 seconds after removal of the test flame.
V-1	<ul style="list-style-type: none"> • Specimens must not burn with flaming combustion for more than 30 seconds after either test flame application.
	<ul style="list-style-type: none"> • Total flaming combustion time must not exceed 250 seconds for each set of 5 specimens.
	<ul style="list-style-type: none"> • Specimens must not burn with flaming or glowing combustion up to the specimen holding clamp.
	<ul style="list-style-type: none"> • Specimens must not drip flaming particles that ignite the cotton.
	<ul style="list-style-type: none"> • No specimen can have glowing combustion remain for longer than 60 seconds after removal of the test flame.
V-2	<ul style="list-style-type: none"> • Specimens must not burn with flaming combustion for more than 30 seconds after either test flame application.
	<ul style="list-style-type: none"> • Total flaming combustion time must not exceed 250 seconds for each set of 5 specimens.
	<ul style="list-style-type: none"> • Specimens must not burn with flaming or glowing combustion up to the specimen holding clamp.

2.4.2 Limited Oxygen Index (LOI)

This test is used to indicate the relative flammability of materials [7]. The value of the LOI is defined as the minimal oxygen concentration $[O_2]$ in the oxygen/nitrogen mixture $[O_2/N_2]$ that will just support flaming combustion of a material initially at room temperature.

The LOI is expressed as:

$$LOI = \frac{[O_2]}{[O_2] + [N_2]} \times 100$$

As air contains 21% oxygen, materials with an LOI below 21 are classified as "combustible" whereas those with an LOI above 21 are classified as "self-extinguishing", because their combustion cannot be sustained at ambient temperature without an external energy contribution. The higher the LOI show the better the flame retardant property.

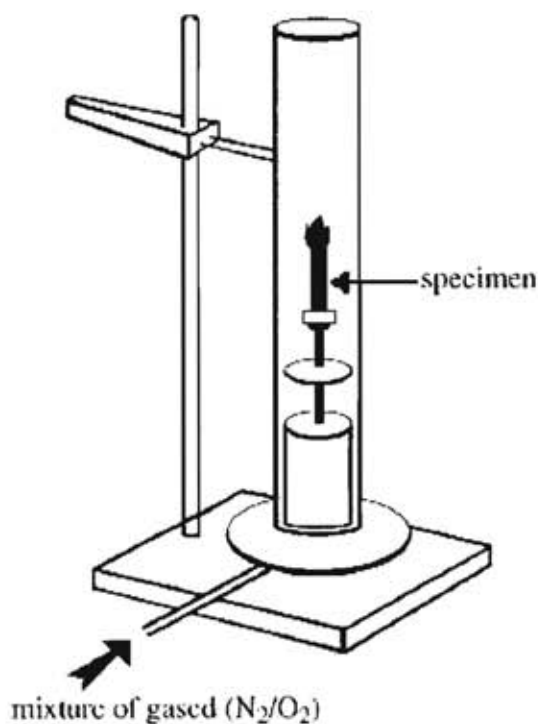


Figure 2.10 Experimental set-up for LOI measurement [9].

CHAPTER III

LITERATURE REVIEWS

The thermal and mechanical properties of effect of polybenzoxazines based on alkyl-substituted aromatic amines were examined by H. Ishida, Daniel P. Sanders, 2000 [5]. A series of benzoxazine resins have been synthesized that upon polymerization produce a varying amount of phenolic Mannich bridges, arylamine Mannich bridges, and methylene linkages. The network structures of *m*-toluidine based benzoxazine (BA-*mt*) and 3,5-xylidine based benzoxazine (BA-35x) contain increasing amounts of arylamine Mannich bridges and methylene linked structures in the network structure as shown in Figure 3.1 which give rise to significantly enhanced glass transition temperatures when prepared with aniline based benzoxazine (BA-*a*), being similar to the phenolic Mannich bridge network as can be seen in Figure 3.2. In addition, it can improve mechanical properties and including higher crosslink densities but no significant effect on the char yield. Properties of arylamine-based benzoxazine resins are shown in Table 2.1.

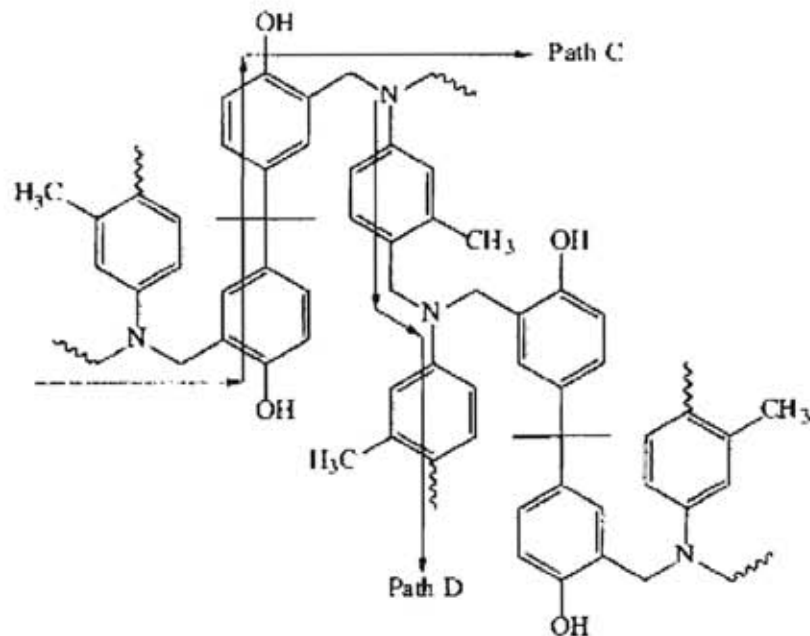


Figure 3.1 The arylamine Mannich bridge network formation

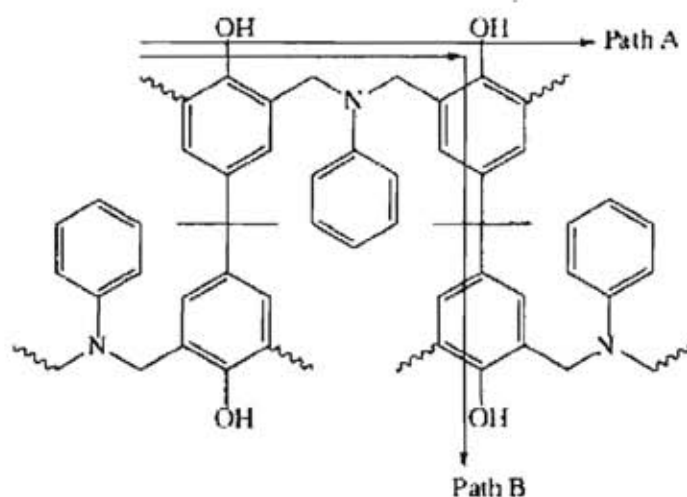
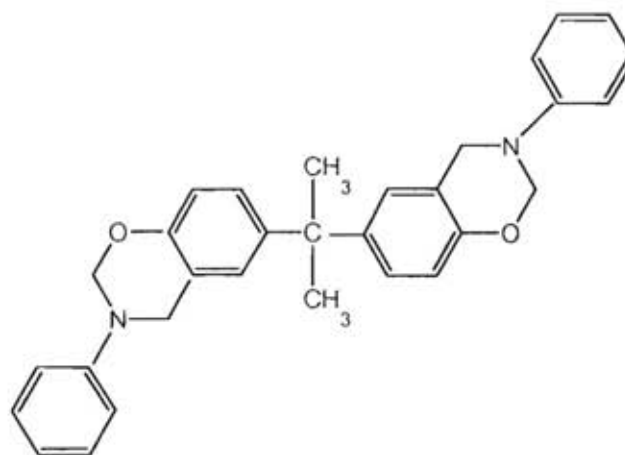
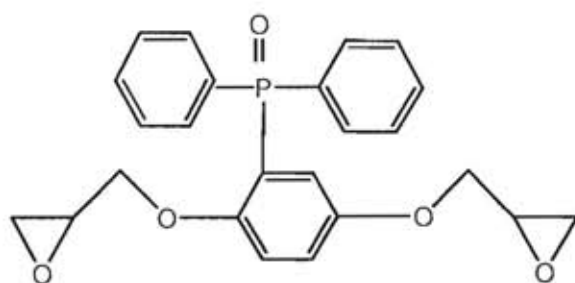


Figure 3.2 The phenolic Mannich bridge network formation.

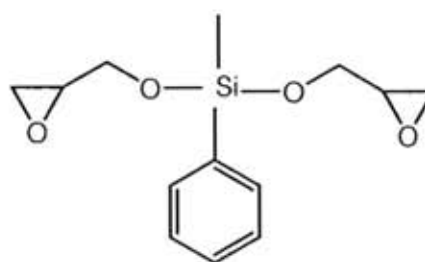
The copolymerisation of benzoxazine of bisphenol A and diglycidyl ether of (2,5-dihydroxyphenyl) diphenyl phosphine oxide were studied by Sponton, M. L. et al. 2009 [20]. Phosphorus- or silicon-containing benzoxazine-epoxy resins with different phosphorus or silicon contents were obtained from Gly-P or Gly-Si and Bz-BA. Table 3.1 summarises the T_g and LOI data. The T_g values of thermosets increased with the epoxy content for the phosphorus-containing benzoxazine-epoxy while the opposite trend was observed for the silicon-containing benzoxazine-epoxy. Moreover, Phosphorus-containing materials have outstanding LOI values, even when the phosphorus content is low, with the corresponding excellent flame retardant properties. In contrast, the presence of silicon in the studied percentages has no effect in the flame retardant behavior of silicon containing resins and their LOI values are similar to those of heteroatom-free resins.



BA-a



Gly-P



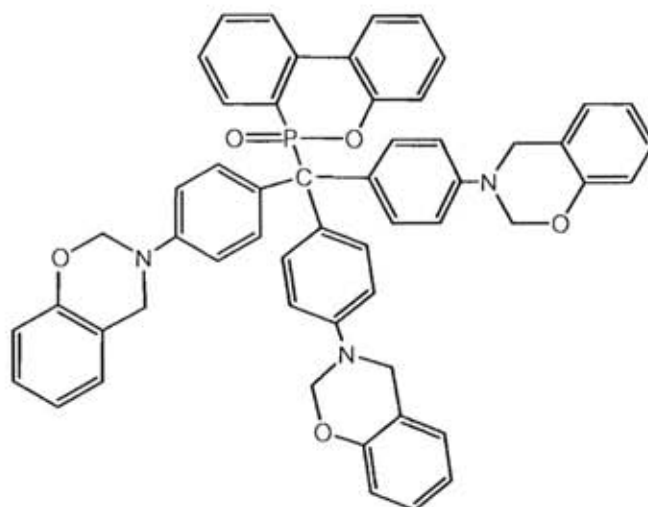
Gly-Si

Figure 3.3 The structures of BA-a, Gly-P and Gly-Si

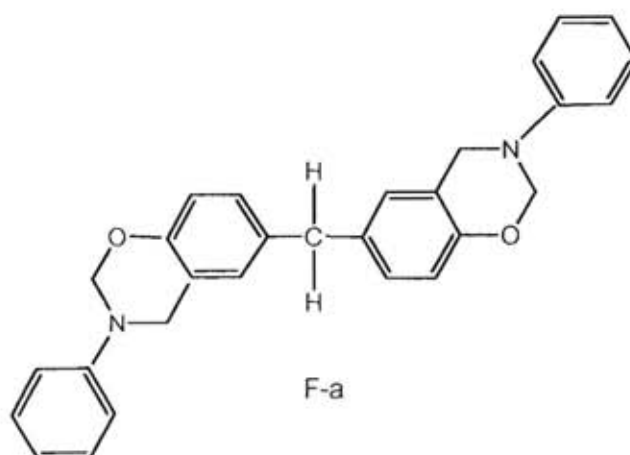
Table 3.1 Thermal properties and LOIs of the polymers.

Epoxy	epoxy/BA-a	P, %	Si, %	Tg(°C) Tan δ_{\max}	LOI, %O ₂ (V/V)
-	0:1	-	-	172	31.8
DGEBA	1:2	-	-	170	32.2
DGEBA	1:1	-	-	161	32.0
DGEBA	2:1	-	-	139	31.6
Gly-P	1:2	2.3	-	179	46.0
Gly-P	1:1	3.5	-	184	48.0
Gly-P	2:1	4.7	-	189	45.5
Gly-Si	1:2	-	2.3	147	32.0
Gly-Si	1:1	-	3.5	122	32.4
Gly-Si	2:1	-	4.7	88	31.9

The flame retardancy of polybenzoxazines were investigated by Chia W.C. et al, 2008 [6]. An aromatic triamine-based flame-retardant benzoxazine was prepared, and then copolymerized with an aromatic biphenol-based benzoxazine (bis(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl) methane, F-a) and an aromatic diamine-based benzoxazine (bis(4-(2H-benzo[e][1,3]oxazin-3(4H)-yl)phenyl)methane, P-d). The flame retardancy of copolybenzoxazines increased with the phosphorus content and UL-94 V-0 grade can be obtained with a phosphorus content of 1.81wt% and 1.08% for F and P-series copolymers, respectively, as shown in Table 3.2. It indicated that phosphorus can improve the fire resistant properties of polymer.



Aromatic triamine-based flame-retardant benzoxazine



F-a

Figure 3.4 The structures of aromatic triamine-based flame-retardant benzoxazine and F-a

Table 3.2 Thermal properties and UL94 data of the polymers.

Sample ID	Weight Ratio of AB/F-a, AB/P-d	P,%	UL-94 grade
F-a 100	0/100	0	Burning
F-a 90	10/90	0.36	V-2
F-a 70	30/70	1.08	V-1
F-a 50	50/50	1.81	V-0
P-a 100	0/100	0	V-2
P-a 90	10/90	0.36	V-1
P-a 70	30/70	1.08	V-0
P-a 50	50/50	1.81	V-0

AB = aromatic triamine-based flame-retardant benzoxazine

The curing and thermal behavior of bis(m-aminophenyl)methylphosphine oxide based benzoxazine and benzoxazine of bisphenol A have been studied by Sponton, M. L. et al., 2008 [21]. The molar ratio of benzoxazine monomers was varied with different phosphorus content. In the Bz-BAMPO/BZ-BA, it exhibited different curing behavior and shift of the main polymerization exotherm of BZ-BA to lower temperature as shown in Figure 3.2. Figure 3.3 showed the weight loss rate of Bz-BAMPO/BZ-BA in nitrogen. The decomposition temperature of phosphorus-free resin is lower than the phosphorus-containing resins. This behaviour is in accordance with the mechanism of improved fire performance via phosphorus modification.

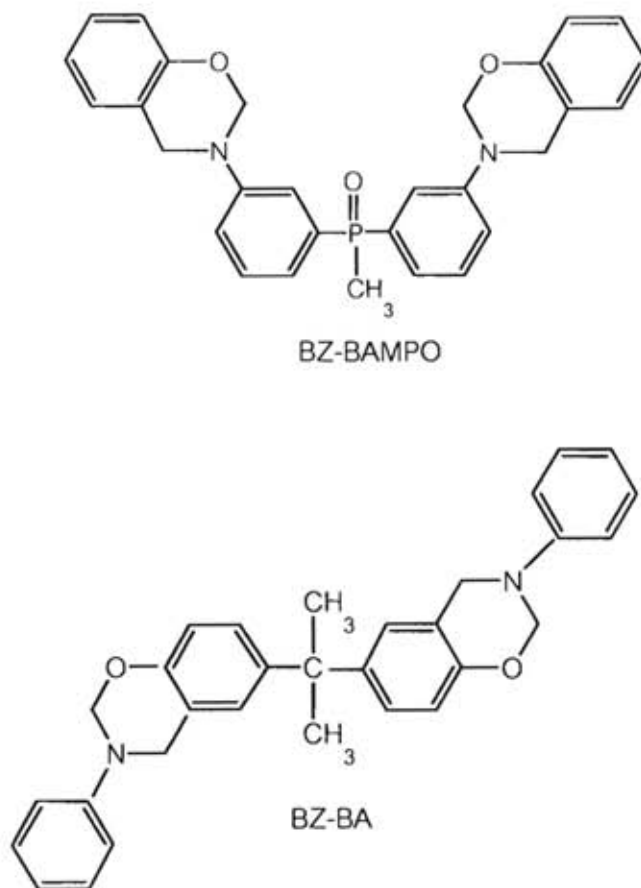


Figure 3.5 The structures of BZ-BAMPO and BZ-BA

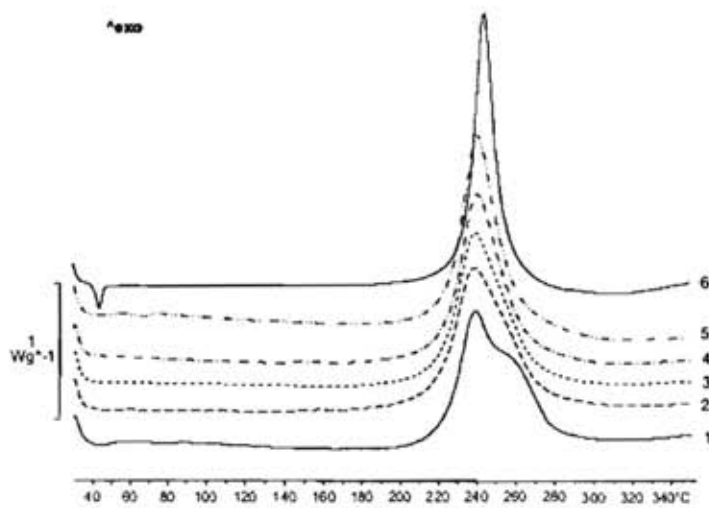


Figure 3.6 DSC plots benzoxazine system: 1 (Bz-BAMPO)
 2 (Bz-BAMPO/BZ-BA, 3:1), 3 (Bz-BAMPO/BZ-BA, 2:1),
 4 (Bz-BAMPO/BZ-BA, 1:1), 5 (Bz-BAMPO/BZ-BA, 1:2),
 6 (BZ-BA).

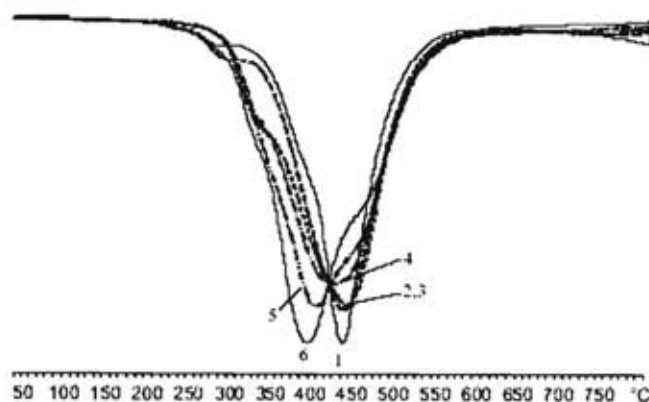


Figure 3.7 DTGA plots in nitrogen of benzoxazine system: 1 (Bz-BAMPO)
 2 (Bz-BAMPO/BZ-BA, 3:1), 3 (Bz-BAMPO/BZ-BA, 2:1),
 4 (Bz-BAMPO/BZ-BA, 1:1), 5 (Bz-BAMPO/BZ-BA, 1:2),
 6 (BZ-BA).

The thermal properties of thermosets based on benzoxazine-phenolic resins and a glycidyl phosphinate were studied by Espinosa, M. A.; Cadiz, V.; and Galia, M., 2003 [22]. They prepared modified novolac resins with benzoxazine rings and copolymerized with a glycidyl phosphinate (DOPO-Gly). The cured phenolic benzoxazines that contains phosphorous were further investigated by TGA. The temperatures of 5% weight loss, temperature of maximum rate weight loss, and char yield at 800°C under air are summarized in Table 3.3. Decomposition temperatures (temperature of 5% of weight loss) of DOPO benzoxazine–novolac resins indicate that they are not as thermally stable as the phosphorous-free benzoxazine–novolac resins. However, in the temperature region above 400°C, the degradation rates of the phosphorous-containing resins were slower than the degradation rates of the phosphorous-free resins. Benzoxazine phenolic resins with the highest content of DOPO-Gly have the high char yield which increased as the phosphorous content increases, it indicated that their flame retardancy would be relatively high. The char yield has been correlated to denote flame retardancy.

Table 3.3 Thermal properties of benzoxazine-modified novolac resins with GlyDOPO.

Sample	Ratio NB:DOPOGly	TGA (Air Atmosphere)		
		T _d 5% (°C)	T _{max} (°C)	%Yield (800°C)
NB	-	342	350	13
NB:DOPOGly	1:0.2	331	360; 437	23
NB:DOPOGly	1:0.4	327	370; 471	28

CHAPTER IV

EXPERIMENTAL

4.1 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-xylydine ($\geq 97\%$ purity), from Fluka Chemicals Co. were used as-received. Triphenylphosphate was purchased from Fluka Chemicals Co.

4.2 Preparation of Arylamine-based Benzoxazine Resins

Aniline-based benzoxazine resin (BA-a) was synthesized from bisphenol-A formaldehyde, and aniline in a molar ratio of 1:4:2. The monomers synthesis were followed a solventless technique disclosed in Ref.3 [3]. All reactants were mixed and heated to 110°C for about 30 minutes to yield a light yellow solid monomer product. The products were dissolved in diethyl ether and washed with 3 N NaOH solution and distilled water. The purified products were dried over sodium sulphate. Finally, the solvent was evaporated. As the same procedure, BA-mt and BA -35x were synthesized by replacing aniline with m-toluidine and 3,5-xylydine, respectively.

4.3 Samples Preparation

4.3.1 Slabs

The three types of benzoxazine monomers were mixed at various weight percentage of TPP i.e. 0, 2, 5, 8, 10 %. The mixtures were heated and mixed until the homogeneous resins mixture were obtained. The step cure for BA-a in an air-circulating oven was 150°C for 1 h, 170°C for 1 h, 190°C for 1 h, 210°C for 2 h, and 220°C for 2 h.

For BA-mt and BA-35x, the final cure at 230°C for 1 h was added. The cured polybenzoxazines were left to cool down and taken out from molding.

4.3.2 films

The polymer films were prepared by mixing monomers at various weight percentage of TPP i.e. 0, 2, 5, 8, 10 % with tetrahydrofuran (THF). The solutions were cast onto a glass plate and the cast films were dried at 60 and 100°C for 1 h each to remove THF. The curing step was followed by thermal cure at 150°C for 1 h, 170°C for 1 h, 190°C for 1 h, 210°C for 2 h, and 220°C for 2 h. For BA-mt and BA-35x, the final cure at 230°C for 1 h was added. The thickness of films was in ca. 100 μm .

4.4 Characterizations

4.4.1 Nuclear Magnetic Resonance (NMR)

The chemical structure of purified benzoxazine monomers were confirmed by ^1H NMR. Deuteriochloroform (CDCl_3) was used as NMR solvent. The spectra were recorded on a Varian Mercury 300 instrument operating at 300 MHz with chemical shift reported in parts per million (ppm).

4.4.2 Fourier Transform Infrared Spectroscopy (FT-IR)

The chemical structure and network formation behavior of each sample was investigated by Fourier transform infrared spectroscopy (FTIR). The sample for infrared analysis were mixed with tetrahydrofuran (THF) and then casted on a potassium bromide (KBr) pellet. The THF was evaporated in vacuum oven. All spectra were recorded with JASCO spectrophotometer model FT/IR-420 in an optical range 650-4000 cm^{-1} .

4.4.3 Differential Scanning Calorimetry (DSC)

Curing behaviors of benzoxazine monomers and its mixture at various weight percentage of TPP were determined using Differential Scanning Calorimetry (DSC) with Rigaku Thermo Plus 2 DSC8230 model. The samples were sealed in aluminum pans by weighing a monomer of approximately 5-10 mg. The calorimetric measurement was performed using a heating rate of 10°C/min and nitrogen flow of 50 ml/min. All samples were heated from room temperature to 300°C.

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

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

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

H_0 = the heat of reaction of the uncured resin, mW/mg.

4.4.4 Dynamic Mechanical Analysis (DMA)

Dynamic viscoelastic measurement were conducted on Automatic Dynamic Viscoelastomer Rheovibron model DDV-01FP at 35 Hz at a heating rate of 4°C/min. The specimens measuring 3 x 30 x 0.1 mm were tested in elongation mode and from room temperature to 300°C. The maximum point of the loss modulus or loss tangent curves by DMA was considered as the glass transition temperatures (T_g).

4.4.5 Universal Testing Machine (Flexural Mode)

Flexural tests of the samples were investigated on a universal testing machine (model 5567) from Instron Co., Ltd., according to ASTM D790M-93 Five specimens with

dimensions of 1.2 x 60 x 3 mm³ were tested for each composition. The test method was a three-point-bending mode with a 48 mm supporting span and 1 kN load cell.

The flexural strength, flexural strain and the modulus were calculated by the following equations:

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

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

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.

4.4.6 Thermogravimetric Analysis (TGA)

The thermal stability of the cured samples were determined using Rigaku Thermo Plus 2 TG-DTA TG8120. The weight of samples were in the range 10-15 mg. Sample was preheated at a heating rate 20°C/min and then maintained at 110°C for 10 min. After cool down to room temperature, the measurement was made at a heating rate rate was used maintained to be constant at 200 ml/min. Weight loss of the sample was measured as a function of temperature. The degradation temperature (T_d) of polybenzoxazines and polybenzoxazines/TPP were reported at their 5% weight loss. Char yield of the above specimens were also reported at 800°C.

4.4.7 UL94 Vertical Test

UL94 tests were performed on vertical testing apparatus as shown in Fig. 4.1. Five specimen bars 120 x 12 x 3 mm were used for each composition. The specimen was placed in a holder in a vertical position the lower end of specimen is contacted by a flame for 10 second thus initiating burning. A second ignition was made after self-extinguishing of the flame at the sample for 10 second. The burning process is characterized by the times t_1 and t_2 pertaining to the two burning steps. The parameters t_1 and t_2 denote the time between removing the methane flame and self-extinguishing of the sample. Moreover, it is always noted whether drips from the sample are released or drips make absorbent cotton flame during the burning times t_1 and t_2 . If $t_1 + t_2$ were less than 10 second with no dripping, it would be considered a V-0 material.

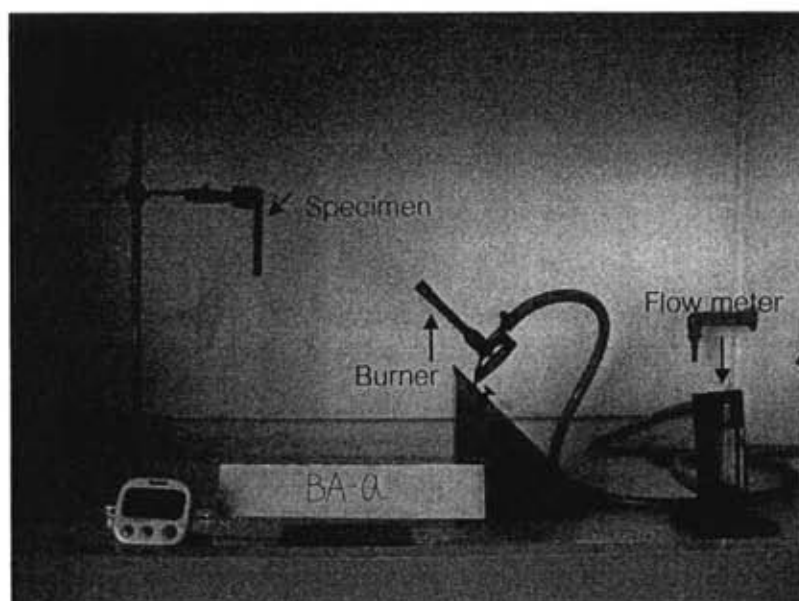


Figure 4.1 Vertical flame test.

4.4.8 Limited oxygen index test (LOI)

LOI values were measured using an LOI instrument on bar (70 x 7 x 3 mm) according to the standard oxygen index test ASTM D2863. The test was based on the determination of the lowest volume concentration of oxygen in a gas mixture of nitrogen

and oxygen (O_2 and N_2) required for ignition and the onset of burning. LOI values were calculated according to the following equation.

$$LOI(\%) = \frac{O_2}{O_2 + N_2}$$

CHAPTER V

RESULTS AND DISCUSSION

5.1 Chemical Structures of Benzoxazine Resins

A series of arylamine based-benzoxazine resins was synthesized from bisphenol-A, paraformaldehyde, and arylamine. The reaction products were purified to eliminate the partially ring-opened oligomers and unreacted reactant. The structure and purity of benzoxazine resins were identified by ^1H NMR. Figure 5.1 shows the ^1H NMR spectrum of three types of benzoxazine resins studied in this work. According to Ishida and Sanders [10], the characteristic protons at approximately 4.57 and 5.32 ppm were assigned to those of $-\text{Ar}-\text{CH}_2-\text{N}-$ and $-\text{O}-\text{CH}_2-\text{N}-$ which are responsible for a formation of a benzoxazine ring. A resonance appearing near 1.57 ppm was associated with the methylene proton of bisphenol-A whereas the signal in the range 6.5 – 7.5 ppm was from aromatic protons. BA-mt and BA-35x showed the development of signal at 2.31 and 2.27 ppm, respectively, which are related to methyl protons on the substituted aniline rings ($\text{Ar}-\text{CH}_3$). Nevertheless, the absence of resonance at 3.6 ppm indicated that opened Mannich base and oligomeric compounds had been removed during the purification procedure [2]. These spectra confirmation that the three types of arylamine-based benzoxazine resins were highly pure.

5.2 Curing Process Investigation

The polymerization of benzoxazine resin can be completed merely by thermal treatment. The curing processes of arylamine-based benzoxazine resins and benzoxazine/TPP mixtures can be observed by a differential scanning calorimeter as shown in Figures 5.2-5.6. The curing behaviors of neat arylamine-based benzoxazine resins are shown in Figure 5.2 revealing BA-mt and BA-35x to exhibited different curing behaviors from BA-a. In the case of BA-mt and BA-35x, two overlapped exothermic peaks at 223°C and 239°C as well as 211°C and 243°C were observed while BA-a

showed only a single dominant exothermic peak at 236°C. This indicated that the curing reaction of BA-mt and BA-35x possessed at least two cure stages. According to Ishida and Sanders, 2000 [12], the curing process in the main exotherm (first peak) at lower temperature was assigned to the oxazine ring opening reaction. Meanwhile, the small shoulder beside the main peak at higher temperature was corresponded to the side reaction at the para position of arylamine ring which generated the biphenolic methylene linkages called arylamine Mannich bridge and methylene linked structures. The onset temperature of the first exothermic peak of BA-a, BA-mt, and BA-35x were at 197, 183, and 170°C, respectively. From the results, polymerization reaction of BA-35x can be initiated at the lowest temperature among the three types of benzoxazine resins due to the lowest onset temperature of the resins. However, to achieve fully cured of BA-35x, relatively higher curing temperature might be needed as a result of the appearance of the highest second exotherm peak at 243°C of the resin.

Figure 5.3 exhibits effect of triphenylphosphate flame retardant (TPP) on curing behaviors of BA-35x. This non-halogenated flame retardant was added in the benzoxazine resins in order to investigate its effect on flammability enhancement and other essential properties such as curing and thermomechanical properties in the benzoxazine resins. The maximum and onset of the exothermic peaks of BA-35x were observed to slightly shifted to lower temperature with an addition of TPP. This phenomenon can also be observed in BA-a/TPP system as shown in Figure 5.4. The maxima of the first exothermic peak of BA-35x : TPP at 100:0, 98:2, 95:5, 92:8, and 90:10 mass ratios were found to be 211, 199, 198, 195, and 191°C, respectively. In addition, the small shoulder, second peak temperature, was also systematically reduced from 236°C to 220°C with 10% by weight of TPP. In the case of BA-a, the exothermic peak was shifted to 221, 218, 214, 212°C for 98:2, 95:5, 92:8, and 90:10 mass ratios, respectively. Moreover, the heat of reaction determined from the area under the main exothermic peak and the second shoulder exothermic peak was also decreased with the TPP addition. The observed curing acceleration suggested that TPP might act as a Lewis acid catalyst or initiator for polymerization of the benzoxazine resins. Only minute amount of TPP was needed to obtain similar curing acceleration i.e. about 2 % by

weight. The addition of larger amount of TPP in those benzoxazine resins was found to show negligible shifting of the exothermic peak to lower temperature and only the reduction of the area under the peak was observed possibly due to the dilution effect of the additive. [23].

The fully cured condition of the benzoxazine and TPP mixtures was determined from the disappearance of the exothermic heat of reaction under the DSC curve. Figure. 5.5 and 5.6 show the DSC thermograms of the neat BA-a and 35x. The neat benzoxazine resins were chosen to represent all the mixture compositions for determining the fully cured condition. From the figures, the area under the exothermic peaks decreased with increasing the curing temperature, using a curing time of 1 hour at each temperature or as specified in the figure, and completely disappeared after curing at maximum temperature of 220°C up to 2 hours. The degree of conversion of the polymerized benzoxazine resins after each curing stages were calculated according to the following relationship.

$$\% \text{ conversion} = \left(1 - \frac{H_{rxn}}{H_o} \right) \times 100 \quad (5.1)$$

where H_{rxn} is a heat of reaction of a partially cured specimen.

H_o is a heat of reaction of an uncured resin.

Both H_{rxn} and H_o values can be obtained from DSC experiments. The heat of reaction of uncured BA-a was determined to be 282 J/g (0% conversion). The heat of reaction was reduced to 193 J/g (32% conversion), 170 J/g (40% conversion), 89 J/g (68% conversion), 17 J/g (94% conversion), 10 J/g (96% conversion), and 3 J/g (98% conversion) after curing at 150°C for 1 hour, and after curing at 150°C for 1 hour, 170°C for 1 hour, 190°C for 1 hour, 210°C for 1 hour, 210°C for 2 hours, and 220°C for 1 hour. Finally, the 100% conversion was obtained after the final cure at 220°C for 2 hours.

However, the area under the exothermic peak still remained after heat treatment at 220°C for 2 hours for BA-35x as shown in Figure 5.6. Therefore, an additional curing step was added at 230°C for 1 hour to get the complete polymerization. As a consequence, the curing step at 150°C for 1 hour, 170°C for 1 hour, 190°C for 1 hour, 210°C for 2 hours, 220°C for 2 hours was chosen as an optimum curing condition for BA-a/TPP systems whereas for BA-mt/TPP and BA-35x/TPP systems, the additional curing step at 230°C for 1 hour was used.

5.3 Functional Groups of Investigation

The important functional groups of the benzoxazine resins were studied by FTIR spectroscopic technique. Figure 5.7 shows the FTIR spectra of arylamine-based benzoxazine monomers and TPP. The absorption bands appeared at 947 and 1498 cm^{-1} were assigned to the oxazine ring and the tri-substituted benzene ring [12] in the benzoxazine ring structure, respectively while the absorption bands at 826 (a), 777 (b) and 756 cm^{-1} (c) were assigned to those of 1,3,5-trisubstituted benzene in BA-35x, meta-substituted benzene in BA-mt, and mono-substituted benzene in BA-a, respectively [23]. For TPP, the main absorption bands at 1188 and 1298 cm^{-1} were assigned to the P=O and P-O-C [29] as shown in Figure 5.10 (d).

Figures 5.8-5.10 represent the FT-IR spectra of the fully cured polybenzoxazines of all three types of the benzoxazine resins. According to the polymerization mechanism reported [10], the oxazine ring was opened by the breakage of a C-O bond to form the network structure. The peak assigned to the oxazine ring (947 cm^{-1}) was thus disappeared. The absorption band of the vibration of tri-substituted benzene ring (1498 cm^{-1}) was shifted to the absorption band at 1487 cm^{-1} which became tetra-substituted benzene ring. It also led to the formation of a phenolic Mannich base polybenzoxazine structure. At the same time, the band attributed phenolic hydroxyl group was found at 3300–3400 cm^{-1} . These confirmed that polymerization reaction of oxazine ring-opening proceeded by thermal curing. In addition, a new absorption band was developed at about 829 cm^{-1} which was assigned to the 3,4-dimethylaniline while BA-35x presented

the new absorption band at 845 cm^{-1} and was assigned to the 1,3,4,5-tetrasubstituted arylamine ring as shown in Figures 5.9 and 5.10, respectively. 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 amount of arylamine Mannich bridge and methylene linked structures [12].

The infrared spectra of arylamine-based benzoxazine resins containing 10 wt% of TPP are shown in Figures 5.11-5.13. The characteristic absorption bands at 1188 cm^{-1} was assigned to the P-O-C due to the presence of TPP. After complete polymerization, no change in the spectra was observed particularly in the positions of the peaks comparing with those of neat polybenzoxazines. This implied that TPP additive was only physically dispersed in the polybenzoxazine matrix with no specific chemical bonding to the polymer network.

5.4 Glass Transition Temperature Determination

Viscoelastic behavior reflects the combined viscous and elastic responses, under mechanical stress, of materials which are intermediate between liquid and solid in character. Glass transition temperatures are characterized by a change from hard, glass-like material to a rubbery solid [26]. The behavior can be examined directly using dynamic mechanical analysis.

The plots of the loss modulus (E'') and $\text{Tan } \delta$ as a function of temperature ($^{\circ}\text{C}$) for the neat arylamine-based Polybenzoxazines are shown in Figure 5.14. The glass transition temperature or T_g was determined from the maximum point on the loss modulus (E'') curves or the α relaxation peak of the loss factor ($\text{Tan } \delta$). The maximum E'' is the most appropriate value to identify T_g as it corresponds to the initial drop from the glassy state into the rubbery plateau region [20-21]. As can be seen from the figure, BA-35x demonstrated the highest T_g at 255°C comparing with those of BA-mt, or BA-a which were found to be 220 and 177°C , respectively. The introduction of aryl-substituted amines was reported to help increase the network crosslink density that occurred at the para position of arylamine ring i.e. arylamine Mannich bridge and methylene linkage

formation. The additional crosslinking would clearly increase the T_g of the network [5]. Figure 5.15 presents the relationship between T_g of the three types of polybenzoxazines with TPP flame retardant content. The T_g s of the three types of polybenzoxazines exhibited the same tendency that were reduced with increasing TPP content, i.e., T_g of BA-a, BA-mt, and BA-35x values decreased to 151, 186, and 201°C, respectively, with an addition of 10 % by weight of TPP. The lower T_g of polybenzoxazines with TPP content can be explained by the small molecules of the TPP used. TPP acts as a plasticizer, gets in between the polymer chains and spaces them apart from each other increasing the free volume, and consequently the ease of segment mobility is increased. As a result, the polymer chains can move around at lower temperatures resulting in a decrease in T_g [24]. Moreover, the reduction of T_g of BA-35x system was greater than BA-mt and BA-a systems, respectively. This is owing to the effect of the methyl pendant groups as well as from TPP additive to significantly increase the free volume of the polymer. In addition, the analysis of the height of the $\text{Tan } \delta$ and the rubbery plateau modulus revealed a trend in the crosslinking densities. From the Figures 5.16-5.18, all polybenzoxazines exhibited the same tendency with increasing TPP content that the height of the $\text{Tan } \delta$ peaks tended to increase and the rubbery plateau region became lower than that of the neat polybenzoxazines. The increasing height is, in principle, associated with higher segmental mobility and more relaxing species [21]. As a consequence, this indicated that the networks of the neat polybenzoxazines were denser than those of polybenzoxazines-TPP systems.

5.5 Thermal Stability Evaluation

Thermal stabilities of the cured polybenzoxazines were compared using the degradation temperature at 5 % weight loss and the percentage char yield at 800°C under argon atmosphere from thermogravimetric analysis (TGA). In TGA thermograms, weight loss is recorded as a function of temperature as shown in Figure 5.19.

TGA thermograms of the neat arylamine-based polybenzoxazines are shown in Figure 5.19. The degradation temperature at 5 % weight loss of BA-mt and BA-35x were

higher than that of BA-a i.e. $T_d = 330, 350, 349^\circ\text{C}$ for BA-a, BA-mt, and BA-35x, respectively. Ishida and Sanders, 2000 [12] reported that in the case of BA-mt and BA-35x, the polymerized network structure was not pure phenolic manich bridge network as BA-a (as also seen in Figure 3.2) but contained additional crosslinking structures, i.e. arylamine Mannich bridge and methylene linkage (see in Figure 3.1). However, 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 Manich bridge unless the phenolic moiety contributes significantly to the degradation mechanism of the phenolic Mannich bridge structure. Moreover, the more rigid network created by the methylene linkages create kinetic barriers to weight loss as well. Those bond formations therefore contribute to the observed enhancement in T_d of BA-mt and BA-35x comparing with BA-a. On the other hand, the char yields of BA-a, BA-mt and BA-35x are not significantly different with the values in a range of 30-31 %. Thus the additional crosslinking from phenolic Mannich bridge and methylene linkage provided insignificant effect on the char formation of the resulting polybenzoxazine networks.

The effect of TPP content on the degradation temperature ($T_{05\%}$) and char yield of polybenzoxazines is shown in Figure 5.20. The three types of polybenzoxazines exhibited the same decreasing trend in 5 % weight loss temperature with increasing TPP content. Due to its relatively low boiling point (245°C), under temperature scan, TPP tended to be released from the specimen before the thermal degradation of benzoxazine matrix. Meanwhile, the char yields of polybenzoxazines in the presence of TPP were observed to be higher than that of the neat polybenzoxazines as illustrated in Figure 5.21. The char yields of BA-a, BA-mt, and BA-35x increased from 30.2, 31.4, 31.0 to 37.7, 39.3, and 35.9 %, respectively, with 10 wt% of TPP content. Char yield of the material has been correlated with its flame retardancy [27]. Increasing char yield implied greater fire resistance of the sample as it was proposed that char formation would limit production of combustion gases, inhibit combustion gases from diffusing to the pyrolysis zone and protect the polymer surface from heat and air. Thus fire resistant property of the polybenzoxazines tended to be improved with the TPP addition.

5.6 Flexural Property Examination

In three-point-bending test the specimen having standard geometry is supported at its ends. A load is then applied at the center of the specimen under standard conditions. The force is measured and registered during the deformation. From the evaluation, the flexural (bending) strength (proportional to the maximal load-bearing capacity), and the flexural modulus (proportional by the stiffness of material) can be determined [28].

Flexural strength represents 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 molecules, which might be transformed to heat, deformation or sound, etc. [28]. The flexural properties of polybenzoxazines at various weight percentage of TPP are shown in Figures 5.22 – 5.24. Figure 5.22 is a plot of the flexural strength (MPa) of the three polybenzoxazines as a function of the TPP content (wt%). In principle, 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 some other contributing factors [29]. As seen in Figure 5.22, the flexural strengths of the neat polybenzoxazines were determined to be 139.6, 129.2, and 116.0 MPa for BA-a, BA-mt, and BA-35x, respectively i.e. BA-a exhibited the highest flexural strength among the three polybenzoxazines. However, the flexural strengths of BA-a, BA-mt, and BA-35x decreased to 122.0, 115.7, and 102.8 MPa, respectively, with an addition of 10 % by weight of TPP. This result was ascribed to the effect of free volume of the modified specimens. A higher free volume with increasing TPP contents might lower interactions and enhance the ability of the polymer chain segments to flow under load by such means as rotationally configurational changes [29]. In addition, as described previously, TPP tended to disperse only physically, without no chemical bonding, in a polybenzoxazine matrix thus provided no contribution to mechanical performance of the polymer.

Figure 5.23 exhibits the plot of the flexural strain at break (%) of the arylamine-based polybenzoxazines as a function of TPP contents (wt%). The flexural strain at break of BA-a, BA-mt and BA-35x was observed to be about 2.40, 2.45 and 2.50 %, respectively. The three types of polybenzoxazines showed slightly difference in their flexural strain at break values i.e. BA-35x demonstrated the highest value. As a result, the methyl side groups on the arylamine ring in this system provided some flexibility in the polymer. The slight increase of flexural strain at break (%) of the three types of polybenzoxazines with an addition of TPP was also observed. The values were found to be 2.9, 2.8, and 2.9 % at 10 % by weight ratio of TPP for BA-a, BA-mt and BA-35x systems, respectively.

The plot of flexural modulus (GPa) of the arylamine-based polybenzoxazines at various weight percent of TPP is shown in Figure 5.24. Flexural modulus defines the relationship between a bending stress and the resulting strain and is, in principle, determined from initial slope of the stress-strain curve. As seen in the figure, BA-a possessed the highest flexural modulus value of 5.8 GPa. For BA-mt and BA-35x, those values were found to be about 5.4 and 4.8 GPa, respectively. Furthermore, the flexural modulus values of BA-a, BA-mt, and BA-35x at 10 % weight of TPP decreased to 4.25, 4.27, and 3.58 GPa, respectively. The observed phenomena also confirmed that TPP was only physically mixed with the polybenzoxazine matrix to yield a homogeneous mixture. The effect of TPP small molecule tended to increase free volume of the polymer matrix thus promoting its strain at break. However, the presence of this small molecular weight additive contributed to the lowering of mechanical strength and modulus of the polybenzoxazine matrices

5.7 Effect of TPP on Flame Retardancy of Arylamine-based Polybenzoxazines

5.7.1 Limiting Oxygen Index (LOI)

The ignitability and fire resistivity of polymers can be characterized by a limiting oxygen index (LOI). The relative flammability is determined by adjusting the

concentration of oxygen. The LOI is the lowest oxygen gas concentration which a material will burn [30]. Figure 5.25 presents the LOI values of the three types of arylamine-based polybenzoxazines at various TPP contents. From the figure, BA-a possessed the highest of LOI values of 23.5 while BA-mt and BA-35x showed LOI values of 23.0 and 22.0, respectively. The LOI values were also found to be systematically enhanced by an addition of TPP. The higher LOI values of 26.0, 25.5, and 24.0 with an addition of 10% by weight of TPP were obtained for BA-a, BA-mt and BA-35x, respectively. The effect of TPP content on the LOI values of polymer has been extensively studied, and usually found that LOI values increased with an addition of TPP content. For example, Mark et al. [31] found that LOI value of polystyrene increased from 18.8 to 20.7 with an addition of 5 % by weight of TPP. Junfeng et al. [32] examined the flame retardant of TPP in polybutylene terephthalate (PBT). They reported the result that LOI value of PBT was significantly increased from 20.9 to 24.6 at 10 % by weight of TPP. L. Kyongho et al [33] also found that LOI values of acrylonitrile-butadiene-styrene (ABS) were increased by adding of TPP. The higher LOI values confirmed that TPP was an effective flame retardant for our polybenzoxazines. These results were also consistent with those char yield values from the TGA results. The char yield also increased with increasing of TPP content. The char formed during combustion can act as a protective layer for polybenzoxazines, which prevents oxygen diffusion to the surface of the specimen thus more oxygen is needed for its combustion [34].

5.7.2 UL94 Vertical Test of TPP-modified Polybenzoxazines

UL94 is the most commonly used standard test for measuring the ignitability and flame-spread of vertical bulk materials exposed to a small flame. Five sample bars of each fully cured polybenzoxazine suspended vertically over surgical cotton were ignited by a methane burner. Two ignitions of 10 seconds were applied to the sample. The flammability of the three arylamines-based polybenzoxazines without the TPP additive is summarized in Table 5.1. It was evident that the neat BA-a provided the shortest total after-flame time (t_1 plus t_2) from 5 tested specimens where t_1 = the after-flame time after the first ignition and t_2 = the after-flame time after the second ignition.

Meanwhile, BA-mt and BA-35x showed the longer times for self-extinction and the flame could propagate the tested specimen up to a holding clamp. It was also observed that BA-35x specimens showed a greater fire spread than BA-mt and were severely burnt after the flame test. However, all three polybenzoxazines exhibited no the dripping of flaming particles in the UL94 vertical test. The total after flame time of the unmodified BA-a, BA-mt, and BA-35x were found to be 100.1, >250, and >250 seconds, respectively thus BA-a was classified as V-1 rating under UL94 test. In the case of BA-mt and BA-35x, both could not pass the vertical rating category. This result indicated that BA-a exhibited the best flame retardancy comparing with BA-mt and BA-35x. The flammability of the polybenzoxazines was ranging in the order of BA-a < BA-mt < BA-35x. The phenomenon might be ascribed to the presence of methyl group on the arylamine ring which, upon pyrolysis, produced relatively flammable CH₃ free radicals. In theory, the flammability of a given material is strongly dependent on the concentration of free radicals [35]. The fire resistance of polybenzoxazines was examined by Wang et al [36]. According to their reported, benzoxazine resins were synthesized from difference of bisphenol i.e. bisphenyl-A and bisphenol-F. The structure of bisphenol-A has an addition of two methyl side groups comparing with bisphenol-F. They found that the burning time of bisphenyl-A based benzoxazine was longer than bisphenol-F based benzoxazine. This result was in good agreement with our result which the methyl side groups have effect on the fire resistance of polybenzoxazines.

The UL94 test results for the three polybenzoxazines with an addition of TPP flame retardant ranging from 0, 2, 5, 8, and 10 % by weight are shown in Table 5.2-5.4. For BA-a type polybenzoxazine, the classification of V-0 rating was achieved in this polymer when at least 5 wt% of TPP was added. The total after-flame time for five specimens for BA-a was reduced substantially from 100.1 to only 16.7 seconds. The flame was observed to extinguish almost immediately after the remove of the burner. Similar effect of TPP on fire resistant behaviors of BA-mt and BA-35x systems was also observed. From Tables 5.3-5.4, UL94 classification of V-0 rating was also achieved with an addition of only 2 wt% and 5 wt% of TPP in BA-mt and BA-35x, respectively. The total

after-flame time for five specimens was significantly reduced from >250 seconds to 21.1 seconds for BA-mt systems and from >250 seconds to 43.43 seconds for BA-35x systems. The visual appearance of those tested specimens can be seen in Figures 5.29-5.32. An addition of TPP flame retardant above those specified levels for each polybenzoxazine provided only a further slight reduction in the burning time. Consequently, maximum fire resistance of V0 category under UL94 test of those arylamine-based polybenzoxazines could be easily obtained with relatively low amount of the TPP flame retardant. This small required amount of TPP would prevent the negative effect on other good properties of the polybenzoxazines.

It had been reported that, during combustion, TPP mainly acted in gas phase as it could vaporize into the gas phase, to yield active radicals, such as PO_2^* , PO^* and HPO^* . These radicals acted as scavengers of H^* and OH^* radicals and thus resulted in suppression of the combustion process [9]. However, TPP was also reported to act in a condensed phase by promoting the formation of char as also observed in our polybenzoxazine systems. In the condensed phase, char formation on the surface inhibited gaseous products from diffusing to the flame as well as shielded the polymer surface from heat and air [20]. As a result, combustion process was suppressed or even terminated.

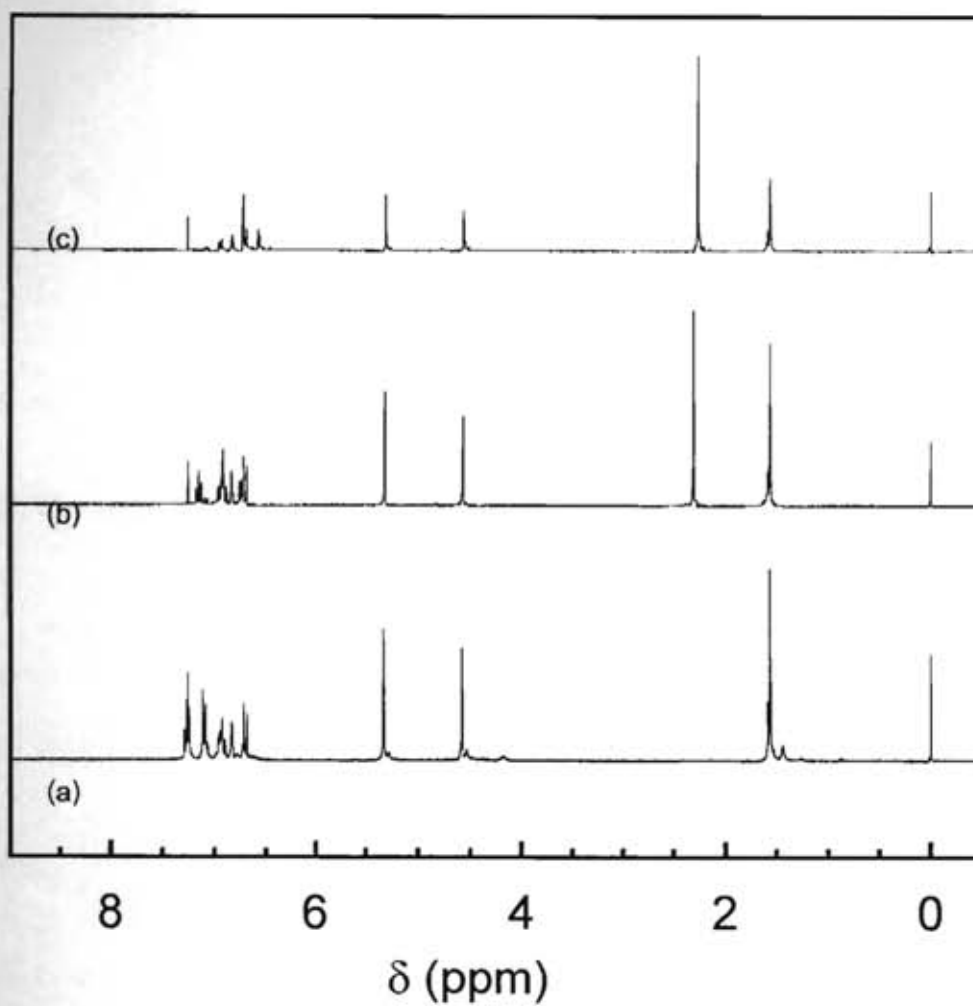


Figure 5.1 ^1H NMR spectra of the neat arylamine-based benzoxazine resins:
(a) BA-a, (b) BA-mt, and (c) BA-35x.

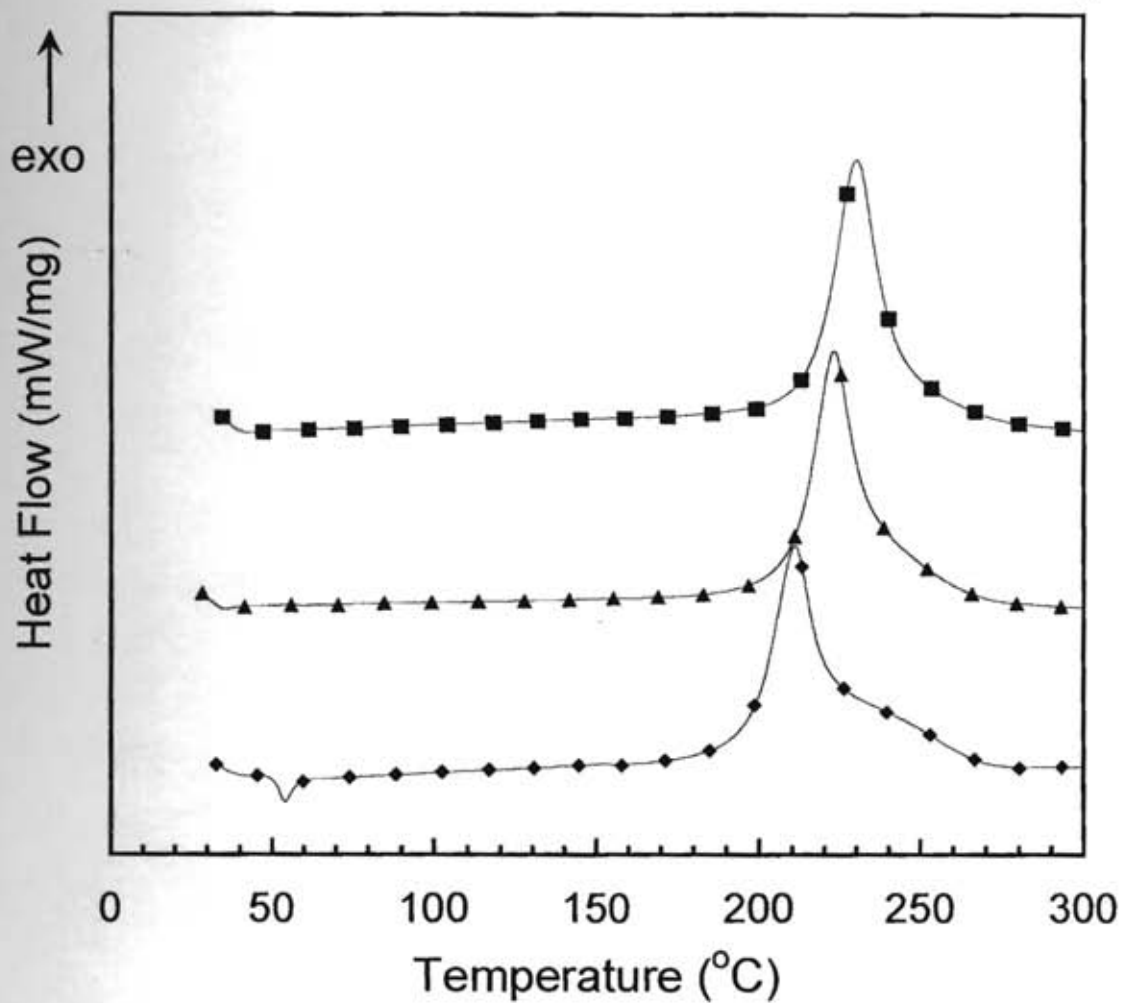


Figure 5.2 DSC thermograms of the neat arylamine-based benzoxazine resins:

(■) BA-a, (▲) BA-mt, and (◆) BA-35x.

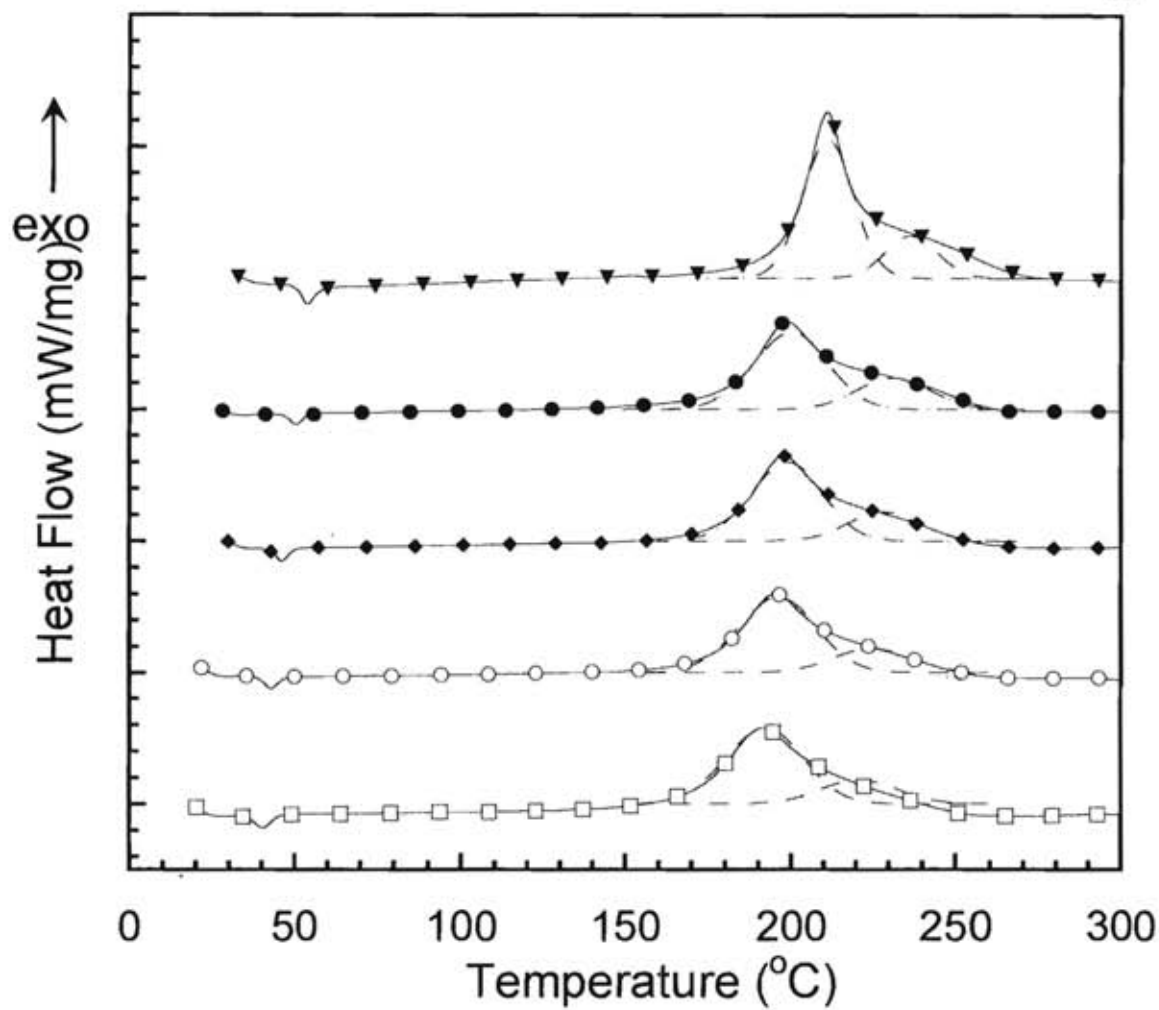


Figure 5.3 Curing behaviors of BA-35x mixed with TPP at various contents:

(▼) 100:0, (●) 98:2, (◆) 95:5, (○) 92:8, and (□) 90:10.

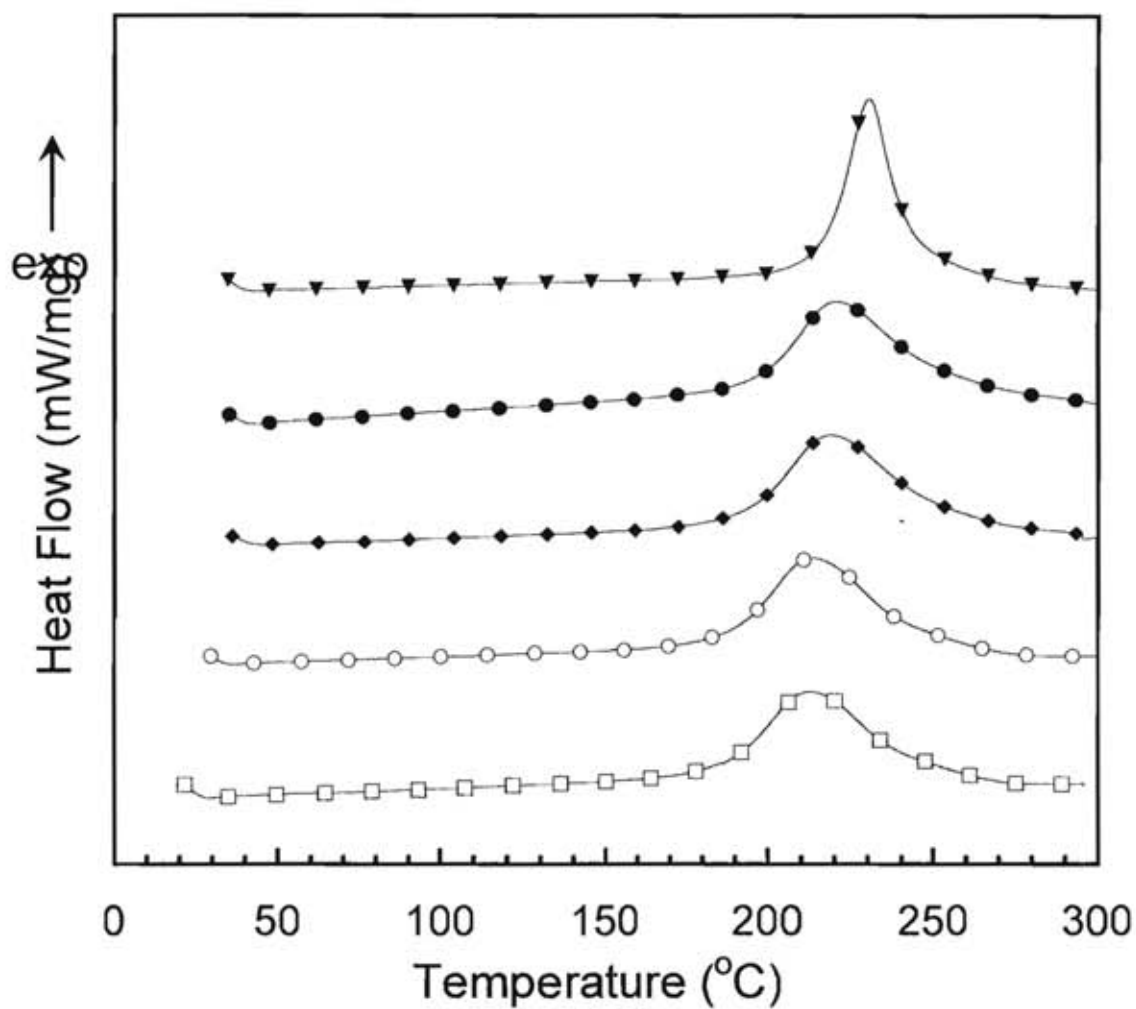


Figure 5.4 Curing behaviors of BA-a mixed with TPP at various contents:

(▼) 100:0, (●) 98:2, (◆) 95:5, (○) 92:8, and (□) 90:10.

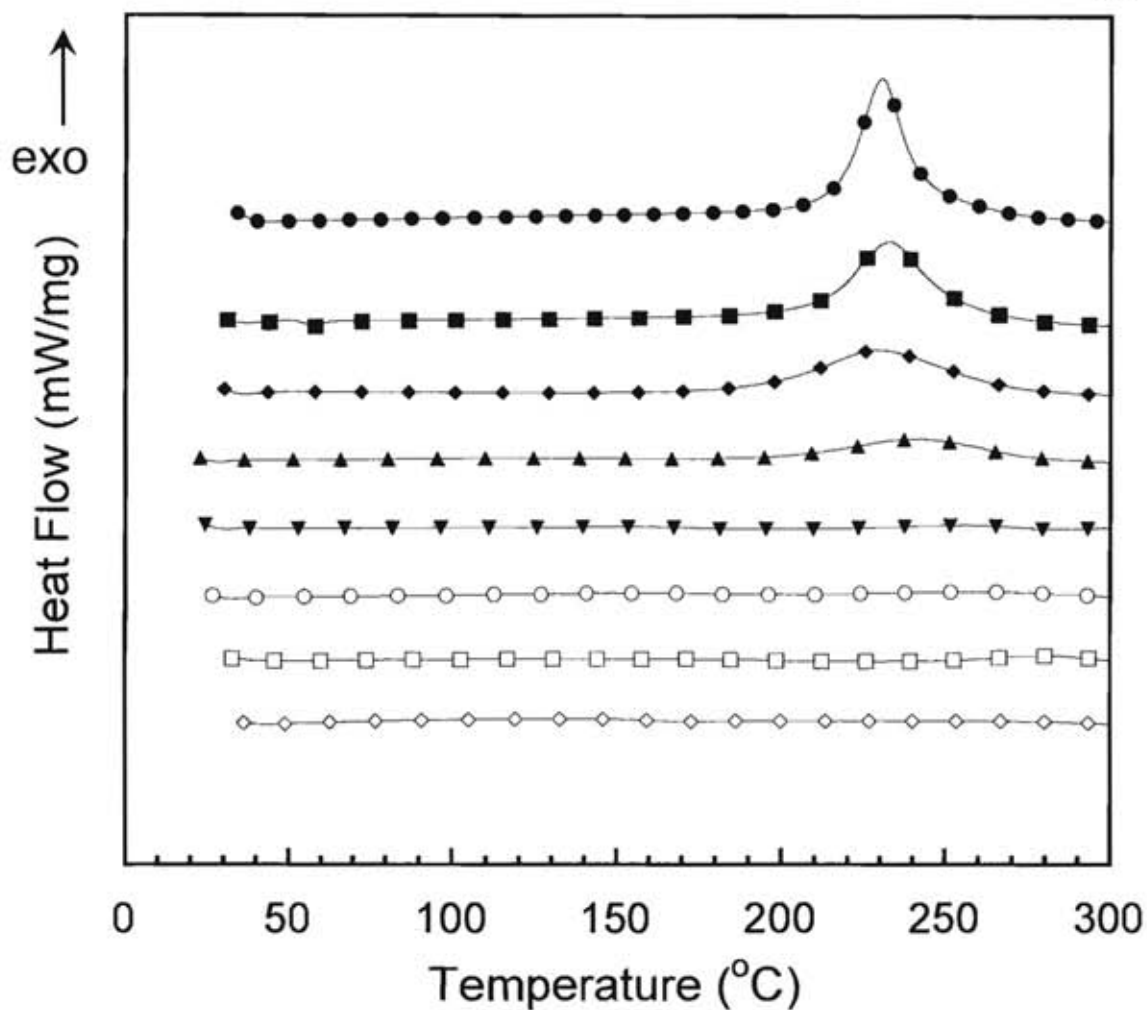


Figure 5.5 DSC thermograms of the neat BA-a at various curing conditions:

- (●) uncured, (■) $150^{\circ}\text{C}/1\text{hr}$, (◆) $150^{\circ}\text{C}/1\text{hr} + 170^{\circ}\text{C}/1\text{hr}$,
- (▲) $150^{\circ}\text{C}/1\text{hr} + 170^{\circ}\text{C}/1\text{hr} + 190^{\circ}\text{C}/1\text{hr}$,
- (▼) $150^{\circ}\text{C}/1\text{hr} + 170^{\circ}\text{C}/1\text{hr} + 190^{\circ}\text{C}/1\text{hr} + 210^{\circ}\text{C}/1\text{hr}$,
- (○) $150^{\circ}\text{C}/1\text{hr} + 170^{\circ}\text{C}/1\text{hr} + 190^{\circ}\text{C}/1\text{hr} + 210^{\circ}\text{C}/1\text{hr} + 210^{\circ}\text{C}/2\text{hrs}$,
- (□) $150^{\circ}\text{C}/1\text{hr} + 170^{\circ}\text{C}/1\text{hr} + 190^{\circ}\text{C}/1\text{hr} + 210^{\circ}\text{C}/1\text{hr} + 210^{\circ}\text{C}/2\text{hrs} + 220^{\circ}\text{C}/1\text{hr}$, and (◇) $150^{\circ}\text{C}/1\text{hr} + 170^{\circ}\text{C}/1\text{hr} + 190^{\circ}\text{C}/1\text{hr} + 210^{\circ}\text{C}/1\text{hr} + 210^{\circ}\text{C}/2\text{hrs} + 220^{\circ}\text{C}/1\text{hr} + 220^{\circ}\text{C}/2\text{hrs}$.

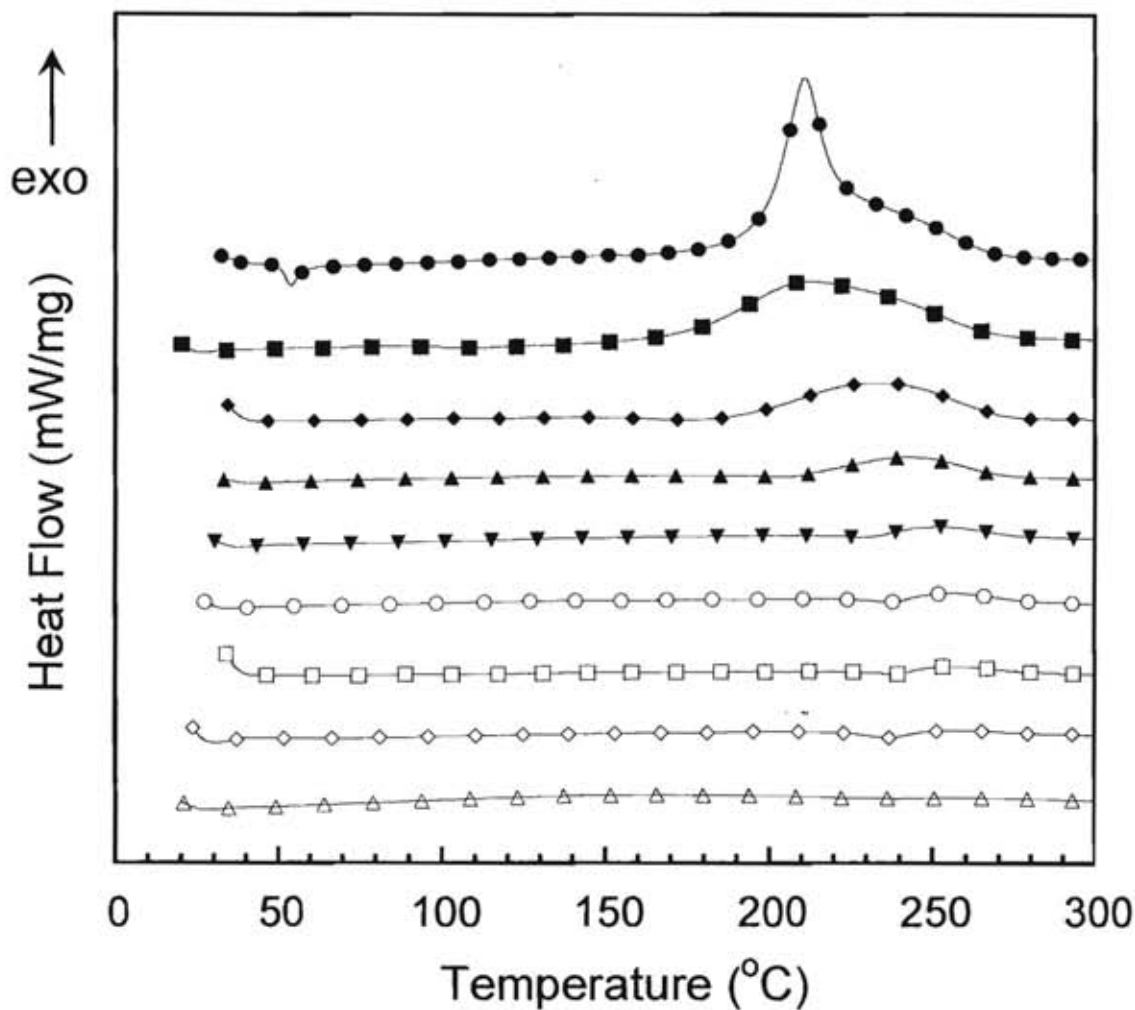


Figure 5.6 DSC thermograms of the neat BA-35x at various curing conditions:

- (●) 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 + 210°C/1hr,
- (○) 150°C/1hr + 170°C/1hr + 190°C/1hr + 210°C/1hr + 210°C/2hrs,
- (□) 150°C/1hr + 170°C/1hr + 190°C/1hr + 210°C/1hr + 210°C/2hrs + 220°C/1hr, and (◇) 150°C/1hr + 170°C/1hr + 190°C/1hr + 210°C/1hr + 210°C/2hrs + 220°C/1hr + 220°C/2hrs,
- (Δ) 150°C/1hr + 170°C/1hr + 190°C/1hr + 210°C/1hr + 210°C/2hrs + 220°C/1hr + 220°C/2hrs + 230°C/1hr.

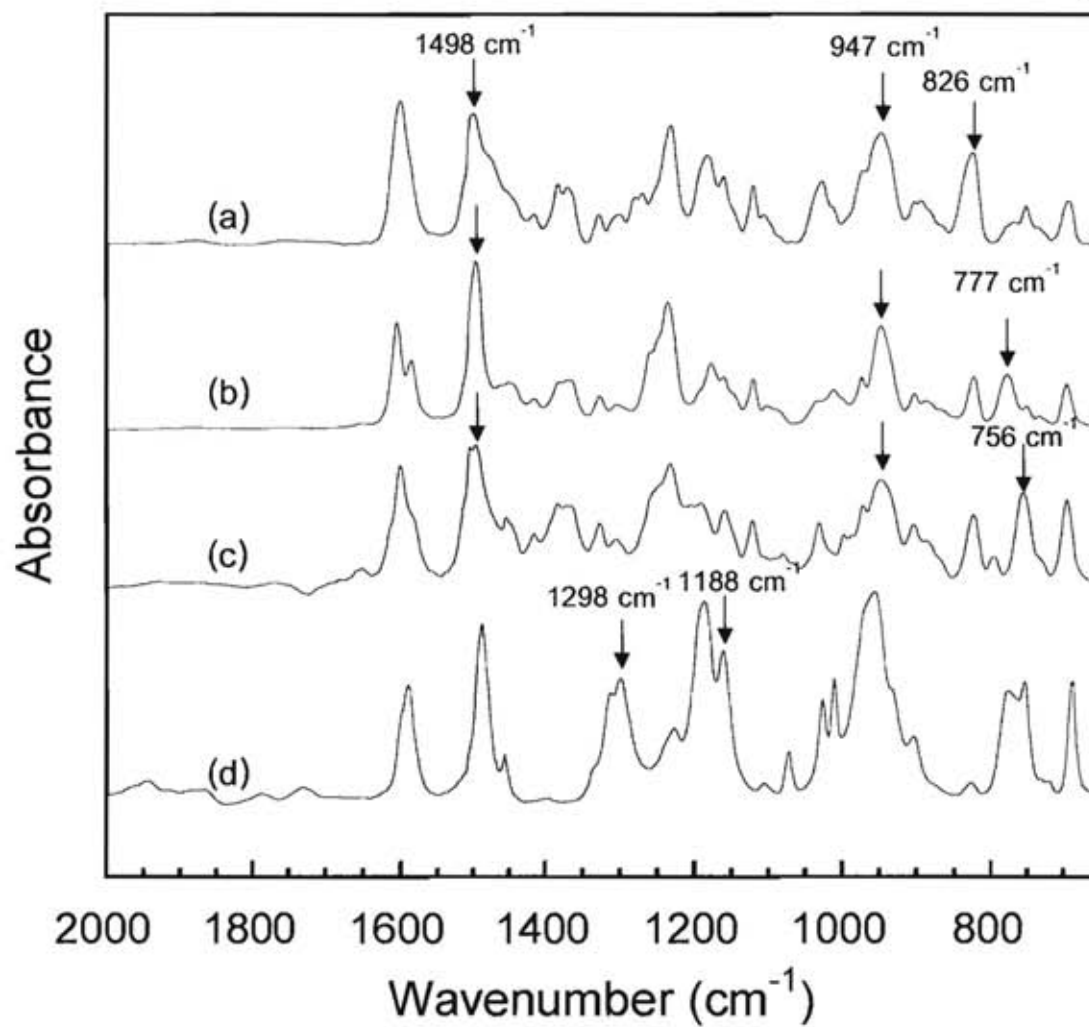


Figure 5.7 FTIR spectra of the neat arylamine-based benzoxazine monomers and TPP: (a) BA-35x, (b) BA-mt, (c) BA-a, and (d) TPP.

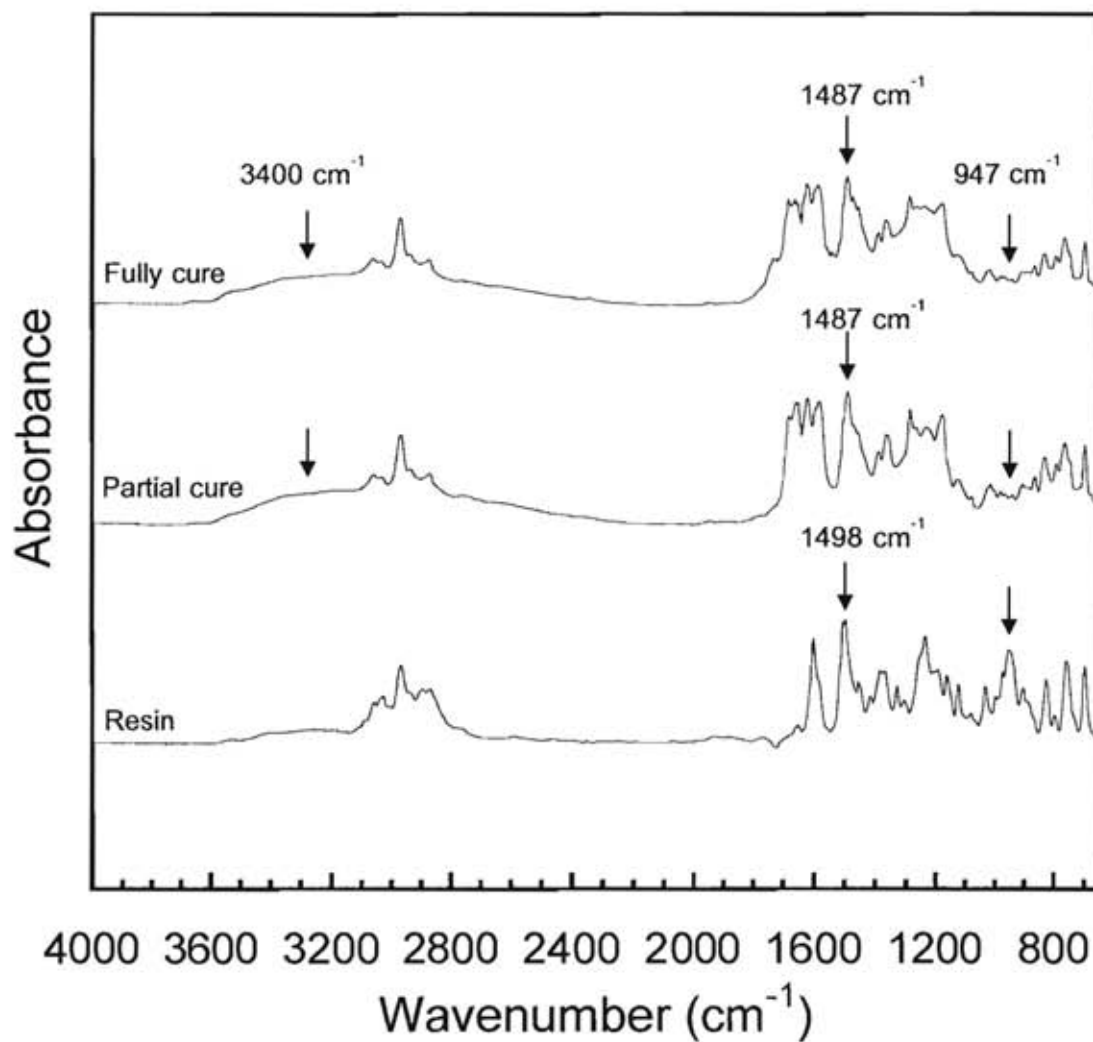


Figure 5.8 FTIR spectra of the neat BA-a formation.

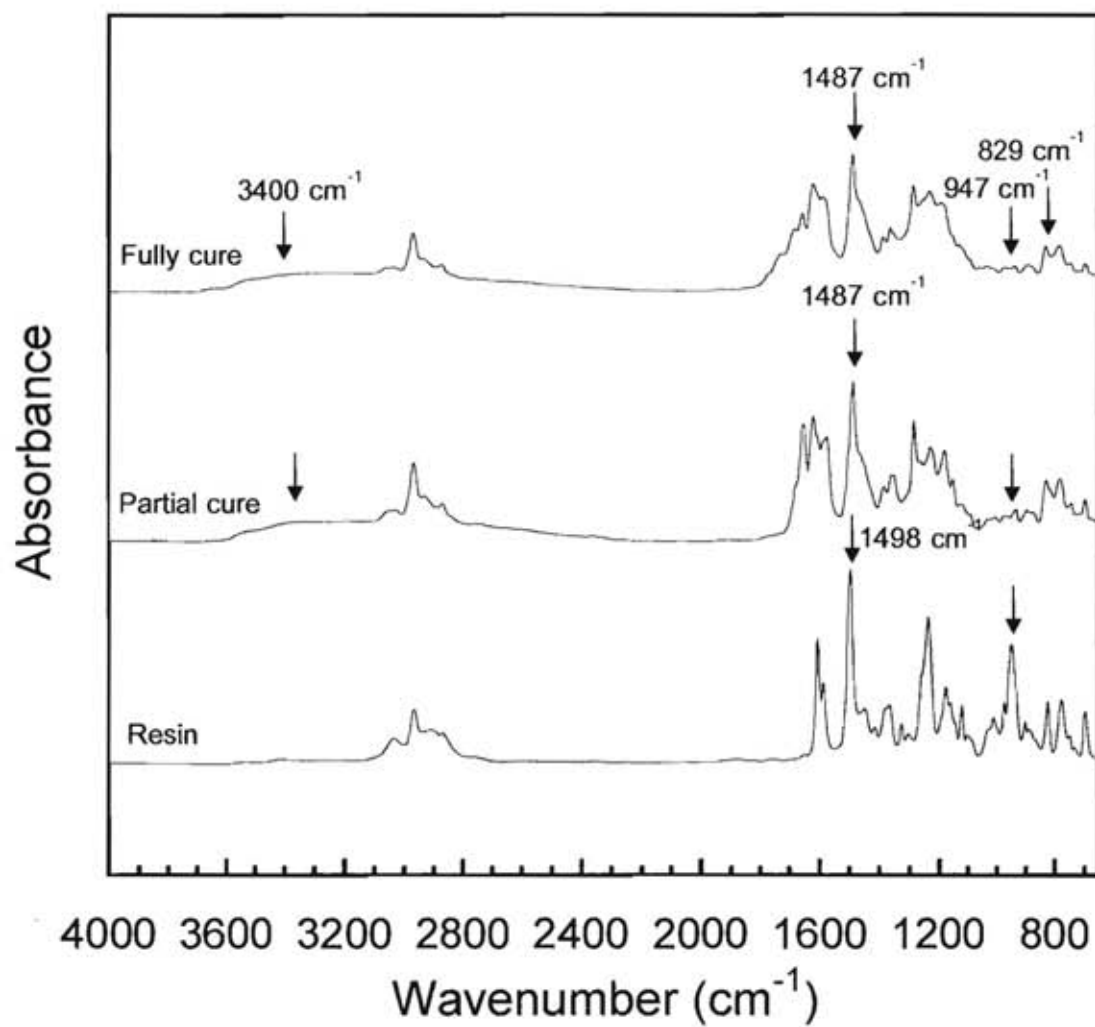


Figure 5.9 FTIR spectra of the neat BA-mt formation.

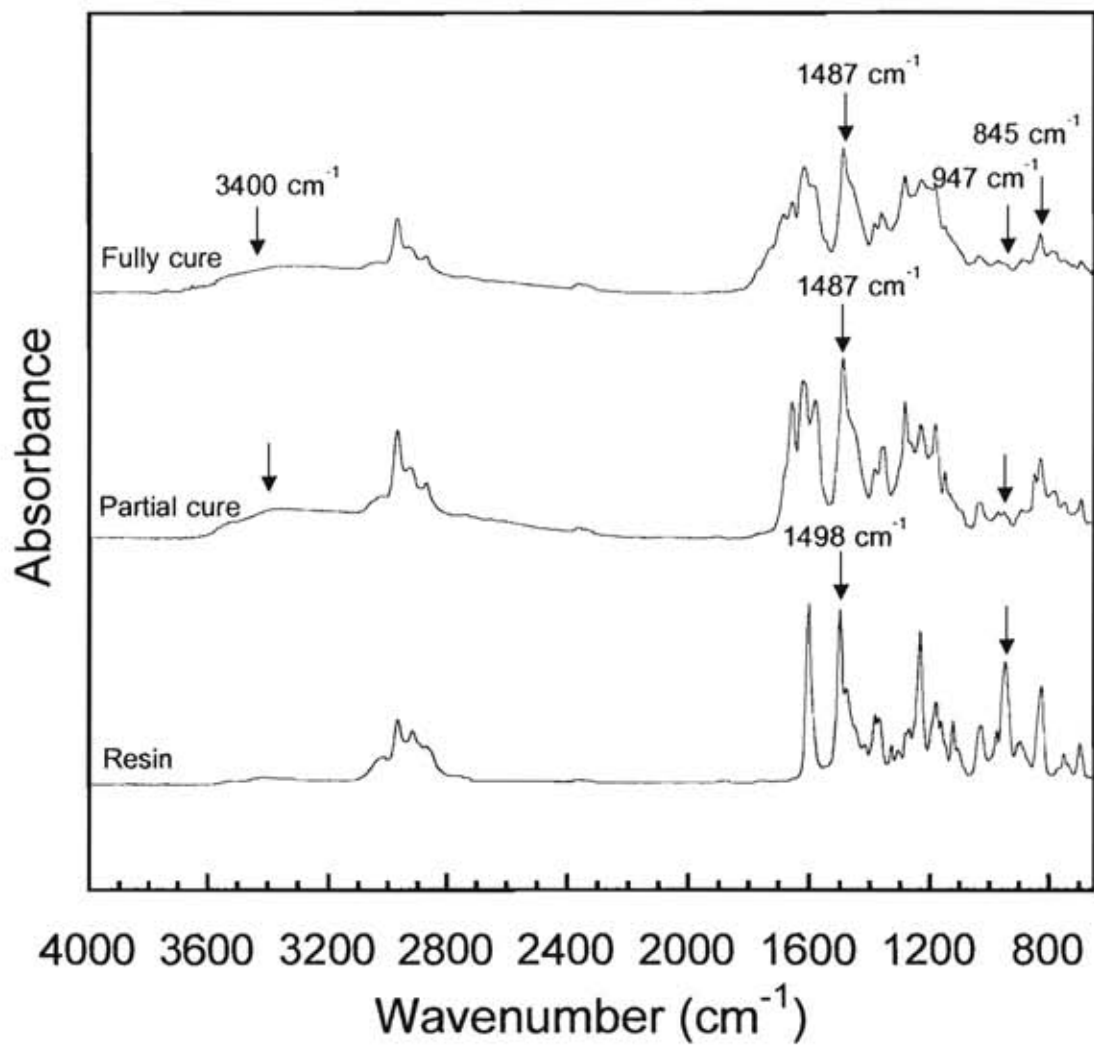


Figure 5.10 FTIR spectra of the neat BA-35x formation:

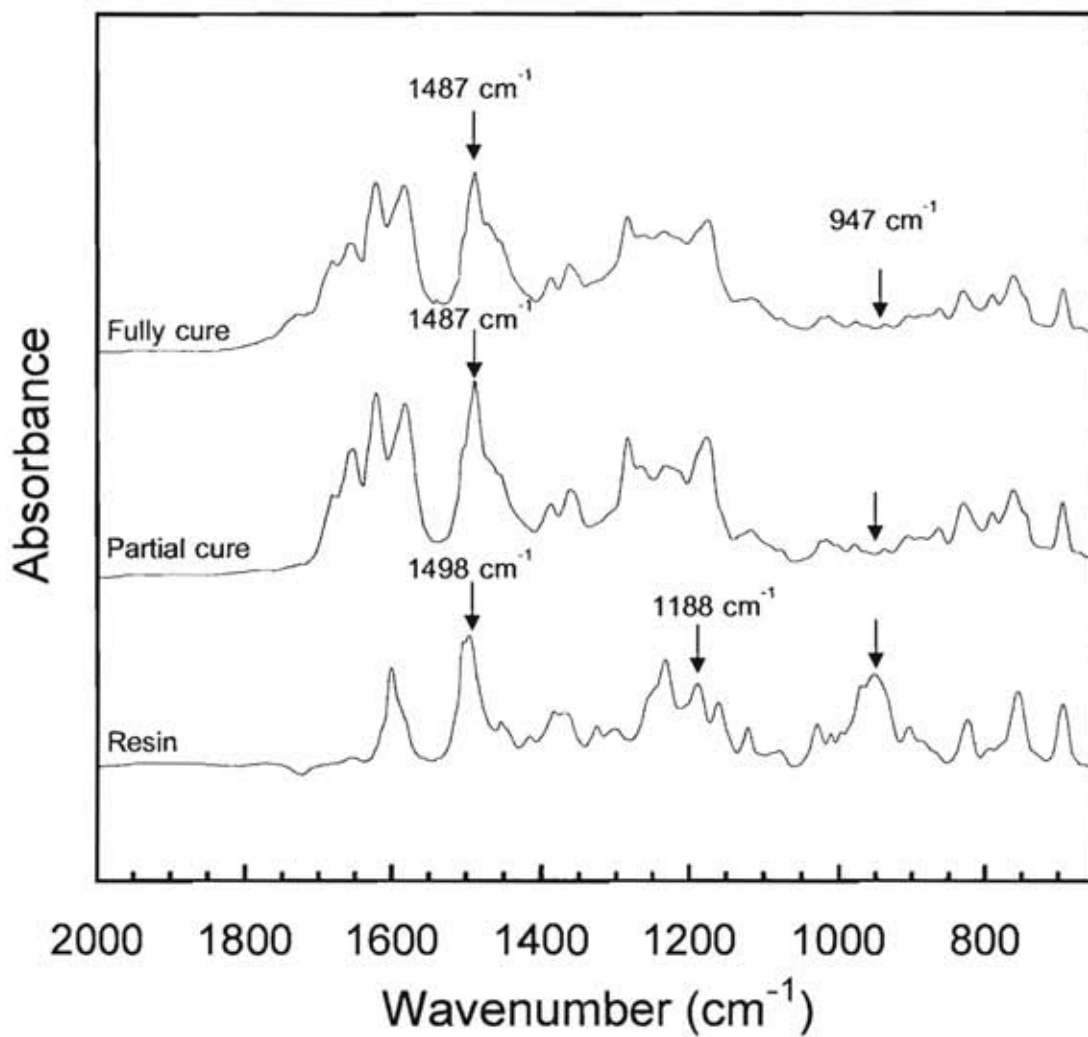


Figure 5.11 FTIR spectra of BA-a/TPP at 90:10 weight ratio.

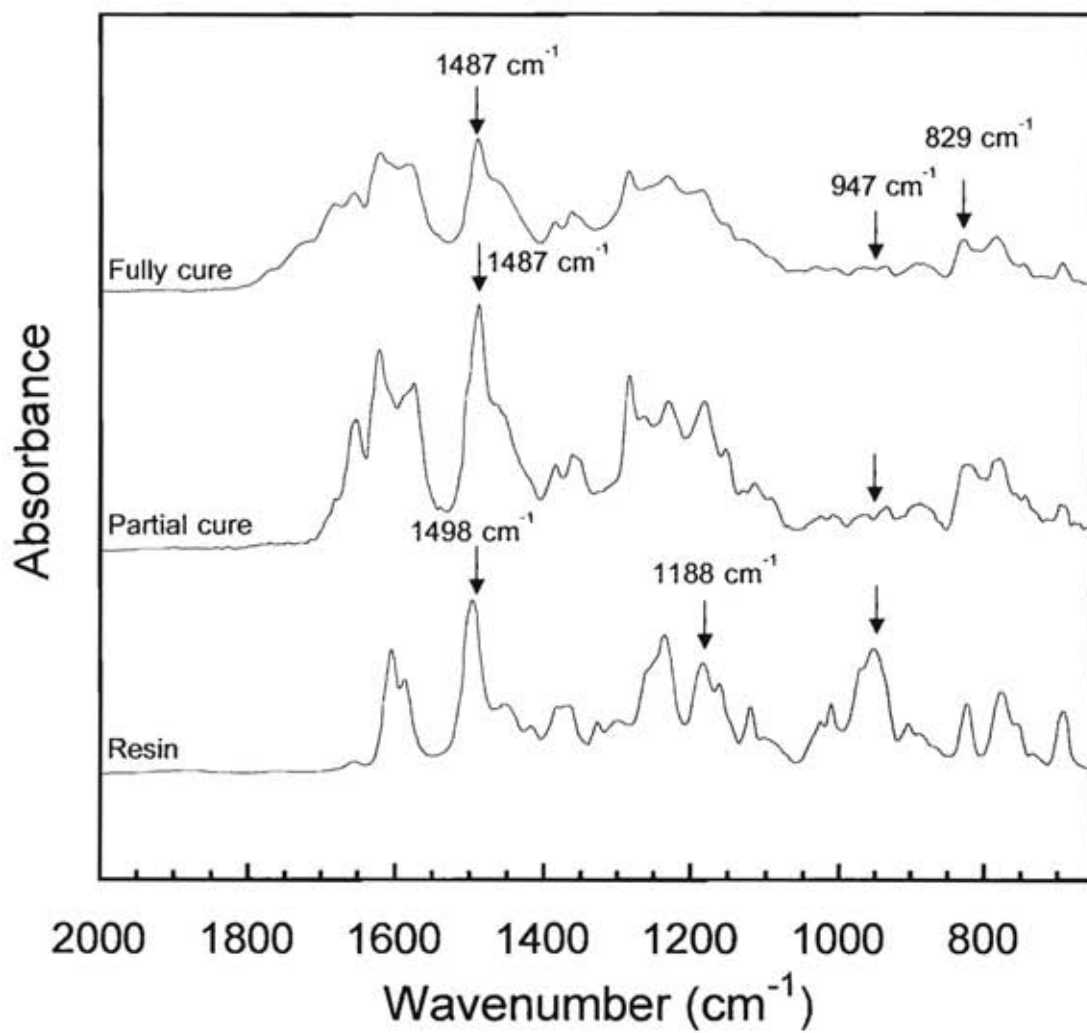


Figure 5.12 FTIR spectra of BA-mt/TPP at 90:10 weight ratio.

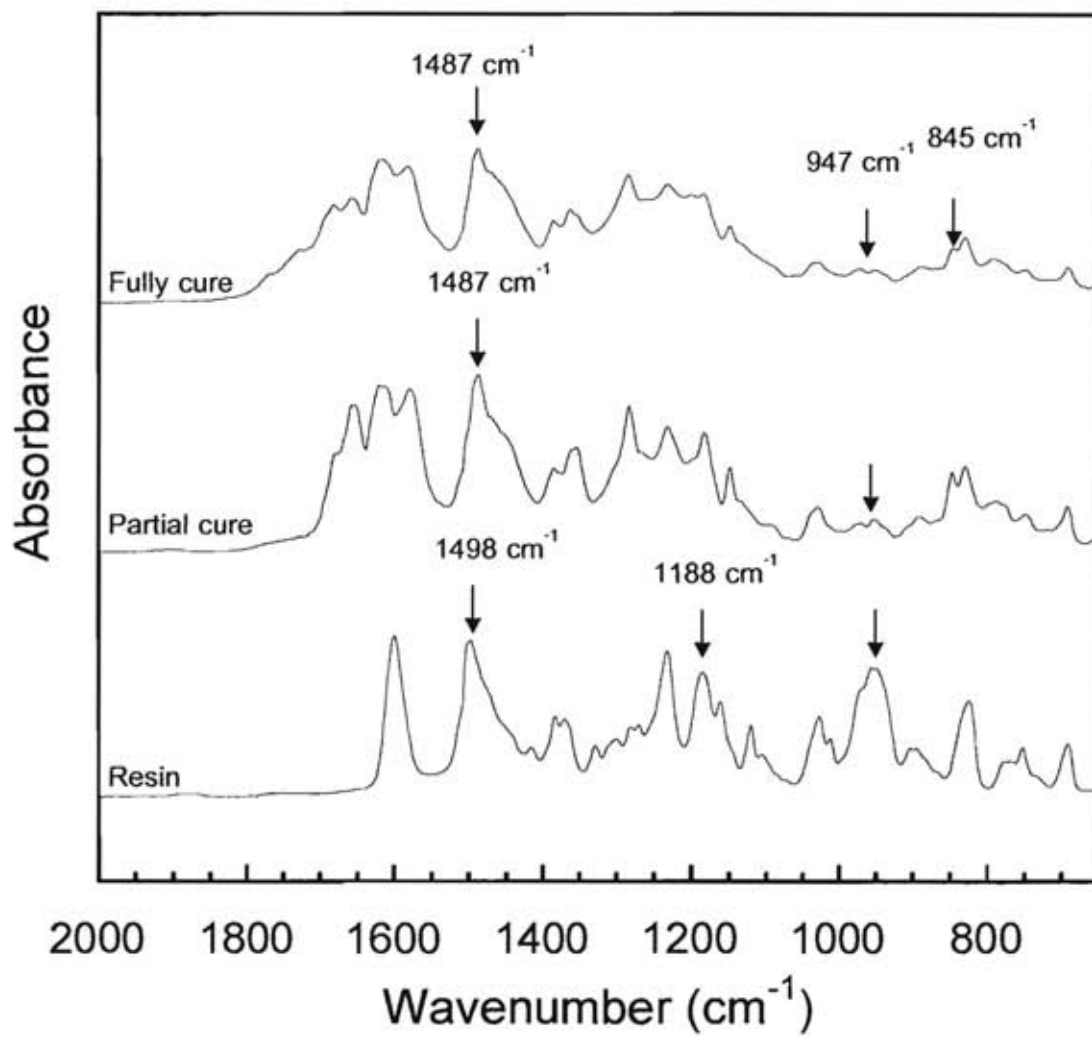


Figure 5.13 FTIR spectra of BA35x/TPP at 90:10 weight ratio.

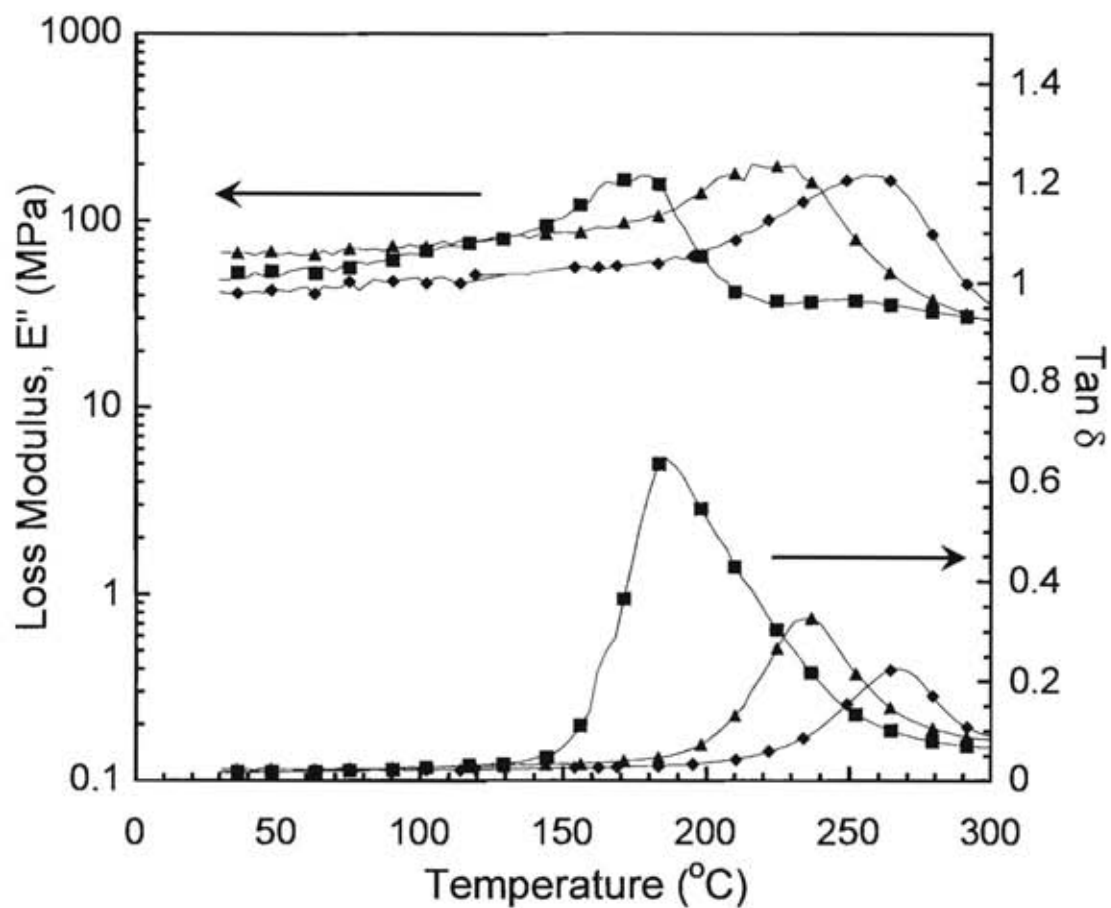


Figure 5.14 Loss modulus and $\tan \delta$ of the neat arylamine-based polybenzoxazines:

(■) BA-a, (▲) BA-mt, and (◆) BA-35x.

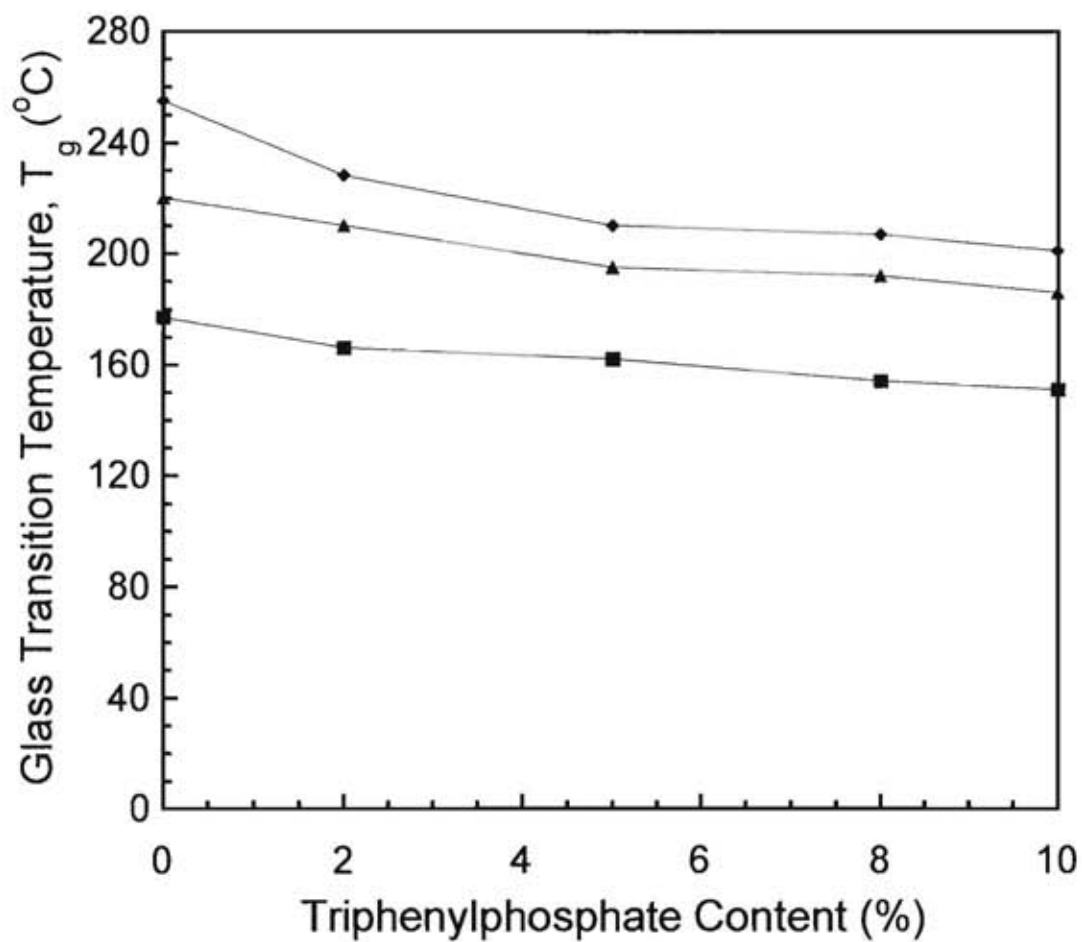


Figure 5.15 Glass transition temperature of arylamine-based polybenzoxazines at various TPP contents: (■) BA-a, (▲) BA-mt, and (◆) BA-35x.

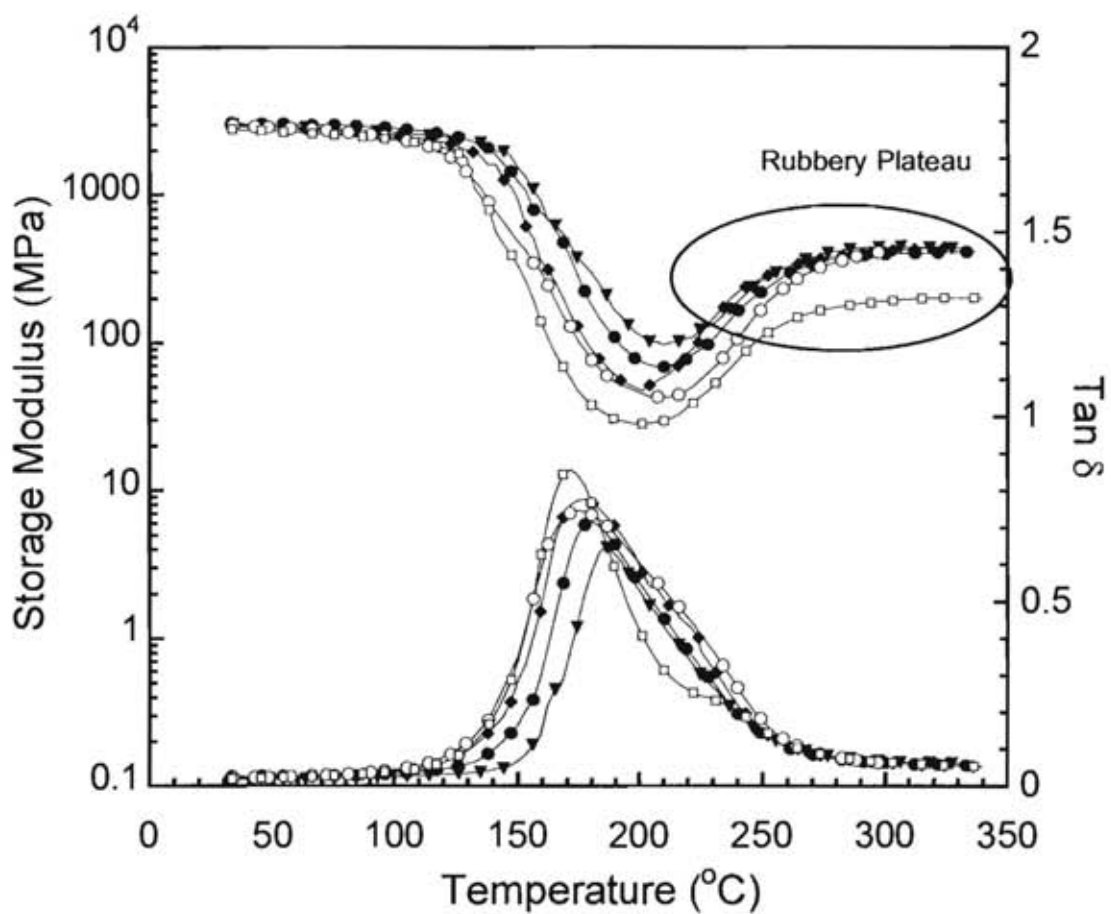


Figure 5.16 Storage modulus and $\tan \delta$ of BA-a at various TPP contents

(▼) 100:0, (●) 98:2, (◆) 95:5, (○) 92:8, and (□) 90:10.

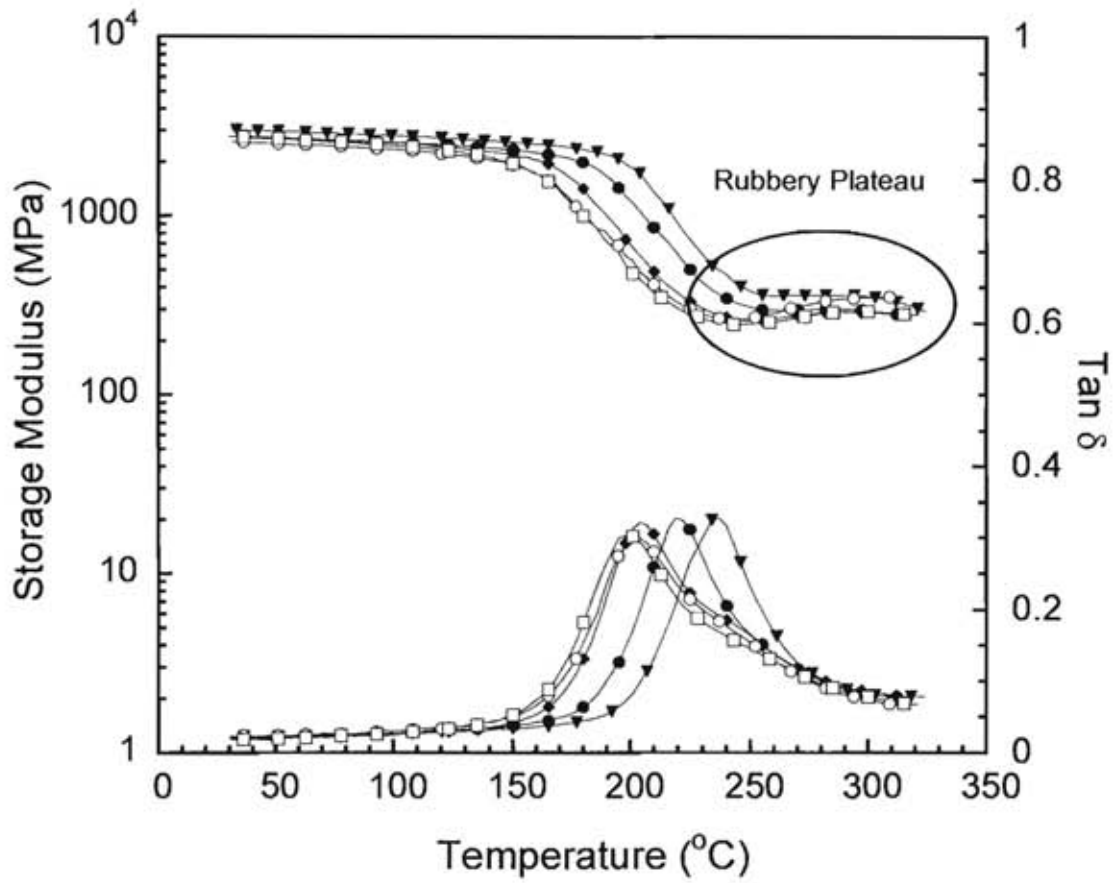


Figure 5.17 Storage modulus and $\tan \delta$ of BA-mt at various TPP contents

(\blacktriangledown) 100:0, (\bullet) 98:2, (\blacklozenge) 95:5, (\circ) 92:8, and (\square) 90:10.

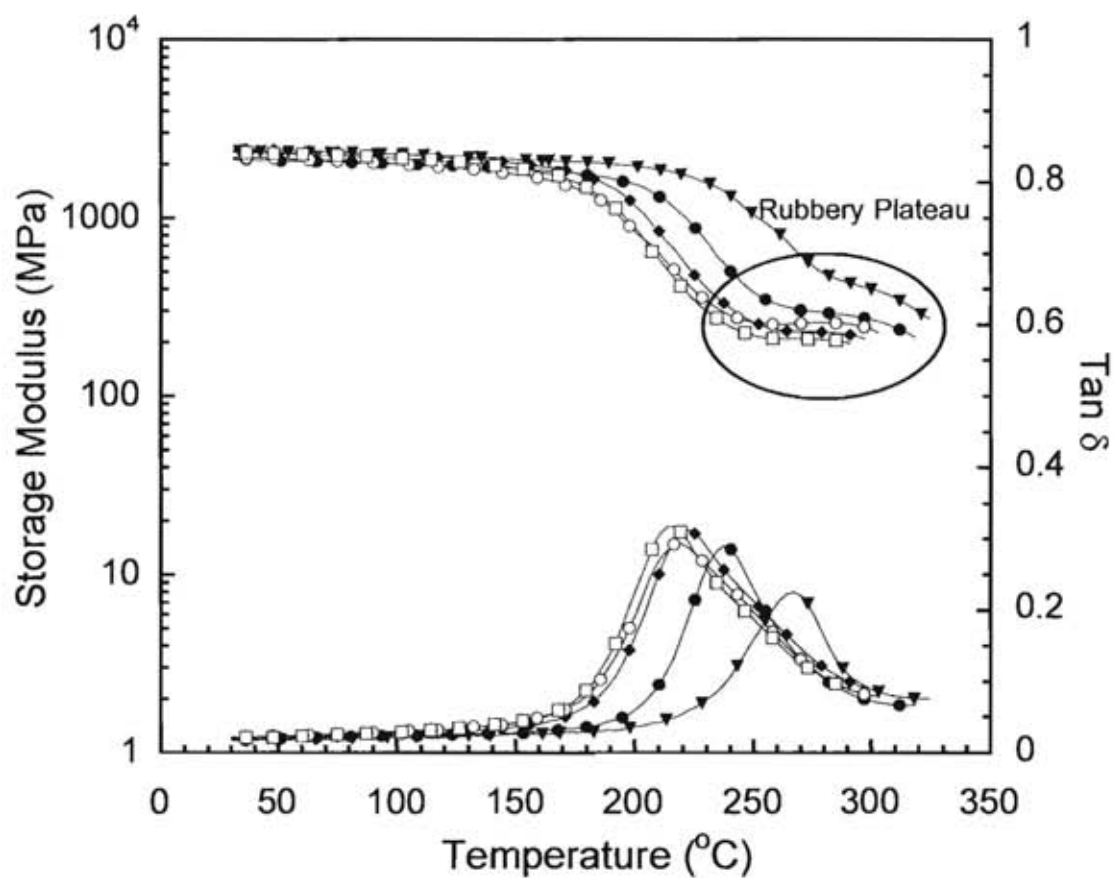


Figure 5.18 Storage modulus and $\tan \delta$ of BA-35x at various TPP contents

(\blacktriangledown) 100:0, (\bullet) 98:2, (\blacklozenge) 95:5, (\circ) 92:8, and (\square) 90:10.

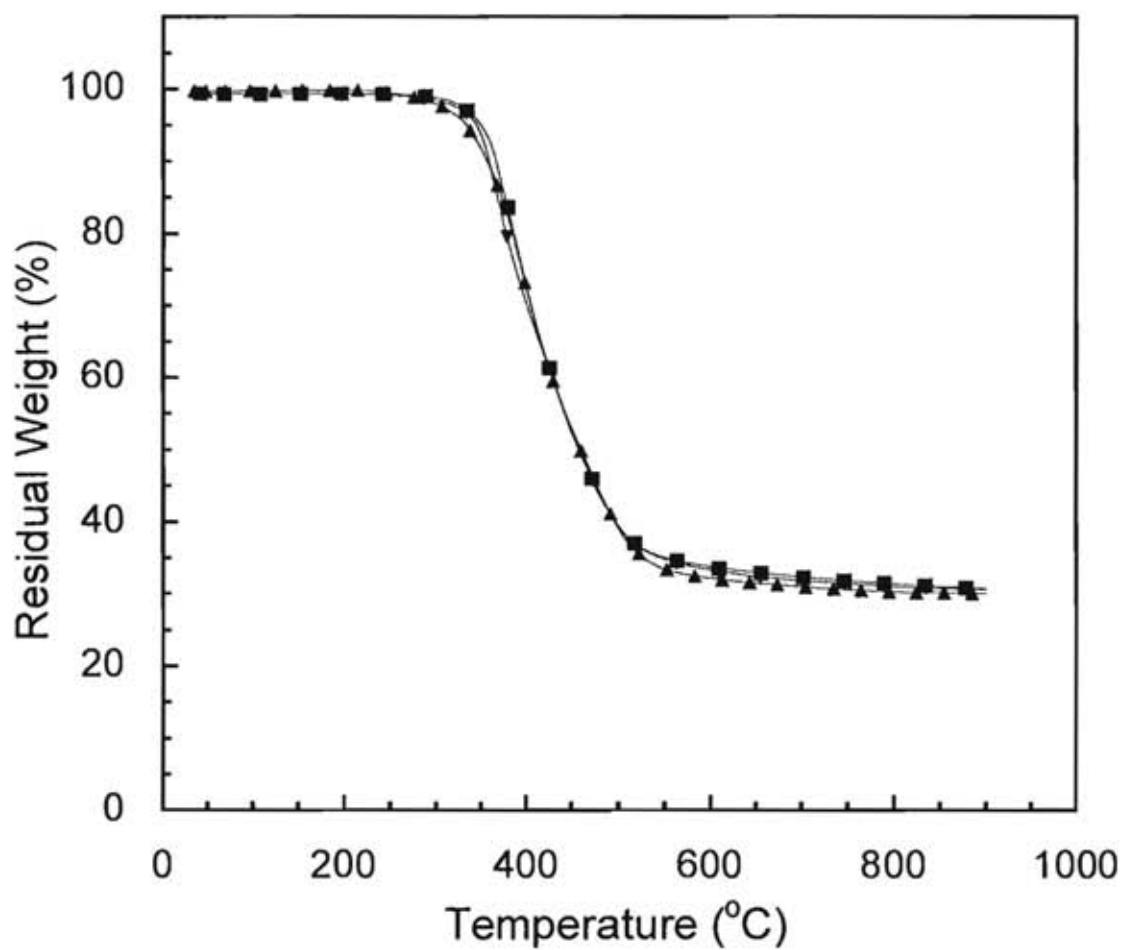


Figure 5.19 TGA thermograms of the neat arylamine-based polybenzoxazines:

(▲) BA-a, (■) BA-mt, and (◆) BA-35x.

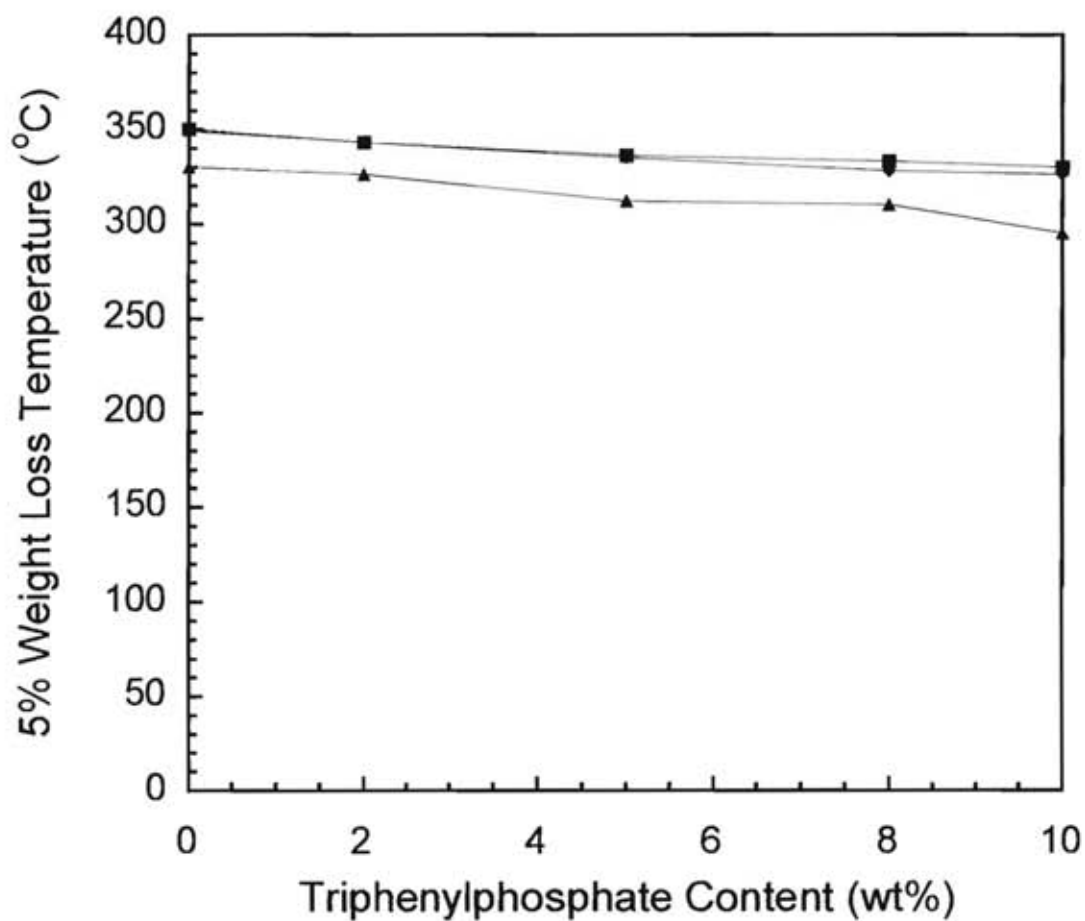


Figure 5.20 Degradation temperature at 5% weight loss of arylamine-based polybenzoxazines at various TPP contents: (■) BA-a/TPP, (▲) BA-mt/TPP, and (◆) BA-35x/TPP.

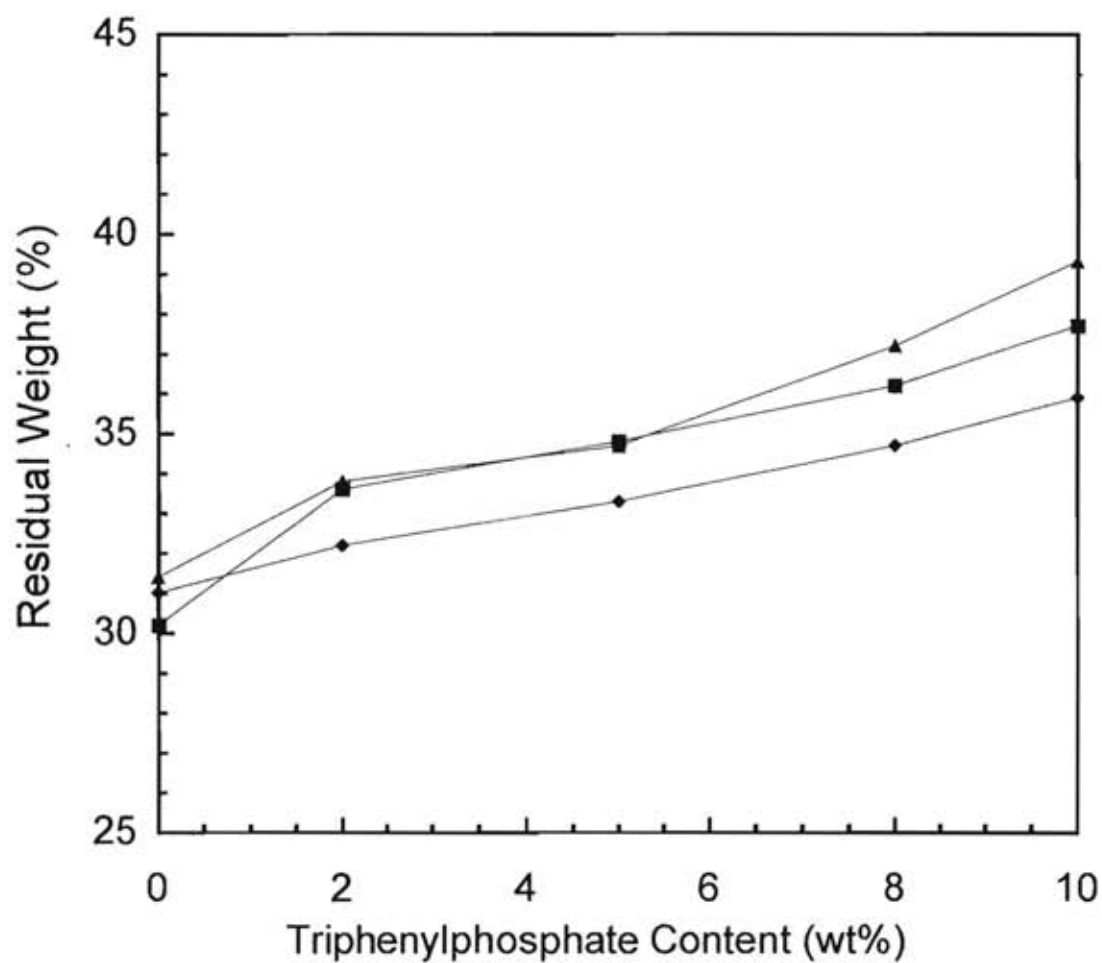


Figure 5.21 Char yield of arylamine-based polybenzoxazines at various TPP contents:

(■) BA-a/TPP, (▲) BA-mt/TPP, and (◆) BA-35x/TPP.

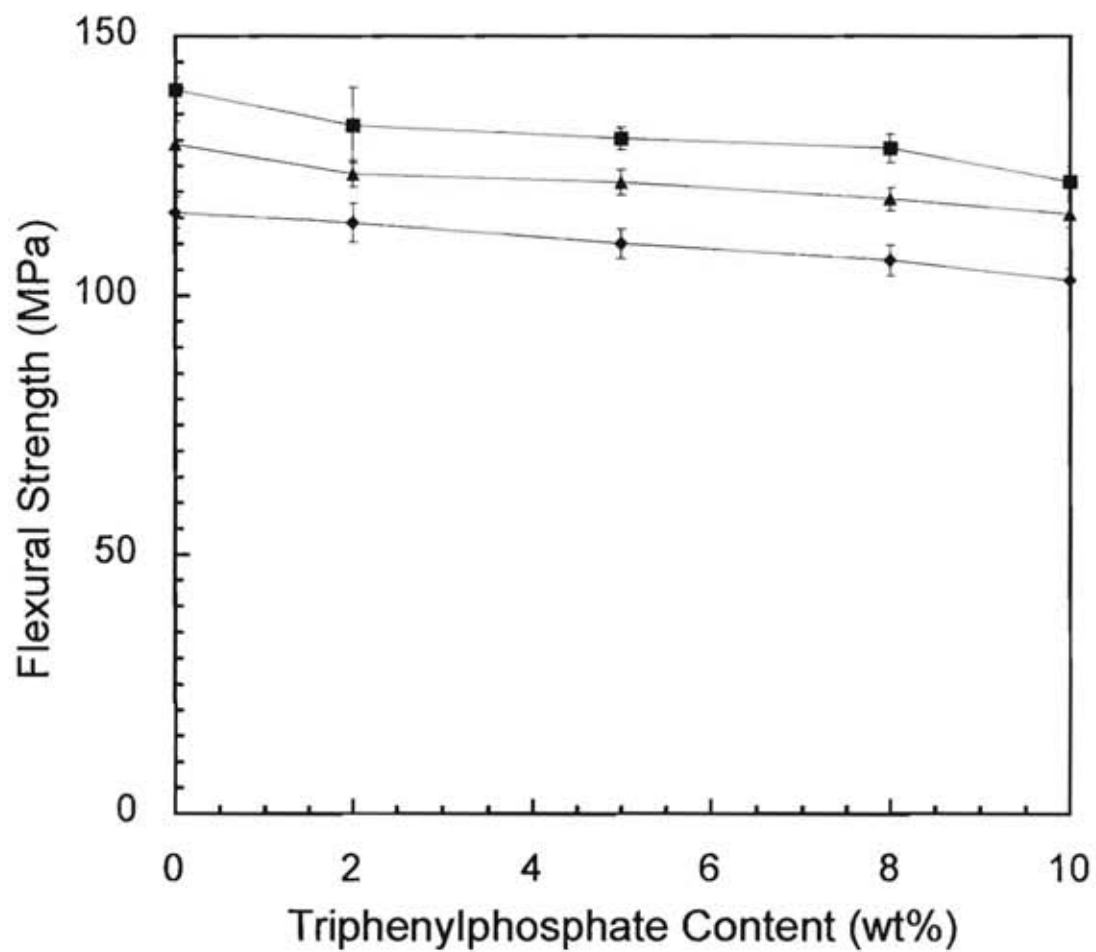


Figure 5.22 Flexural strength of arylamine-based polybenzoxazines at various TPP contents: (■) BA-a, (▲) BA-mt, and (◆) BA-35x.

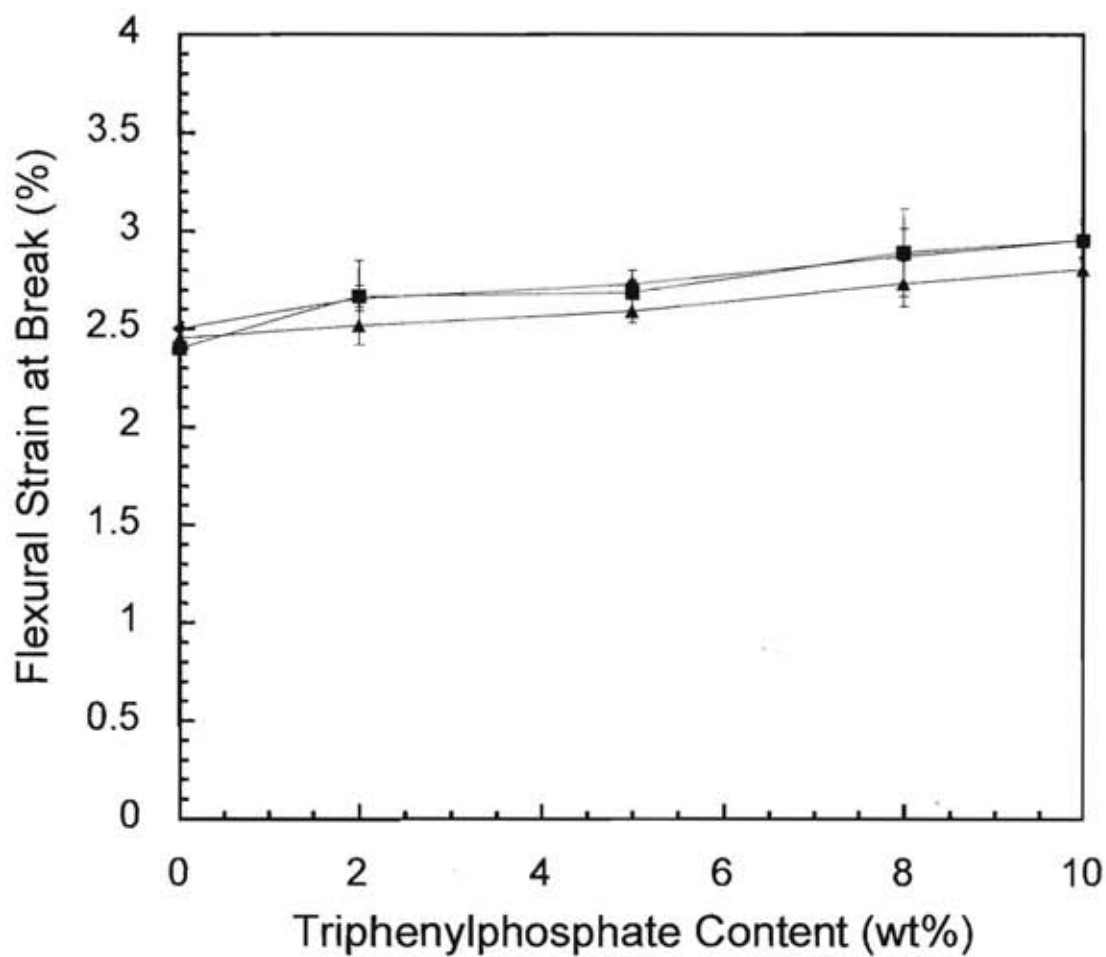


Figure 5.23 Flexural strain at break of arylamine-based polybenzoxazines at various TPP contents: (■) BA-a, (▲) BA-mt, and (◆) BA-35x.

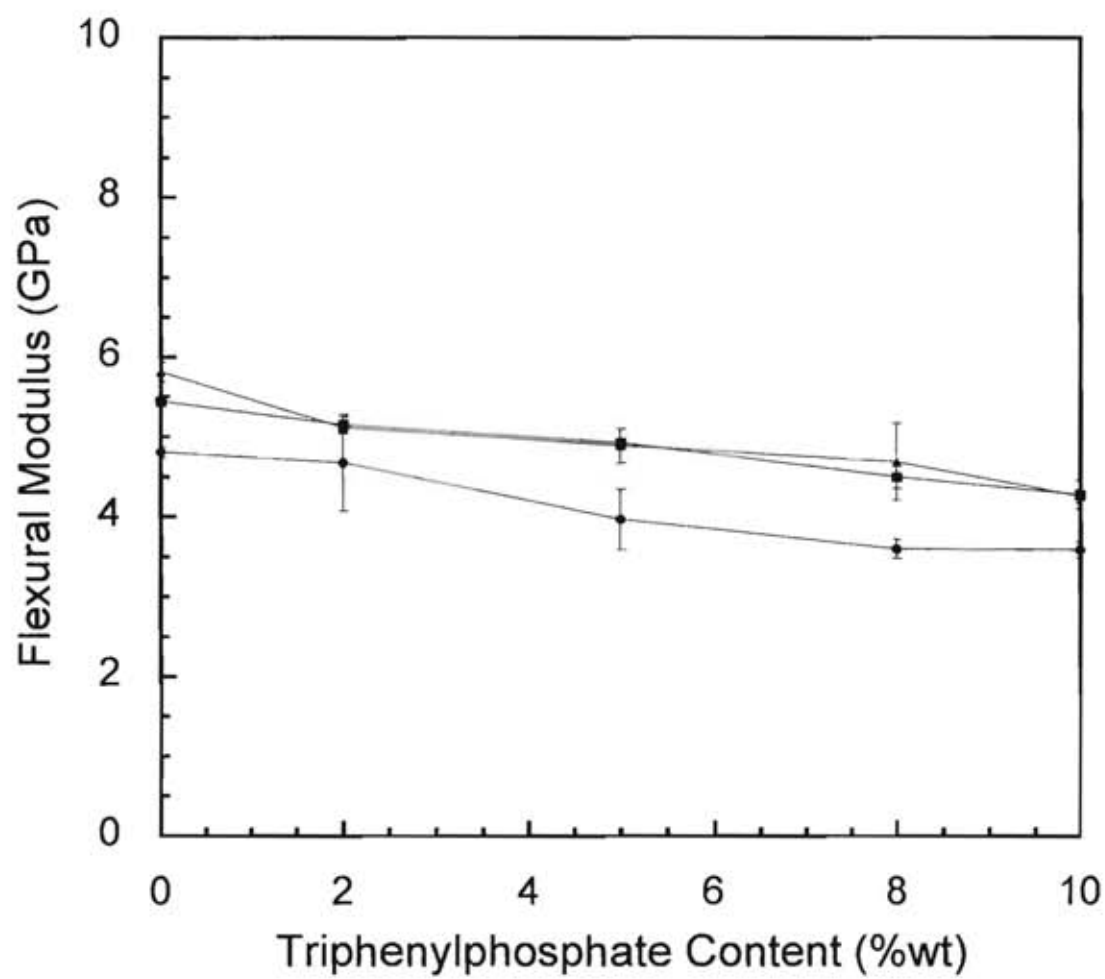


Figure 5.24 Flexural modulus of arylamine-based polybenzoxazines at various TPP contents: (■) BA-a, (▲) BA-mt, and (◆) BA-35x.

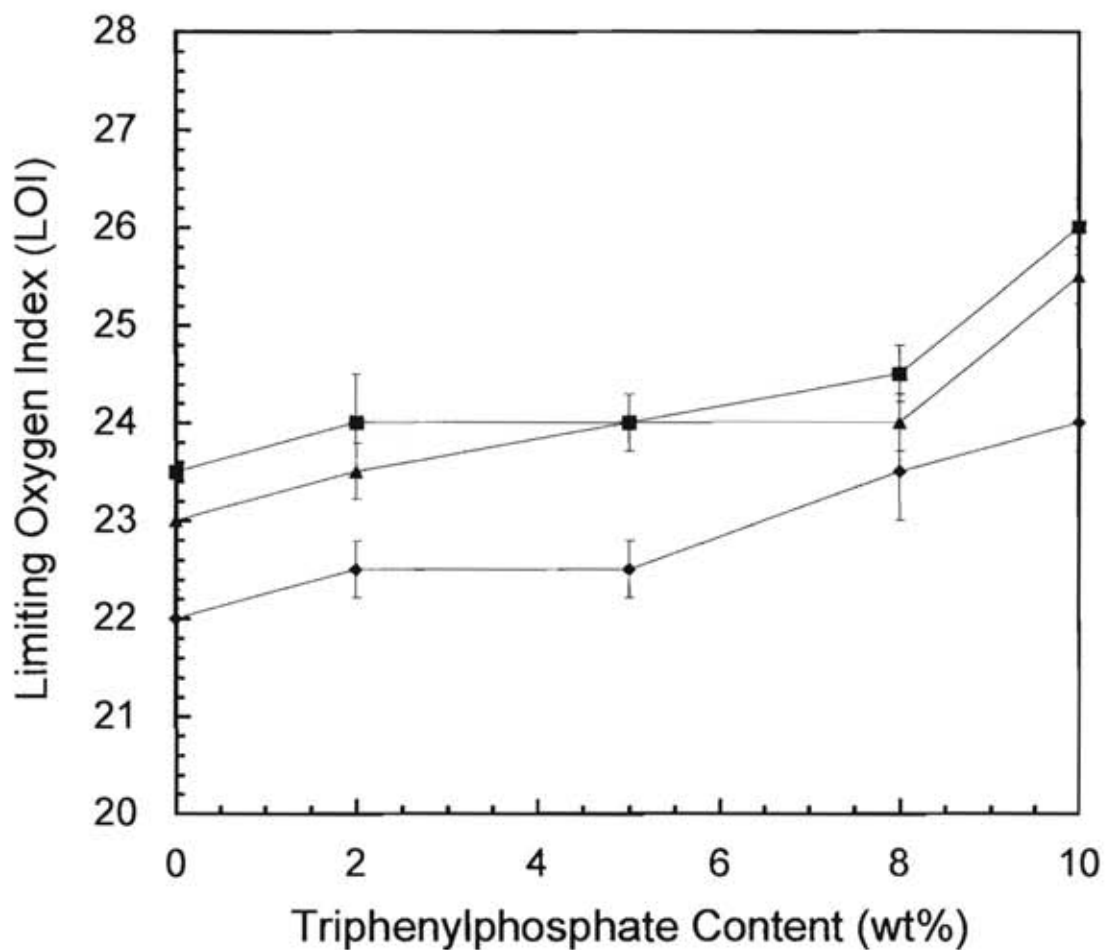
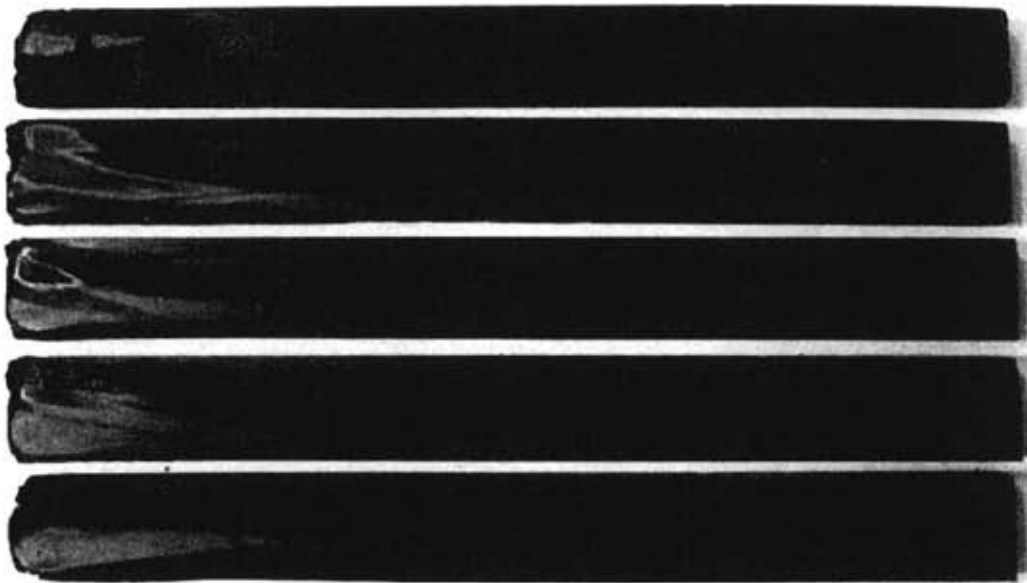
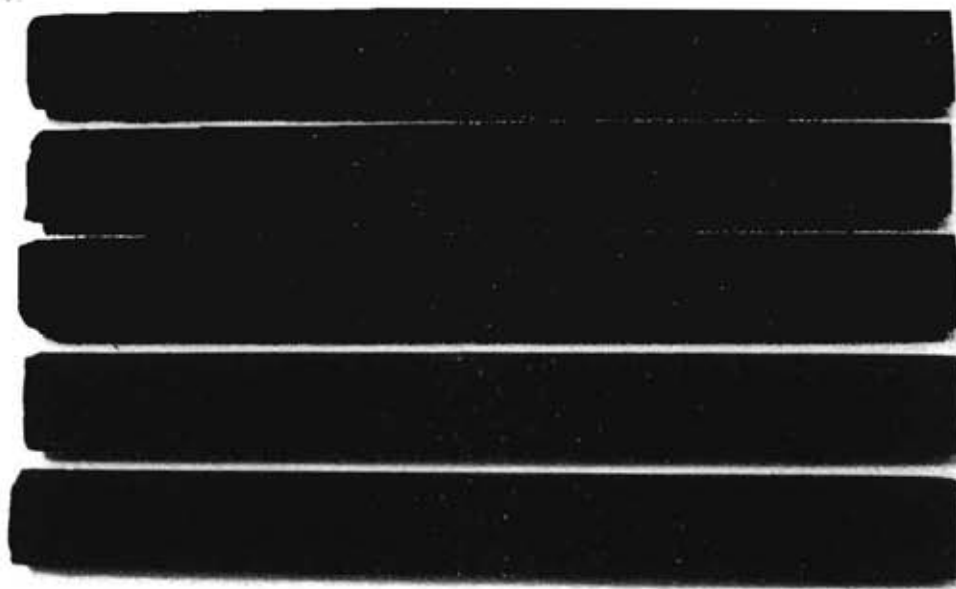


Figure 5.25 Limiting oxygen index (LOI) of arylamine-based polybenzoxazines at various TPP contents: (■) BA-a, (▲) BA-mt, and (◆) BA-35x.



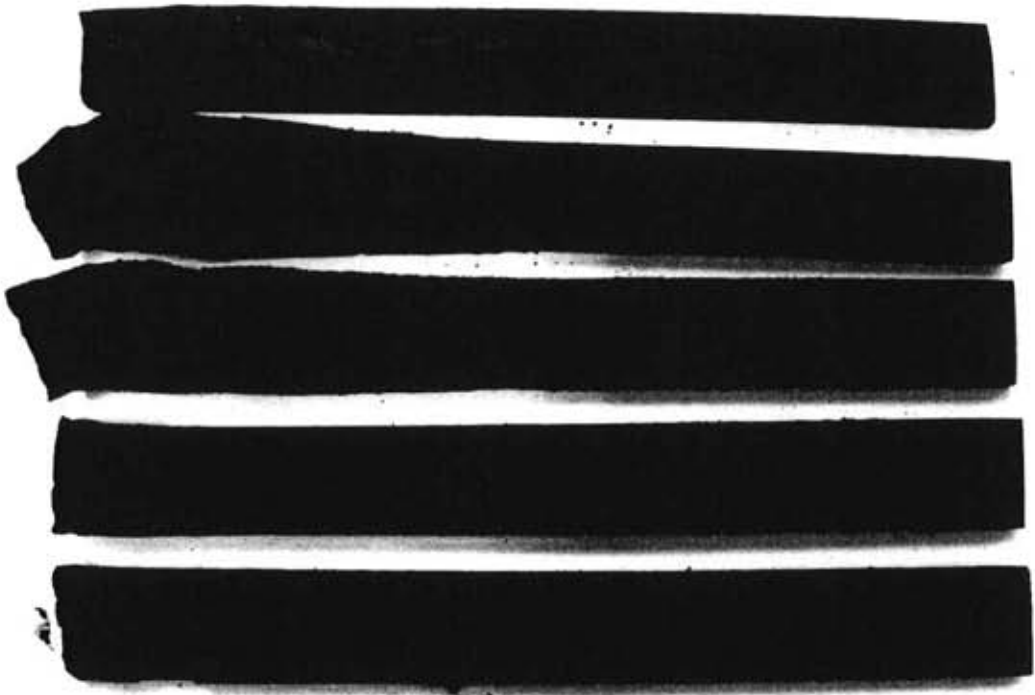
V-1

Figure 5.26 UL94 vertical test of BA-a without TPP flame retardant.



V-0

Figure 5.27 UL94 vertical test of BA-a at 5 wt% TPP flame retardant.



Burning

Figure 5.28 UL94 vertical test of BA-mt without TPP flame retardant.

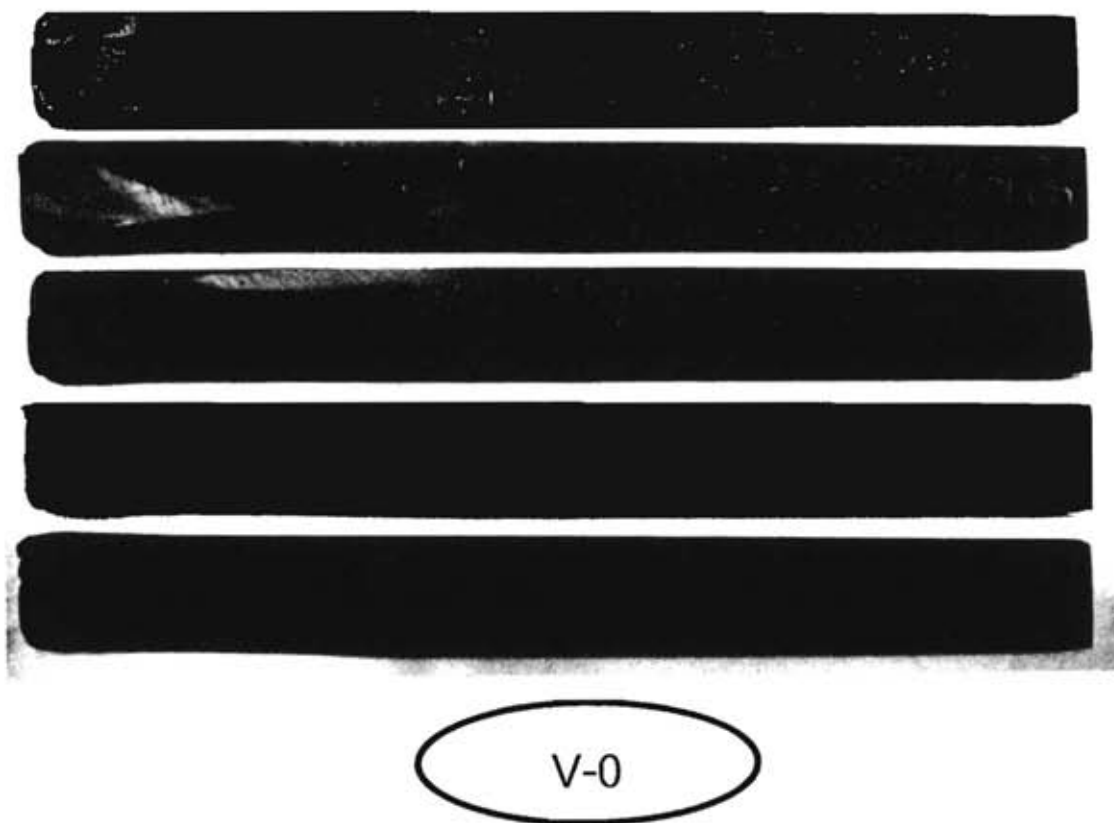


Figure 5.29 UL94 vertical test of BA-mt at 2 wt% TPP flame retardant.

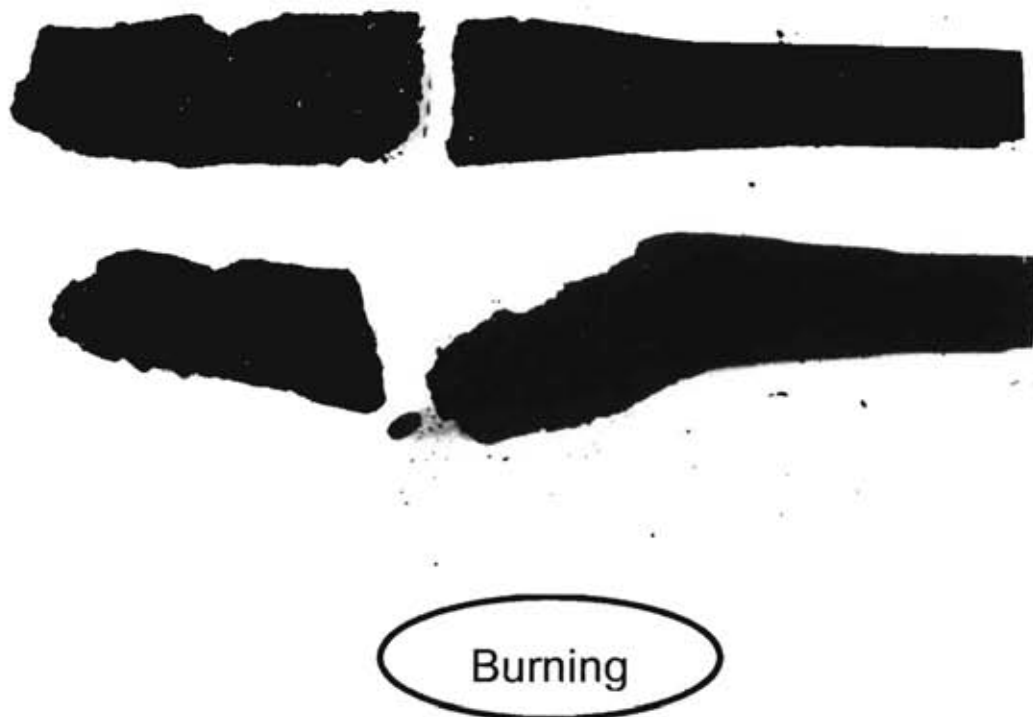
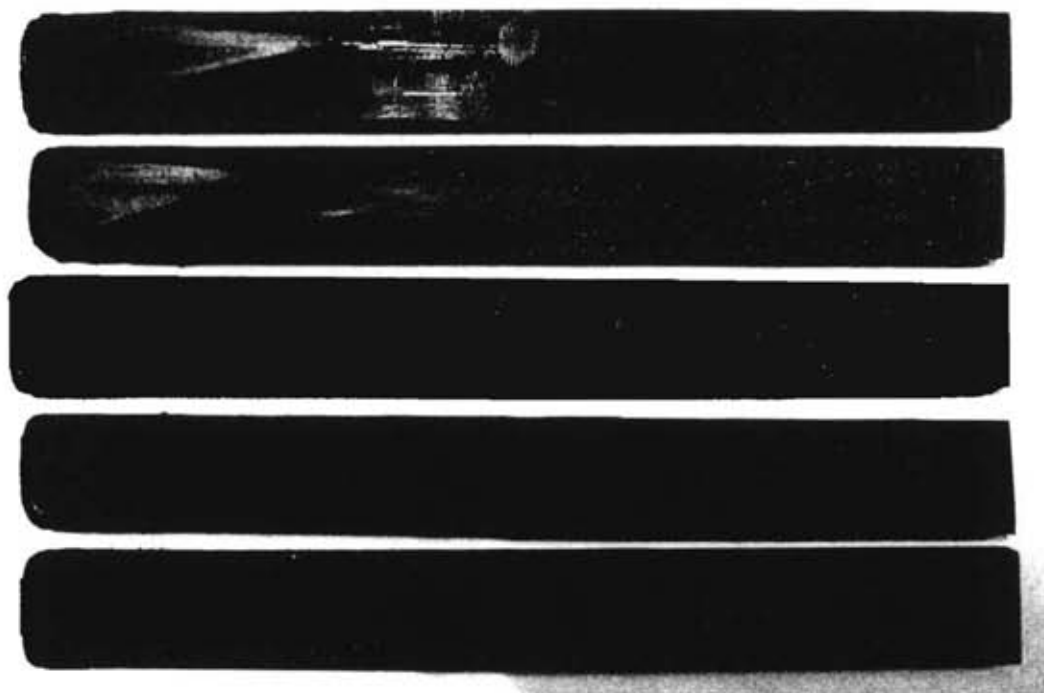


Figure 5.30 UL94 vertical test of BA-35x without TPP flame retardant.



V-0

Figure 5.31 UL94 vertical test of BA-35x at 5 wt% TPP flame retardant.

Table 5.1 : Flammability of the three types of arylamines-based polybenzoxazines without TPP flame retardant (3 mm thick sample).

Criteria for classification	BA-a	BA-mt	BA-35x
- After flame time for each individual specimen t1 or t2 (s)	14.4, 5.7	>250	>250
- Total after flame time for any condition set (s) (t1 + t2 for the 5 specimens)	100.1	>250	>250
- After flame plus after flow time for each individual specimen after the second flame application (t2 + t3) (s)	5.7	-	-
- After flame or after flow of any specimen up to the holding clamp	No	Yes	Yes
- Cotton indicator ignited by flaming particales of drops	No	No	No
Classification	V-1	Burning	Burning

Table 5.2 : Flammability of BA-a at various TPP contents (3 mm thick sample).

Criteria for classification	TPP 0%	TPP 2%	TPP 5%	TPP 8%	TPP 10%
- After flame time for each individual specimen t1 or t2 (s)	14.4, 5.7	8.5, 0.9	2.3, 0.9	0.9, 0.9	0.9, 0.7
- Total after flame time for any condition set (s) (t1 + t2 for the 5 specimens)	100.1	47.1	16.7	8.7	8.3
- After flame plus after flow time for each individual specimen after the second flame application (t2 + t3) (s)	5.7	0.9	0.9	0.9	0.7
- After flame or after flow of any specimen up to the holding clamp	No	No	No	No	No
- Cotton indicator ignited by flaming particulates of drops	No	No	No	No	No
Classification	V-1	V-1	V-0	V-0	V-0

Table 5.3 : Flammability of BA-mt at various TPP contents (3 mm thick sample).

Criteria for classification	TPP 0%	TPP 2%	TPP 5%	TPP 8%	TPP 10%
- After flame time for each individual specimen t1 or t2 (s)	>250	3.2,1.0	1.7,0.9	1.0,1.0	0.9, 0.7
- Total after flame time for any condition set (s) (t1 + t2 for the 5 specimens)	>250	21.1	13.1	8.7	8.3
- After flame plus after flow time for each individual specimen after the second flame application (t2 + t3) (s)	-	1.0	0.9	1.0	0.9
- After flame or after flow of any specimen up to the holding clamp	Yes	No	No	No	No
- Cotton indicator ignited by flaming particales of drops	No	No	No	No	No
Classification	Burning	V-0	V-0	V-0	V-0

Table 5.4 : Flammability of BA-35x at various TPP contents (3 mm thick sample).

Criteria for classification	TPP 0%	TPP 2%	TPP 5%	TPP 8%	TPP 10%
- After flame time for each individual specimen t1 or t2 (s)	>250	26.9,1.0	7.6,1.1	7.3,0.8	3.0,0.6
- Total after flame time for any condition set (s) (t1 + t2 for the 5 specimens)	>250	139.5	43.43 1	40.57	17.23
- After flame plus after flow time for each individual specimen after the second flame application (t2 + t3) (s)	-	1.0	1.1	0.8	0.6
- After flame or after flow of any specimen up to the holding clamp	Yes	No	No	No	No
- Cotton indicator ignited by flaming particales of drops	No	No	No	No	No
Classification	Burning	V-1	V-0	V-0	V-0

CHAPTER VI

CONCLUSIONS

Effect of triphenylphosphate flame retardant (TPP) at various weight ratios in three types of arylamines-based benzoxazine resins were investigated. Among those polybenzoxazines, BA-a showed the best fire resistant properties, provided a V-1 rating, while BA-mt and BA-35x did not pass UL-94 vertical test standard. All three polybenzoxazines achieved the highest V-0 rating of UL94 standard with only a small addition of TPP. That is BA-mt passed V-0 rating with an addition of 2 wt% of TPP. Whereas, BA-a and BA-35x achieved V-0 rating at 5 wt% of TPP addition. Limiting oxygen index (LOI) of these polybenzoxazines were also enhanced with increasing amount of TPP. As a result, it can be concluded that the flame retardancy of polybenzoxazines can be improve by the addition of relatively small amount of TPP,

TGA results revealed that the degradation temperature at 5 % weight loss of the polybenzoxazines decreased with increasing TPP content in the polymers. On the other hand, residual weight at 800 °C increased from 30.2, 31.4, and 31.0 to 37.7, 39.3, and 35.9% at 10 wt% of TPP for BA-a, BA-mt, and BA-35x, respectively. From the DSC experiment, ring opening polymerization of benzoxazine resins was observed to be accelerated by a presence of TPP that possibly acted as a Lewis acid catalyst of benzoxazine resins.

The glass transition temperature obtained from the peaks of loss moduli of the polybenzoxazines were observed to be reduced with an addition of TPP. In dynamic mechanical property measurement, flexural strength and flexural modulus of all polybenzoxazines were also found to slightly decrease with increasing amount of the TPP. Meanwhile, the flexural strain-at-break was increased with increasing TPP. Finally TPP was found to disperse homogenously in polybenzoxazines. However, no chemical bonding between the additive and those polybenzoxazines was observed.

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APPENDICES

APPENDIX A

Arylamine-based Benzoxazine Resins and TPP Characterization

Appendix A-1 Curing temperature of the neat arylamine-based benzoxazine resins.

Benzoxazine resin	Curing temperature (°C)	
	Major	Minor
BA-a	236	-
BA-mt	221	239
BA-35x	211	243

Appendix A-2 Major of the curing temperatures of BA-a at various TPP contents.

BA-a/TPP	curing temperature (°C)
100:0	236
98:2	221
95:5	218
92:8	214
90:10	212

Appendix A-3 Major of the curing temperatures of BA-35x at various TPP contents.

Benzoxazine resin	Curing temperature (°C)	
	Major	Minor
100:0	211	243
98:2	199	230
95:5	198	228
92:8	195	220
90:10	191	220

APPENDIX B

Characterization of Arylamine-based Polybenzoxazines and TPP Mixtures

Appendix B-1 Glass transition temperature (T_g) and storage modulus at room temperature (E') of arylamine-based polybenzoxazine at various TPP contents.

Benzoxazine:TPP	BA-a		BA-mt		BA-35x	
	T_g (°C)	E' (GPa)	T_g (°C)	E' (GPa)	T_g (°C)	E' (GPa)
100:0	177	3.03	220	3.02	255	2.37
98:2	166	3.07	210	2.78	228	2.13
95:5	162	2.93	195	2.77	210	2.40
92:8	154	2.98	192	2.60	207	2.18
90:10	151	2.79	186	2.77	201	2.32

Appendix B-2 Degradation temperatures (T_d) at 5% weight loss and residue weights (char yield) at 800°C of arylamine-based polybenzoxazine at various TPP contents.

Benzoxazine:TPP	BA-a		BA-mt		BA-35x	
	T_d (°C)	Char(%)	T_d (°C)	Char(%)	T_d (°C)	Char(%)
100:0	330	30.2	350	31.4	349	31.0
98:2	326	33.6	343	33.8	343	32.2
95:5	312	34.8	336	34.7	335	33.3
92:8	310	36.2	333	37.2	328	34.7
90:10	295	37.7	330	39.3	326	35.9

Appendix B-3 Flexural strength of arylamine-based polybenzoxazine at various TPP contents.

Benzoxazine:TPP	Flexural strength (MPa)		
	BA-a	BA-mt	BA-35x
100:0	139.6	129.2	116.0
98:2	132.8	123.4	114.0
95:5	130.2	121.8	109.9
92:8	128.4	118.5	106.7
90:10	122.0	115.7	102.8

Appendix B-4 Flexural strain at break of arylamine-based polybenzoxazine at various TPP contents.

Benzoxazine:TPP	Flexural strain at break (%)		
	BA-a	BA-mt	BA-35x
100:0	2.40	2.45	2.50
98:2	2.66	2.51	2.65
95:5	2.68	2.58	2.72
92:8	2.88	2.72	2.86
90:10	2.95	2.80	2.94

Appendix B-5 Flexural modulus of arylamine-based polybenzoxazine at various TPP contents.

Benzoxazine:TPP	Flexural modulus (GPa)		
	BA-a	BA-mt	BA-35x
100:0	5.81	5.44	4.80
90:10	5.11	5.14	4.67
80:20	4.88	4.92	3.96
70:30	4.68	4.49	3.60
60:40	4.25	4.27	3.58

Appendix B-6 The Limiting oxygen index (LOI) of arylamine-based polybenzoxazine at various TPP contents.

Benzoxazine:TPP	LOI values		
	BA-a	BA-mt	BA-35x
100:0	23.5	23.0	22.0
90:10	24.0	23.5	22.5
80:20	24.0	24.0	22.5
70:30	24.5	24.0	23.0
60:40	26.0	25.5	24.0

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- Polymer Bulletin
- Polymers and Polymer Composites
- Polymer Degradation and Stability
- Journal of the American Ceramic Society
- Journal of Biobased Materials and Bioenergy
- Composites Part A: Applied Science and Manufacturing
- Journal of Applied Polymer Science
- Express Polymer Letters
- Songklanakarin Journal of Science and Technology
- Journal of Non-Crystalline Solids
- International Journal of Biological Macromolecules
- Biomacromolecules
- Journal of Metals, Materials, and Minerals

PROFESSIONAL AFFILIATIONS:

Society of Plastic Engineers, USA.
 Engineering Institute of Thailand
 Forest Production Society, USA

COMMERCIALIZED RESEARCH PRODUCT:

Breast training model for breast cancer examination, Thailand patent pending (see website for details)
http://pioneer.netserv.chula.ac.th/~schompun/INDEX_files/page0005.htm

CURRENT RESEARCH TOPICS:

- 1) Natural fiber reinforced composites: a development of environmentally friendly wood substitutes.
- 2) Composites from polybenzoxazine and polybenzoxazine alloys.
- 3) Processing and characterization of PC/ABS blends and their composites.
- 4) Impact property enhancement of PVC wood composites using styrenic copolymers.
- 5) Non-phosgene condensation polymerization of polycarbonate.
- 6) Characterization of polyurethane coatings: Water-borne, UV cure.
- 7) Fire resistance of polymers: Formulation and Testing.

(ภาษาไทย)นางสาวนิตินาต สุกภาณัจญ์.....ตำแหน่งทางวิชาการ ผู้ช่วยศาสตราจารย์ประจำสาขา
 วิศวกรรมพอลิเมอร์(ภาษาอังกฤษ)Ms.Nitinat Suppakarn.....
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Case Western Reserve University, USA	Ph.D.	Macromolecular Science	2542

ผลงานวิจัยที่พิมพ์เผยแพร่ (ระบุแหล่งพิมพ์และปีที่พิมพ์)

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EDUCATION:

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- D. Eng., Department of Chemical Engineering Chulalongkorn University, Bangkok, Thailand.
Dissertation: “Development of Benzoxazine-Based Resins for Wood Composite Application.”
Grade of dissertation: Very good
- 2001- 2002
- M.Eng., Department of Chemical Engineering Chulalongkorn University, Bangkok, Thailand.
Thesis: “Wood-substituted Composites from Highly-filled Polybenzoxazine.”
Grade of Thesis: Very good
- 1999 – 2001
- B.Eng., Department of Chemical Engineering King Mongkut’s University of Technology Thonburi, Bangkok, Thailand.
Senior Project: “Development of Management System for Environmental Safety and Health in KMUTT: Chromium Removal from COD Waste by Reduction- Neutralization Method.”
- 1996-1999
- Diploma (Industrial Chemistry Technology) Rajamangala University of Technology Krungthep, Thailand.

WORK EXPERIENCES:

- Oct. 2008-present
- Lecturer, Dept. Chemical Engineering, Faculty of Engineering, Srinakharinwirot University
- Jun. 2008-Sep. 2008
- Guest Lecturer (Chemical Engineering Thermodynamic I) Dept. Chemical Engineering, Faculty of Engineering, Srinakharinwirot University
- Jan. 2008- Dec. 2008
- Researcher
Polymer Engineering Research Laboratory, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University.
PTT Phenol Company Limited: An Affiliated Company of PTT Group.
Vinythai Public Company Limited.
- Jun. 2007-Jan. 2008
- Research Assistant
PTT Phenol Company Limited: An Affiliated Company of PTT Group.
- Jul. 2007-Oct. 2007
- Research Assistant
Collaboration between National Metal and Materials Technology Center and Department of Chemical Engineering, Chulalongkorn University:
Development of Light Weight Ballistic Armor from Polybenzoxazine Alloys and Kevlar™ Fiber.
- Jun. 2006-May 2007
- Research Assistant
PTT Chemical Public Company Limited: An Affiliated Company of PTT Group: Innovation Project.
- Jan. 2005-Dec. 2006
- Breast Model Production Team for Utilizing in Teaching Breast Self Examination
Collaboration between Department of Chemical Engineering and Faculty of Nursing, Chulalongkorn University.
- Nov. 2006
- Solving material problems of composite industry e.g. Eastern Hobas Pipes Co.,Ltd (Thailand), Viking Life-Saving Equipment (Thailand) Ltd.
- Jun. 2005-Oct. 2005
- Guest Lecturer (General Chemistry), Department of Chemistry, Faculty of Science and Technology, Rajamangala University of Technology Krungthep

ANALYTICAL TECHNIQUES:

- Thermal Analysis including DMA, DSC, TGA, and TMA
- SEM, FTIR, Rheometer, GPC, Nanoindentation, Contact angle, LCR meter, Universal testing machine
- Single and Twin Screw Extrusion, Injection Molding, Compression Molding

FILED OF INTEREST: Polymer Blend/Alloy and Polymer Composite
Polymer Networks (Thermosets)

PUBLICATIONS:

PATENT:

- S. Rimdusit and C. **Jubsilp**, Polymer from Anhydride Modified Polybenzoxazine, Thailand Patent pending (2007).

INTERNATIONAL PAPERS:

- C. **Jubsilp**, T. Takeichi, S. Rimdusit, "Curing kinetics of Benzoxazine-Epoxy Novolac Copolymer Investigated by Non-isothermal Differential Scanning Calorimetry". *Polym. Degrad. Stab.* 2010; **95**: 918. (impact factor = 2.154) ISI : Journal Citation Reports, 2009.
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- C. **Jubsilp**, T. Takeichi, S. Hiziroglu, and S. Rimdusit. "Effect of Resin Composition on Microwave Processing and Thermophysical Properties of Benzoxazine-Epoxy-Phenolic Ternary Systems Filled with Silicon Carbide (SiC) Whisker." *Polym. Eng. Sci.* 2009; **49**: 1022. (impact factor = 1.248) ISI : Journal Citation Reports, 2009.
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INTERNATIONAL AND LOCAL CONFERENCES:

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- C. **Jubsilp**, T. Takeichi, S. Tiptipakorn, W. Tanthapanichakoon, and S. Rimdusit, "Characterization of High Performance Silicon Carbide-filled Polybenzoxazine", Proceedings of Asian Pacific Confederation of Chemical Engineering (11th APCChe), Oral Presentation, Kuala Lumpur, Malaysia, 28-30 August 2006.
- C. **Jubsilp**, T. Takeichi, W. Tanthapanichakoon, and S. Rimdusit, "Kinetic Studies of Curing Reaction of Polyfunctional Benzoxazine Resins by Dynamic DSC Methods", Proceedings of Eco-Energy and Materials Science and Engineering Symposium (3rd EMSES), Oral Presentation, Chiang Mai, Thailand, 6-9 April 2005.
- C. **Jubsilp**, T. Takeichi, S. Covavisaruch, W. Tanthapanichakoon, and S. Rimdusit, "Thermal and Mechanical Characterization of High Performance Silicon Carbide-filled Polybenzoxazine", Undergraduate and Graduated Academic Conference for the Year 2004, Poster Presentation, Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand, 17-18 March 2005.
- C. **Jubsilp**, T. Takeichi, and S. Rimdusit, High Performance Wood Composites based on Benzoxazine-Epoxy Alloys, The 5th Research Progress Meeting in Particle Technology and Material Processing Laboratory (PTMP), Oral Presentation, Dept. Chemical Engineering, Chulalongkorn University, Bangkok, Thailand, 6-7 March 2004.
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- C. **Jubsilp**, W. Tanthapanichkoon, and S. Rimdusit, "High Performance Wood Composite Made of Highly Filled Polybenzoxazine", Proceedings of the 2nd Asian Particle Technology Symposium, Oral Presentation, Penang, Malaysia, 17-19 December 2003.
- **Jubsilp**, C., Tanthapanichkoon, W., and Rimdusit, S. Wood-substituted Composites from Highly-filled Polybenzoxazine System. The 2nd Research Progress Meeting in Particle Technology and Material Processing Laboratory (PTMP), Oral Presentation, Dept. Chemical Engineering, Chulalongkorn University, Bangkok, Thailand, 24-25 August 2002.
- **Jubsilp**, C., Tanthapanichkoon, W., and Rimdusit, S. Wood-substituted Composites from Highly-filled Polybenzoxazine System. 28th Congress on Science and Technology of Thailand, Poster Presentation, The Science Society of Thailand under the Patronage of His Majesty the King. Queen Sirikit National Convention Center, Bangkok, Thailand, 24-26 October 2002.

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EDUCATION

- 2008-2010 Chulalongkorn University
Master of Engineering in Chemical Engineering GPA: 3.75
- 2004-2007 Chulalongkorn University
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Coursework includes: Material and Energy Balances, Process Dynamics and control, Chemical Process and Plant Design, and Petroleum Technology

OCCUPATION

- Michelin Siam Co.,Ltd.
Position: Quality Obtenion Engineer (Jan 2011-Present)
Responsibilities:
 - Facilitate the process control approach in the shop and initiate qualification of the process evolutions.
 - Define methods and manage process parameters

EXPERINCES

- Completed an internship program at Thai Oil Co.,Ltd in Commercial Marketing, Crude Supply (March – May 2007)
- Elected as Special Research Student of the programme of "Educational System for Future Environment Leader in East Asia" at Toyohashi University of Technology under the Implementation of JASSO, Japan Student Services Association (May 2009 – March 2010)

RESEARCH PROJECTS

- Studied in the Tropic of "DME Synthesis at Low Temperature" for Senior Project
- Studied in the Tropic of "Effect of Triphenylphosphate Flame Retardant on Properties of Polybenzoxszines" for Thesis

PROCEEDING PAPERS AND PRESENTATIONS

- "DME Synthesis at Low Temperature"
Oral Presentation in the Science Forum 2008, Chulalongkorn University, Thailand
- "Effect of Triphenylphosphate Flame Retardant on Properties of Polybenzoxazines"
Oral Presentation in the Thailand-Japan International Academic (TJIA) Conference 2009, Kyoto, Japan
Oral Presentation in the 6th Thailand Materials Science and Technology (MSAT) Conference 2010, Miracle Grand Convention Hotel, Bangkok, Thailand

SKILLS

- Language: Fluent in English and Thai
- Computer: Knowledge of Microsoft Office (Word, Excel, PowerPoint, Outlook, and Publisher), MATLAB, HYSYS and Chem-draw

