ผลของชนิดและปริมาณของฟีนอลิกเรซินต่อภาวะการบ่ม สมบัติทางความร้อนและพฤติกรรมการติดไฟของพอลิเมอร์แอลลอยด์เบนซอกซาซีน/ฟีนอลิก

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EFFECTS OF TYPES AND AMOUNT OF PHENOLIC RESINS ON CURING CONDITION, THERMAL PROPERTIES AND IGNITION BEHAVIOR OF BENZOXAZINE/PHENOLIC POLYMER ALLOYS

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พอลิเมอร์แอลลอยด์ระหว่างเบนซอกซาซีนเรซินและฟีนอลิกเรซินสามารถเตรียมได้โดยการผสมองค์ประกอบทั้งสองแล้วให้ความร้อนจนเกิดการบ่มอย่างสมบูรณ์ จากการศึกษาด้วยเทคนิค DSC พบว่า ภาวะการบ่มที่เหมาะสมสำหรับแอลลอยด์เบนซอกซาซีน/ฟีนอลิกเรซินชนิดโนโวแลกคือ 150 องศาเซลเซียส/1 ชั่วโมงและ180 องศาเซลเซียส/1 ชั่วโมง เมื่อปริมาณของโนโวแลกต่ำกว่า 50 เปอร์เซ็นต์โดยน้ำหนัก และภาวะการบ่มที่เหมาะสมที่ 150 องศาเซลเซียส/ 1 ชั่วโมงและ180 องศาเซลเซียส/2 ชั่วโมง เมื่อปริมาณของโนโวแลกสูงกว่า 50 เปอร์เซ็นต์โดยน้ำหนัก ในขณะที่ภาวะการบ่มที่เหมาะสมสำหรับแอลลอยด์เบนซอกซาซีน/ฟีนอลิกเรซินชนิดรีโซลคือ 100 องศาเซลเซียส/2 ชั่วโมงและ180 องศาเซลเซียส/1.5 ชั่วโมง เมื่อปริมาณของรีโซลต่ำกว่า 50 เปอร์เซ็นต์โดยน้ำหนัก และภาวะการบ่มที่เหมาะสมที่ 100 องศาเซลเซียส/2 ชั่วโมงและ180 องศาเซลเซียส/2 ชั่วโมง เมื่อปริมาณของรีโซลสูงกว่า 50 เปอร์เซ็นต์โดยน้ำหนัก ฟีนอลิกเรซินทั้งสองชนิดช่วยปรับปรุงเสถียรภาพทางความร้อนและเพิ่มการหน่วงไฟของเบนซอกซาซีน โดยมีแนวโน้มว่าเมื่อปริมาณฟีนอลิกทั้งสองเพิ่มขึ้น อุณหภูมิการสลายตัวด้วยความร้อนและค่า LOI ของแอลลอยด์มีค่าสูงขึ้น ในขณะที่อัตราการเผาลดต่ำลง แต่จะเห็นได้ชัดเจนว่า ณ ปริมาณผสมที่เท่ากัน แอลลอยด์ระบบเบนซอกซาซีน/รีโซลจะให้ปริมาณการเกรียมสูงกว่าแอลลอยด์ระบบเบนซอกซาซีน/โนโวแลก ซึ่งเป็นข้อบ่งชี้ว่าแอลลอยด์ระบบเบนซอกซาซีน/รีโซลมีการหน่วงไฟที่ดีกว่าแอลลอยด์ระบบเบนซอกซาซีน/โนโวแลก

ภาควิชา วัสดุศาสตร์ ลายมือชื่อนิสิต..

สาขาวิชา วิทยาศาสตร์พอลิเมอร์ประยุกต์-และเทคโนโลยีสิ่งทอ ลายมือชื่ออาจารย์ที่ปรึกษา..........................

ปีการศึกษา 2546 ลายมือชื่ออาจารย์ที่ปรึกษาร่วม......................

4472259623: MAJOR APPLIED POLYMER SCIENCE AND TEXTILE TECHNOLOGY
KEYWORDS: BENZOXAZINE / PHENOLIC / THERMAL PROPERTY / CURING CONDITION / POLYMER ALLOYS

NATTAPONG JALONGWONGSHA: EFFECTS OF TYPES AND AMOUNT OF PHENOLIC RESINS ON CURING CONDITION, THERMAL PROPERTIES AND IGNITION BEHAVIOR OF BENZOXAZINE/PHENOLIC POLYMER ALLOYS. THESIS ADVISOR: ASSISTANT PROFESSOR VIMOLVAN PIMPAN, Ph.D., THESIS COADVISOR: SARAWUT RIMDUSIT, Ph.D. 101 pp. ISBN 974-17-3649-5

Polymer alloys between benzoxazine and phenolic resins were prepared by mixing these two components followed by heating until the alloys were completely cured. From DSC studies, it was found that the suitable curing condition for benzoxazine/novolac phenolic alloys was 150°C/1 hour and 180°C/1 hour when the amount of novolac resin was lower than 50% by weight and the suitable curing condition was 150°C/1 hour and 180°C/2 hours when the amount of novolac resin was higher than 50% by weight. On the other hand, the suitable curing condition for benzoxazine/resole phenolic alloys was 100°C/2 hours and 180°C/1.5 hours when the amount of resole resin was lower than 50% by weight and the suitable curing condition was 100°C/2 hours and 180°C/2 hours when the amount of resole resin was higher than 50% by weight. Both phenolic resins improved thermal stability and increased flame retardation of benzoxazine resin. It can be seen that as the amounts of both phenolic resins in the alloys increased, thermal decomposition temperatures and LOI values increased while burning rates decreased. However, it is clearly seen that at the same blending ratio, benzoxazine/resole alloys gave higher char yield than benzoxazine/novolac alloys. This indicates that the former has better flame retardation than the latter.

Department Materials science Student's signature..............................
Field of study Applied Polymer Science and Textile Technology Advisor's signature..............................
Academic year 2003 Co-advisor's signature...........................

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LIST OF SYMBOLS

B : Benzoxazine resin
N : Novolac resin
R : Resole resin
F : Formaldehyde
P : Phenol

CHAPTER 1

INTRODUCTION

1.1 General Introduction

In recent years, fire and burning are taking place almost everywhere due to the tremendous amount of flammable interior decoration and construction materials which are used. In the United Kingdom (UK.), about 16,000 fires a year result from ignition of materials most of them domestic fires. Fires in dwellings produce about 6,000 casualties per year, 650 of them fatal (Office of Information, 1985)[29]. A major proportion of deaths (at least 50%) are attributable to toxic fumes and smoke, but in clothing fires and interior decoration the major hazard is burns. In the USA one person is burned to death every 44 minutes in clothing and other fires. If fire happens in public places horrific loss of life has occurred, as the following examples illustrate. The notorious Ring Theatre Disaster in Vienna, Austria, caused 450 deaths when a back-stage fire spread rapidly to the auditorium. A whole range of aircraft, train and auditorium fires have been influential in both highlighting dangers and generating legislation to control risks. The main reason for serious damage to life and property is that these kinds of material can catch fire very easily and can keep burning to propagate the flame, so that a large amount of toxic gas and heavy smoke are generated. Heat and fumes feed back readily burned gases and give increased ignition. The rate of combustion increases, and can reach explosive violence in so called ‘flashover’ events. Such an event caused major loss of life in the Kings Cross Underground station disaster in London, UK, in 1989[29]. A major contribution to saving life is to ‘retard’ the combustion process. By slowing down the developing situation, crowds can escape, fires can be extinguished, and garments removed. Time is available to formulate and execute the necessary measures. Therefore, the development of polymer flame retardant technology regains a focus in the Western countries, Japan and Taiwan for the past few years. Such technology seeks the development of a flame retardant, low toxic, dimensional stability at elevated temperatures, corrosion resistant, creep resistant, minimal smoke generating and good heat resistant material. Generally speaking, various flame retardant additives are currently used in engineering plastic materials to achieve the objectives. However, polymer blends or polymer alloy techniques are believed to be the key studies to overcome the problems in the near future.

Phenol-formaldehyde resins or phenolic resin have found many industrial applications ranging from aerospace to electronics and consumer. Phenolic resin is thermoset plastics has evolved considerably from the early 1900s when Dr. Leo Baekeland discovered that a hard, infusible polymer made from phenol-formaldehyde could lend itself to hundreds of applications. With phenolics' excellent properties, products made with phenolic resins are increasingly being developed, manufactured, and distributed throughout North America and the world. Phenol and formaldehyde are among the most basic building blocks in polymer chemistry. The condensation reaction may be initiated by a number of alkali or acidic catalysts. Resins that are produced by employing an alkaline catalyst and that are reacted with sufficient formaldehyde to completely cure are referred to as *single-stage resins* or *resole resins.* Resins that are produced by employing an acid catalyst and that are reacted with insufficient formaldehyde to completely cure are referred to as *two-stage resins* or *novolac resins.* The two-stage resins require the addition of another material to provide the proper mole ratio of phenol-to-aldehyde to completely cure. it produce reaction by-products after reacted. Hexamethylenetetramine (HMTA) is usually the curing agent added to the novolac resins. But resole resins can crosslinking (curing) is carried out by heating at temperatures up to 180°C [8] without the need of a curing agent or catalyst. The crosslinking process involves the same chemical reactions as for synthesizing the prepolymer. This polymer, in conjunction with various organic and inorganic reinforcing systems, offers a variety of unique properties and characteristics. The polymer acts as a matrix for binding together a number of substrates such as wood; paper; fibers (e.g., fiberglass, carbon fiber); or particles (e.g., wood flour, foundry sand) to form a highly crossed-linked composite. The characteristics of these intermediate products are engineered to satisfy a wide array of processing and finished product requirements. When cured, the resins are transformed from the fusible, thermoplastic state to a densely, cross-linked thermoset matrix. Methylene bridges join the phenol molecules in three dimensions. The resulting structure provides a number of advantages over other materials. Its inherent hardness, rigid polymers that are produced have superior resistance to a wide range of chemicals, high heat resistance, low flammability and relatively high char yield, smoke, and toxicity properties. They satisfy critical requirements for diverse applications in a cost-effective manner.

Polybenzoxazine is a newly developed thermosetting polymer with interesting properties. It was developed recently as a high temperature polymer for electronic aviation industries. As a noval class of phenolic resins, it has been developed and modified to overcoming tradition thermoset resins including very low melt viscosity above its melting point. Polybenzoxazine has excellent properties commonly found in the traditional phenolics such as heat resistance, good electrical properties and flame retardance. Polybenzoxazine or oxazine-based phenolic resins are an alternative to traditional phenolics. It is synthesized by the ring-opening polymerization of aromatic oxazines, which can be modified by changing the functional groups on the backbone. Furthermore, it does not produce reaction by-products and can be synthesized via a simple (without strong acid or alkaline catalysts) solventless technology. The resin has been reported to possess some intriguing properties such as low viscosity, low water absorption, high-temperature properties, near-zero volumetric changes upon polymerization, and ease of processing due to self-polymerization upon heating via ring-opening polymerization. The latter property renders no volatile by-products; therefore, giving no void formation in the curing step[16,17]. Low melt viscosity is one of the outstanding properties of polybenzoxazine which results in the ability to accommodate relatively large quantity of filler.

Recently, Ishida,H., and Rimdusit, S.[20,21] studied, a new polymer system base on the ternary mixture of benzoxazine, epoxy, and phenolic novolac resins, have shown promising propreties suitable for a wide range of applications. It investgate the effect of phenolic novolac on the curing of epoxy-diluted benzoxazine resin since phenolic novolac is typically used as a hander for epoxy resin as well as an initiator for benzoxazine resin. Through the addition of a small amount of phenolic novolac to the systems, the T_g of the obtained materials is enhanced about 170°C because of the higher crosslink density in the resulting materials. The curing reaction can also occur at a lower temperature through the addition of phenolic resin. Synergism in the T_g can be observed in both the binary and ternary systems studied. The material properties present a high thermal stability, high glass transition temperature, low melt viscosity and high char yield.

1.2 The objective of this research

1.To study the interaction of benzoxazine resin with phenolic resins.

2.To compare effect of types and amount of phenolic resins on curing conditions, thermal properties and ignition behavior of polymer alloy benzoxazine/phenolic.

3.To find optimum composition of the obtained polymer alloys with good thermal properties and fire retardability.

CHAPTER 2

THEORY

2.1 Polymer blends and alloys

Mixing two or more polymers together to produce blends or alloys is a well-established strategy for achieving a specified portfolio of physical properties, without the need to synthesize specific polymer systems. The subject is vast and has been the focus of much work, both theoretical and experimental. Much of the earlier work in this field was necessarily empirical and many of the blends produced were of academic rather than commercial interest.

The manner in which two (or more) polymers are compounded together is of vital importance in controlling the properties of blends. Moreover, particularly through detailed rheological studies, it is becoming apparent that processing can provide a wide range of blend microstructures. In an extreme, this is exemplified by the *in situ* formation of blends, when in the solution or melt state. The microstructures produced in this case transform the blend into fibre composite; this parallels earlier work on the deformation of metal alloys. This type of processing-structure-property correlation opens up many new possibilities for innovative application.

Polymer materials may be grouped in different ways. An overview of the most common two-phase systems consisting of polymers is shown in figure 2.1

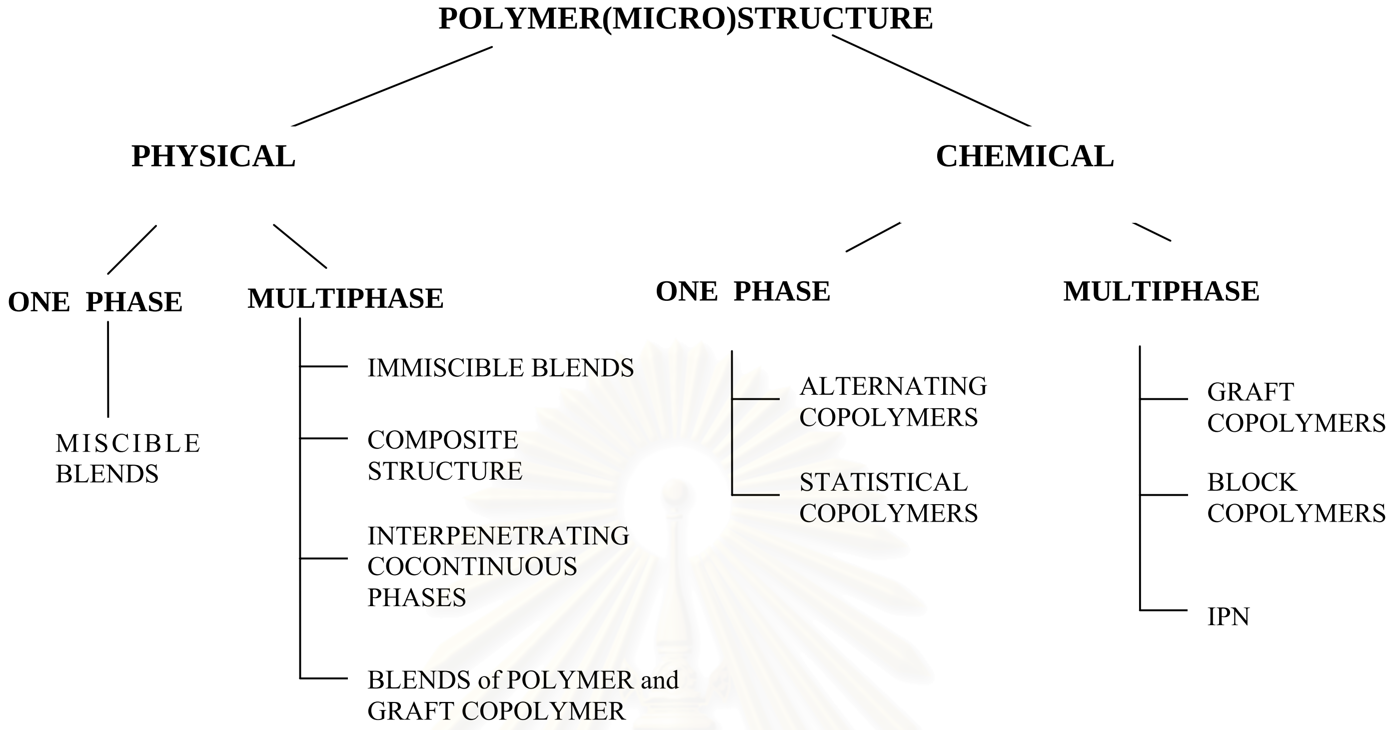


Figure 2.1 Microstructure of polymer blends and alloys.

Compatibilization, that is to say modification of normally immiscible blends to give alloys with improved end-use performance, is an important factor in almost all commercial blends, and has been the subject of an enormous amount of experimental investigation, much of which remains proprietary.

2.1.1 Achievement of thermodynamic miscibility.

Compatibilization by the achievement of true thermodynamic miscibility is a concept which has been exploited in only a handful of situations to produce commercial blends. Briefly, it is recognised that miscibility between polymers is determined by a balance of enthalpic and entropy contribution to the free energy of mixing. While for small molecules the entropy is high enough to ensure miscibility, for polymers the entropy is almost zero, causing enthalpy to be decisive in determining miscibility. The change in free energy on mixing (ΔG) is written as

$$\Delta G = \Delta H - T\,\Delta S$$

Where H is enthalpy, S is entropy and T is temperature. For spontaneous mixing, ΔG must be negative, and so

$$\Delta H - T\,\Delta S < 0$$

This implies that exothermic mixtures (ΔH <0) will mix spontaneously, whereas for endothermic mixtures miscibility will only occur at high temperatures. For two-component blends it is possible to construct a phase diagram, which may exhibit lower or upper critical solution temperature (LCST or UCST) (Figure 2.2). In practice, LCST behavior is more commonly seen, phase separation occuring as temperature increase, because the intermolecular attractive forces responsible for the miscible behavior tend to disappear as the internal energy of the molecules becomes high enough to overcome them.

In principle it should be possible to tailor the structure of polymers in some circumstances to modify their phase diagram in blends, and thereby to achieve miscible blends.

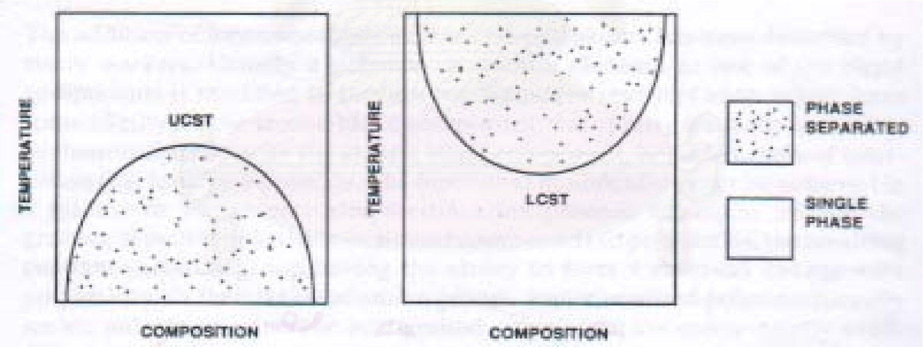


Figure 2.2 Schematic phase diagrams for binary blends showing LCST and UCST behaviors.[26]

Polymer blend is defined as a mixture of at least two polymers or copolymers.

Miscible polymer blend is defined as polymer blend homogeneous down to molecular level: $\Delta G_m \cong \Delta H_m \leq 0$.

Immiscible polymer blend. $\Delta G_m \cong \Delta H_m > 0$.

Compatible polymer blend. Homogeneous to the eye, commercially attractive polymer blend

Polymer alloy. Immiscible polymer blend having a modified interface and/or morphology.

2.1.2 Compatibilization mechanisms

In most cases, melt mixing two polymers results in blends which are weak and brittle; while the low deformation modulus may follow an approximately linear mixing rule, the ultimate properties certainly will not. This is because the incorporation of a dispersed phase in a matrix leads to the presence of stress concentrations and weak interfaces, arising from poor mechanical coupling between phase. It is most common for compatibilization to be *in situ* chemical reaction, leading to modification of the polymer interfaces in two-phase blends, and thereby tailoring of the phase structure, and hence properties

The factors contributing to end-use properties during manufacture of a blend by melt compounding, and subsequent conversion processing to produce a finished article, are illustrated in Figure 2.3

The mechanical properties of a blend or alloy will be determined not only by the properties of its components, but also by the phase morphology and the interphase adhesion, both of which are important from the viewpoint of stress transfer within the blend in its end-use application. The phase morphology will normally be determind by the processing history to which the blend has been subjected, in which such factor as the (mixer type, rate of mixing and temperature history), the rheology of the blend components and the interfacial tension between phase in the melt are important. The phase morphology is unlikely to be in thermodynamic equilibrium, but generally will have been stabilized against de-mixing by some methods or others; this usually means via quenching to below the glass transition temperature of one or both phases, or via the occurrence of crystallinity in one or both phases, or occasionally by crosslinking

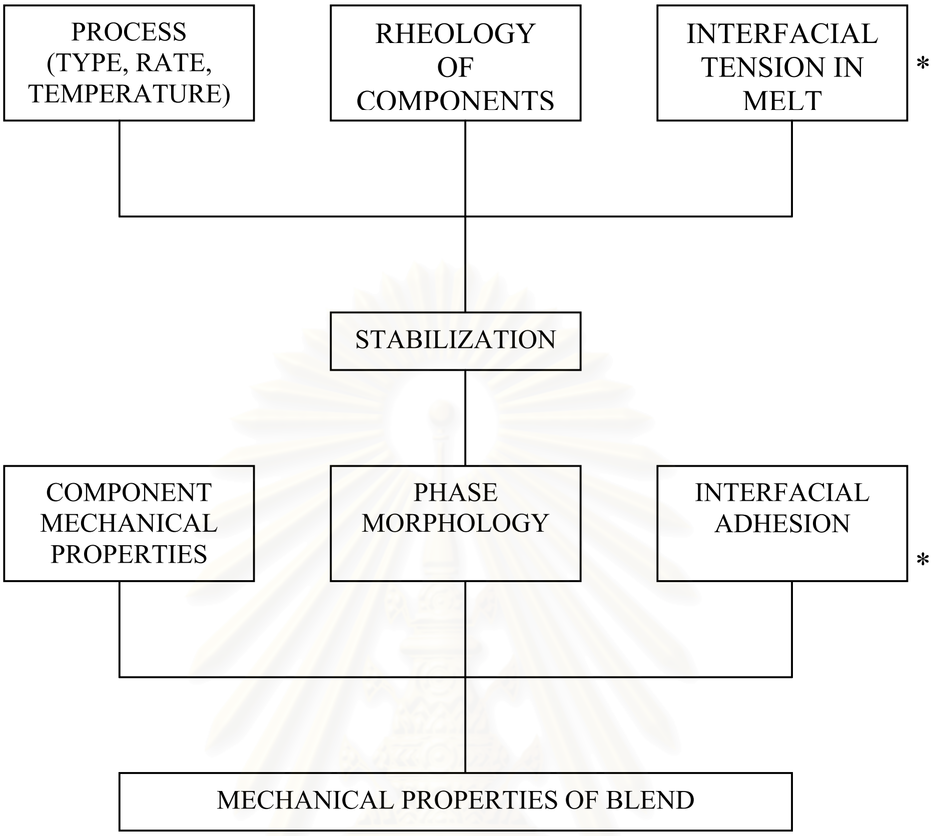


Figure 2.3 Summary of the factors contributing to end-use properties in melt compounded blends, highlighting the role of compatibilization*.[26]

2.1.3 Methods of compatibilization

Pursuing our technological definition of compatibilization as modification of blends to produce a desirable set of properties, it is perhaps unhelpful to attempt to categorise methods too narrowly. However, a number of different lines of approach can be defined which may assist the materials developer. Broadly, these are:

2.1.3.1 Addition of block and graft copolymers

Addition of block or graft copolymers represents the most extensively researched approach to compatibilization of blends. Block copolymers have been more frequently investigated than graft copolymers, and in particular block copolymers containing blocks chemically identical to the blend component polymers. It is perhaps not surprising that block and graft copolymers containing segments chemically identical to the blend components are obvious choices as compatibilizers, given that miscibility between the copolymer segments and the corresponding blend component is assured, provided the copolymer meets certain structural and molecular weight requirements, and that the copolymer locates preferentially at the blend interfaces.

2.1.3.2 Addition of functional polymers

The addition of functional polymers as compatibilizers has been described by many workers. Usually a polymer chemically identical to one of the blend components is modified to contain functional (or reactive) units, which have some affinity for the second blend component; this affinity is usually the ability to chemically react with the second blend component, but other types of interaction are possible. The functional modification may be achieved in a reactor or via an extrusion-modification process.

2.1.3.3 Reactive blending

A comparatively new method of producing compatible thermoplastics blends is via reactive blending, which relies on the *in situ* formation of copolymers or interacting polymers. This differs from other compatibilization routes in that the blend components themselves are either chosen or modified so that reaction occurs during melt blending, with no need for addition of a separate compatibilizer.

2.2 Composite materials

A composite material can be defined as a macroscopic combination of two or more distinct materials, having a recognizable interface between them. However, because composites are usually used for their structural properties, the definition can be restricted to include only those materials that contain a reinforcement (such as fibers or particles) supported by a binder (matrix) material. Composite materials were developed because no single, homogeneous structural material could be found that had all of the desired attributes for a given application. The advantage of composites is that they usually exhibit the vest qualities of their constituents and often some qualities that neither constituent possessed. The Properties that can be improved by forming a composite material include such as strength, stiffness, weight, temperature-dependent behavior, and thermal conductivity. Naturally, not all of the above properties are improved at the same time nor is there usually any requirement to do so.

2.2.1 Classification and characterization of composite materials.

Composites can be divided into classes in various manners. Depending on the types of matrix, composites can be categorized as polymer matrix composites, metal matrix composites, ceramic matrix composites, carbon-carbon composites, intermetallic composites or hybrid composites. Other simple classification scheme is to separate them according to reinforcement forms.

2.2.1.1 Particulate-reinforced composites

Particulate composites are composed of particles in a matrix. A reinforcement is considered to be a “particle” if all of its dimensions are roughly equal. Thus, particulate-reinforced composites include those reinforced by spheres, rods, flaked, and many other shapes of roughly equal axes.

2.2.1.2 Fiber-reinforced composites

Fiber-reinforced consist of fibers in a matrix. They contain reinforcements having lengths much greater than their cross-sectional dimensions. Such a composite is considered to be a discontinuous fiber or short fiber composite if its properties vary with fiber length.

2.2.1.3 Laminated composites

Laminated composites consist of layers of at least two different materials that are bonded together in a matrix. Sandwich and honeycomb component as well as the term high-pressure laminates are included. Lamination is used to combine the best aspects of the constituent layers in order to achieve a more useful material.

2.2.2 Matrices

The role of the matrix in a fiber-reinforced composite is

(1) to transfer stresses between the fibers

(2) to provide a barrier against an adverse environment, and

(3) to protect the surface of the fibers from mechanical abrasion.

The matrix plays a minor role in the tensile load-carrying capacity of a composite structure. However, selection of a matrix has a major influence on the interlaminar shear as well as on in-plane shear properties of the composite material. The interlaminar shear strength is an important design consideration for structures under bending loads, whereas the in-plane shear strength is important for structures under torsional loads. The matrix provides lateral support against the possibility of fiber buckling under compression loading, thus influencing to some extent the compressive strength of the composite material. The interaction between fibers and matrix is also important in designing damage-tolerant structure. Finally, the processability of and defects in a composite material depend strongly on the physical and thermal characteristics, such as viscosity, melting point, and curing temperature of the matrix. Additional functions of a matrix are to keep the fibers in place in the structure, help distribute of transfer load, the protect the filaments, both in the structure and before fabrication, control the electrical and chemical properties, carry interlaminar shear. The needs or desired properties of a matrix, depending on the purpose of the structure, are to minimize moisture absorption, wet and bond to fiber, flow to penetrate completely and eliminate voids during the compacting and curing process, have strength at elevated temperature (depending on the application), have low shrinkage, have dimensional stability. In addition; have reasonable strength, modulus, and elongation.

2.3 Thermoseting resins

Thermoset resins are the most widely used class of matrix materials in polymer based composite where thermoplastics cannot complete because of either properties or costs. For example, phenolic resins constitute a first option when fire resistance is required because they are self-extinguishing and exhibit low smoke emission. Though well established, they suffer from a number of well-known limitations and it is to address these problems that current research efforts are largely devoted. Reinforced thermoset plastics are plastic resins such as polyester, phenolic, silicone, and epoxy reinforced by fibrous glass, graphite, carbon, or aramid, as well as paper, cotton, flakes, beads, or powders. The reinforcement adds strength and toughness to inherent weather resistance, moldability, good mechanical property, high thermal property, colorability and, in many case, lower costs.

One of the most important parameters characterizing a thermosetting polymer is the location of its glass transition temperature (T_g) with respect to the temperature at which it is used (T_{use}). Most thermosetting polymers are formulated and selected so that their T_g is higher than T_{use}; therefore, they behave as glasses during their use materials exhibiting a T_g lower than T_{use} are classified as rubbers, but they can also be regarded as thermosetting polymers operationg in the rubbery state.

2.4 Phenolic polymers

Figure 2.4 Phenolic polymer.

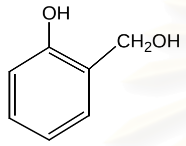
The field of thermoset plastics has evolved considerably from the early 1900s when Dr. Leo Baekeland discovered that a hard, infusible polymer made from phenol-formaldehyde could lend itself to hundreds of applications. With phenolics' excellent properties, products made with phenolic resins are increasingly being developed, manufactured, and distributed throughout North America and the world. This report outlines the development of phenolic resins from phenol through its use in industrial and consumer products.

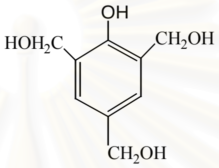
Phenol and formaldehyde are among the most basic building blocks in polymer chemistry. The condensation reaction may be initiated by a number of alkali or acidic catalysts, resulting in a polymer. This polymer, in conjunction with various organic and inorganic reinforcing systems, offers a variety of unique properties and characteristics. The polymer acts as a matrix for binding together a number of substrates such as wood; paper; fibers (e.g., fiberglass); or particles (e.g., wood flour, foundry sand) to form a highly crossed-linked composite.

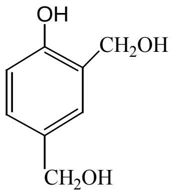
Resins that are produced by employing an alkaline catalyst and that are reacted with sufficient formaldehyde to completely cure are referred to as *single-stage resins* or *resole resins*. Resins that are produced by employing an acid catalyst and that are reacted with insufficient formaldehyde to completely cure are referred to as *two-stage resins* or *novolac resins*. The two-stage resins require the addition of another material to provide the proper mole ratio of phenol-to-aldehyde to completely cure. Hexamethylenetetramine (HEMA) is usually the curing agent added to the novolac resins.

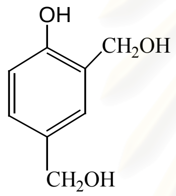
2.4.1 Resole phenolics

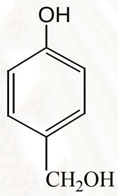
Phenolic polymers are obtained by the polymerization of phenol (*f* = 3) with formaldehyde (*f* = 2)[1,3]. The polymerization rate is pH – dependent, with the highest reaction rates occurring at both high and low pH. The strong base – catalyzed polymerization yields mixtures, referred to as *resoles, resole prepolymers, or resole phenolics,* of mononuclear methylolphenols and various dinuclear and polynuclear compounds such as[8]



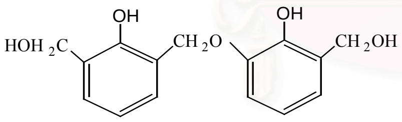


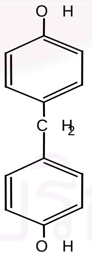


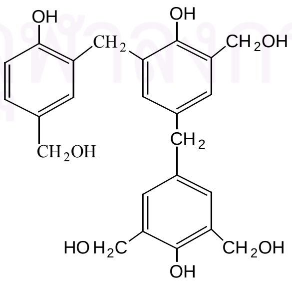


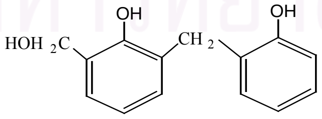


Only some of the possible products such as[8]









The other products are those differing in the position of ring substitution (i.e., ortho versus para) and the type of bridge between rings (methylene versus ether). The polymerization is carried out using a molar ratio of formaldehyde to phenol of 1.2 – 3.0: 1. A 1.2: 1 ratio is the typical formulation. The formaldehyde is supplied as a 36 – 50 % aqueous solution (referred to as *formalin*). The catalyst is 1 – 5 % sodium, calcium, or barium hydroxide. Heating at 80 – 95°C for 1 – 3 hr is sufficient to form the prepolymer[8]. Vacuum dehydration is carried out quickly to prevent overreaction and gelation. Although phenol itself is used in the largest volume, various substituted phenols such as Cresol (o-, m-, p-), p-butylphenol, resorcinol, and bisphenol A are used for specialty applications. Some use is also made of aldehydes other than formaldehyde – acetaldehyde, glyoxal, 2-furaldehyde. The exact composition and molecular weight of the resole depend on the formaldehyde to phenol ratio, pH, temperature and other reaction conditions[8]. For example, higher formaldehyde compositions will yield resoles containing more of the mononuclear compounds. The resole prepolymer may be either a solid or liquid polymer and soluble or insoluble in water depending on composition and molecular weight. Molecular weights are in the range 500 – 5000, with most being below 2000. The resoles are usually neutralized or made slightly acidic. The pH of the prepolymer together with its composition determine whether it will be slow curing or highly reactive. Crosslinking (curing) is carried out by heating at temperatures up to 150°C. The crosslinking process involves the same chemical reactions as for synthesizing the prepolymer – the formation of methylene and ether bridges between benzene rings to yield a network structure

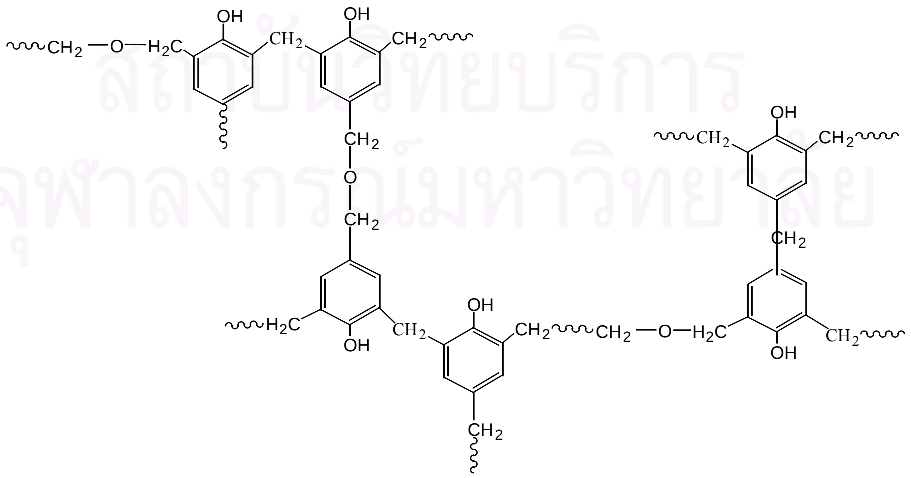


Figure 2.5 Network structure of resole.

The relative importance of methylene and ether bridges is dependent on temperature[3]. Higher curing temperatures favor the formation of methylene bridges but not to the exclusion of ether bridges.

The polymerization and crosslinking of phenol – formaldehyde is a highly useful industrial process. However, the reactions that take place are quite difficult to handle in a quantitative manner for a number of reasons. The assumption of equal reactivity of all functional groups in a monomer, independent of the other functional groups in the molecule and of whether the other are reacted, is dubious in this polymerization. Consider, for example, the routes by which trimethylolphenol[3] (Figure 2.6) can be produced in this system:

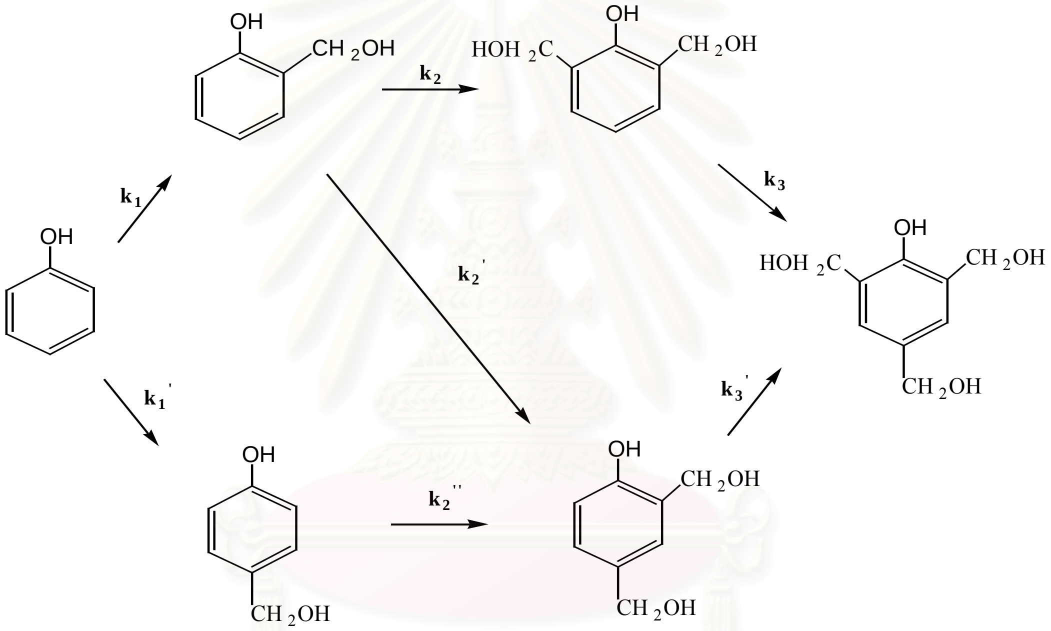


Figure 2.6 The routes by which trimethylolphenol can be produced in this system.[8]

Table 2.1[8] shows the rate constants for the various reactions. It is apparent that there are significant differences in the reactivities of the different functional groups in phenol (i.e., in the different positions on the ring). The reaction between phenol and formaldehyde involves a nucleophilic attack by the phenolate anion on formaldehyde (Figure 2.7) or its hydrated form. The electron – pushing methylol groups generally increase the reactivity of phenol toward further substitution although steric hindrance modifies this effect.

Table 2.1 Reaction of phenol with formaldehyde catalyzed by base.

Reaction	Rate Constant x 10^4 (liters/mole-sec)
k_1	14.63
$k_1^{/}$	7.81
k_2	13.50
$k_2^{/}$	10.21
$k_2^{//}$	13.45
k_3	21.34
$k_3^{/}$	8.43

It is difficult to quantitatively discuss the reasons for the specific differences in reactivity, since there is no general agreement on even the relative values of the seven different rate constants. The evaluation of the different rate constants is difficult from both the viewpoints of chemical analysis of the mono-, di-, and trimethylolphenols and the mathematical analysis[8] of the kinetic data.

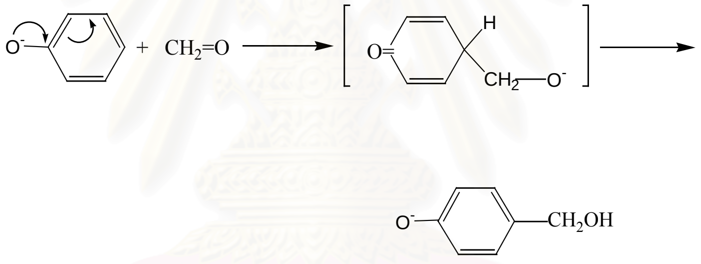


Figure 2.7 The reaction between phenol and formaldehyde involves a nucleophilic attack by the phenolate anion on formaldehyde.

Not only are the different ring positions on phenol of different reactivity, but one expects that the two functional groups of formaldehyde would also differ. The second functional group of formaldehyde actually corresponds to the methylol group, since the reaction of a methylolphenol with a phenol molecule (or with a second methylolphenol) probably proceeds by a sequence such as

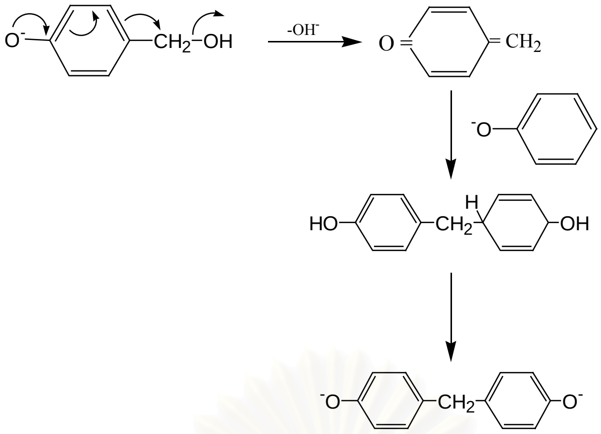


Figure 2.8 The reaction of a methylolphenol with a phenol molecule.

Direct kinetic measurements are not available to show the reactivity of the methylol group in this reaction compared to the initial reaction of formaldehyde. However, the general observation that the amounts of di- and polynuclear compounds present in resole prepolymers differ widely depending on the reaction condition (temperature, pH, specific catalyst used, concentrations of reactants) indicates that the two functional groups of formaldehyde differ in reactivity.

A further complication in the phenol – formaldehyde polymerization is that it may involve a decrease in functional group reactivity with molecular size. This can easily happen in systems that undergo extensive crosslinking. Such systems may cease to be homogeneous solutions before the experimentally determined gel point. The gel point may be preceded by the formation of microgel particles which are too small to be visible to the naked eye[8]. Functional groups in the microgel particles would be relatively unreactive due to their physical unavailability. Similar considerations would apply for the reaction period subsequent to the gel point. A decrease in reactivity with size may not be due to molecular size but a consequence of steric shielding of ortho or para positions of benzene rings within a chain compared to those positions on rings at the chain ends.

2.4.2 Novolac phenolics

Phenol – formaldehyde prepolymers, referred, to as *novolacs*, are obtained by using a ratio of formaldehyde to phenol of 0.75 – 0.85: 1[2,8], sometimes lower. Since the reaction system is starved for formaldehyde, only low molecular weight polymers can be formed and there is a much narrower range of products compared to the resoles. The reaction is accomplished by heating for 2 – 4 hr at or near reflux temperature in the presence of an acid catalyst. Oxalic and sulfuric acids are used in amounts of 1 – 2 and <1 part, respectively, per 100 parts phenol[2]. The polymerization involves electrophilic aromatic substitution, first by hydroxymethyl carbocation and subsequently by benzyl carbocation – each formed by protonation of OH followed by loss of water[8].

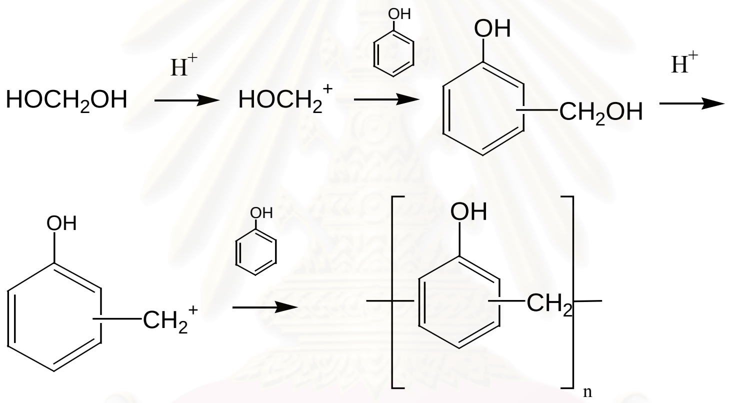


Figure 2.9 Phenol - formaldehyde reactions under acidic condition.

There is much less benzyl ether bridging between benzene rings compared to the resole prepolymers.

Some novolacs are synthesized without strong acid present by using a carboxylate salt of zinc, calcium, manganese, cobalt, or other divalent metal ion (2% or more relative to phenol). These novolacs contain a higher degree of ortho substitution on the benzene rings and cure faster compared to the novolacs synthesized with the stronger acids. The mechanism for this ortho effect probably involves simultaneous complexation of the divalent metal ion with the phenol and carbocation hydroxyl groups. Similar effects of divalent ions on the relative amounts of ortho and para substitution are observed in the formation of resole prepolymers on comparison of catalysis by divalent metal hydroxides versus monovalent metal hydroxides.

The reaction mixture is dehydrated at temperatures as high as 160°C (higher temperatures can be tolerated than with resoles). The prepolymer is cooled, crushed, blended with 5 – 15 % hexamethylenetetramine, $(CH_2)_6N_4$, and sold to the fabricator. Hexamethylenetetramine, referred to as *hexa*, is the product of the reaction of 6 moles of formaldehyde and 4 moles of ammonia. Curing occurs rapidly on heating with the formation of both methylene and benzylamine crosslinking bridges between benzene rings. The crosslinked network is pictured as

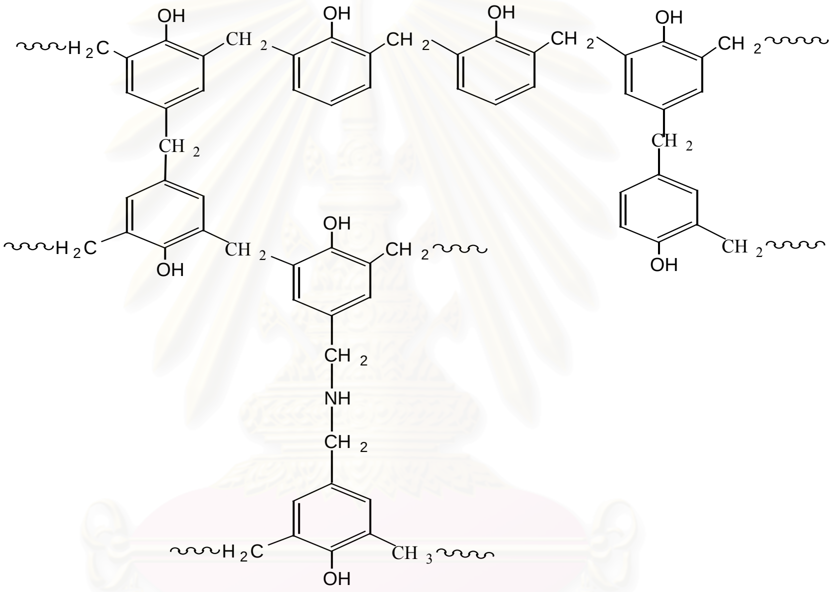


Figure 2.10 The crosslinked network of novolac.

2.4.3 Characteristics of phenolic resins

* Dimensional stability at elevated temperatures

* Creep resistant

* Excellent fire performance

* Cost effective

* Outstanding durability

* Excellent strength-to-weight ratio

* Excellent thermal insulation properties

* Excellent sound-damping properties

* Corrosion resistant

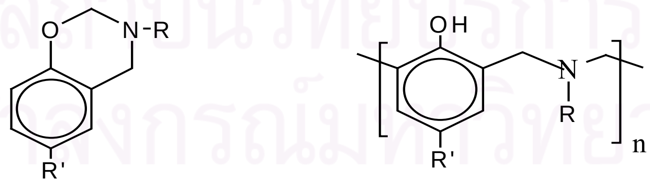
2.4.4 Phenolic applications

Phenolic polymers, the first commercial synthetic plastics, were introduced by Baekeland in 1909 through his Bakelite Company. Bakelite dominated this product until 1926 when its patent expired. Phenolic polymers are the largest-volume thermosetting plastics. More than 3 billion pounds are produced annually in the United States. Phenolics have high strength and dimensional stability combined with good resistance to impact, creep, solvents, and moisture. Most phenolics contain fillers or reinforcements. General-grade phenolics are filled with mica, clay, wood or mineral flour, cellulose, and chopped fabric. Engineering-grade phenolics, reinforced with glass or organic fibers, elastomers, graphite, and polytetrafluoroethylene, are rated for continuous use at 150 - 170°C.

The largest – volume application of phenolic polymers is the adhesive bonding material for the manufacture of plywood, particle board, wafer board, and fiberboard. The phenolic constitutes up to one – third of the weight of such products. Other adhesive applications include the binder for aluminum oxide or silicon carbide in abrasion wheels and disks and contact adhesives, usually blends of rubber and phenolic, used extensively in the furniture, automotive, construction, and footwear industries. Phenolics are used in a variety of coatings applications – baked – on coatings, coatings on cans, drums, metal pipe, electrical insulation, varnishes, and metal primers. The phenolic resins are generally too hard and brittle to be used alone for the coatings applications but blends with alkyds, polyethylene, and epoxy resins perform well. Laminates of cellulose paper, cotton fabric, glass and asbestos cloths, and wood veneer with phenolics are made in various forms (sheet, rod, tubes) that can be machined. These find wide uses as printed – circuit boards, gears, cams and protective and decorative surfaces for tables, furniture, kitchen and bathroom countertops, and walls. Composites containing phenolics are used as the ablative coating for space reentry vehicles, aircraft interiors and brakes.

2.5 Polybenzoxazine resin

The chemistry of benzoxazines dated back to the early 1940s. Phenolic resins have been widely used in polymer and composite applications. However, their attractiveness is compromised by the problematic nature of their chemistry, Well-known shortcomings of phenolic resins are the production of water during polymerization, poor processibility, short shelf life for resole-types, use of chemically harsh catalysts, and limited molecular design flexibility. The chemistry of benzoxazines dated back to the early 1940s. polybenzoxazine resins overcome almost all shortcomings of convention standard phenolic resins, Also, the materials exhibit a number of special propertied that have been only rarely observed in other commonly used polymers. Polybenzoxazine resin is a newly developed class of thermosetting resins that are based on the ring-opening polymerization of benzoxazine precursors. These new materials are synthesized by the ring-opening polymerization of benzoxazines. The chemistry of benzoxazine synthesis offers superb of molecular design flexibility, performance properties can be tailored and optimized to meet specific application requirements. The benzoxazine resin can be synthesized from phenolic derivatives, primary amine, and aldehyde. The polymerization occurs by a simple ring-opening addition reaction and did not yield any reaction by-product. Benzoxazines cure without the aid of the strong acid catalysts required by other phenolic materials. Molecular structures of the monomer and resulting polymer are shown in Figure 2.11



(a) (b)

Figure 2.11 Molecular structures of (a) benzoxazine mononer and (b) polybenzoxazine.

Benzoxazine is a single benzene ring fused to another six-membered heterocycle group containing one oxygen atom and a single nitrogen atom, called an oxazine ring. The oxazine ring is the reactive site for curing of the benxozaxine. There are a number of possible isomers of benzoxazine depending on the relative positions of the two heteroatoms and the degrees of oxidation of this oxazine ring system. Benzoxazine were synthesized may be monofunctional or difunctional. The latter can produce crosslinked structures. The polymerization of monofunctional benzoxazines produces only linear oligomeric phenolic structures. However, difunctonal benzoxazine monomers are tetrafunctional in terms of reactive sites and polymerize to form crosslinked networks, resultion in phenolic materials with substantial mecchanical integrity. Their chemical structures are shown in Figure 2.12

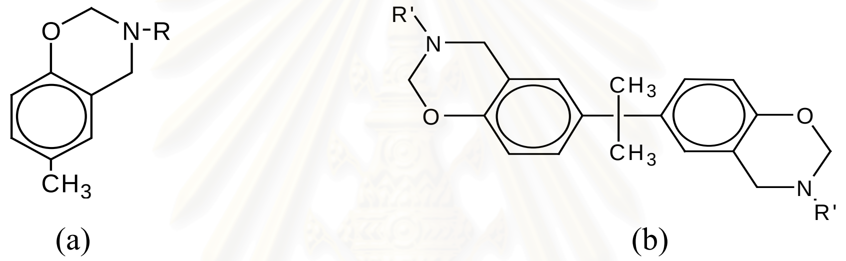


Figure 2.12 Chemical structures of benzoxazine resin, (a) monofunctional, (b) bifunctional.

The polybenzoxazines overcome many of the traditional shortcomings of conventional novolak and resole type phenolic resins, while retaining their benefits. The physical and mechanical properties feature a wide range. The material property balance of these resins exhibit good thermal, chemical, electrical, mechanical, and physical properties make the polybenzoxazine family an attractive option in many existing applications. In addition, these new materials possess high glass transition temperatures, high char yield, high moduli, low water absorption despite the large amount of hydroxyl groups in the backbone structure, excellent resistance to chemicals and UV light, low melt viscosities compared to conventional phenolics. in, near-zero volumetric shrinkage or expansion upon polymerization and relatively low coefficients of thermal expansion. The polybenzoxazines suited for high-performance adhesives and composite.

2.5.1 Polymerization of polybenzoxazine

Benzoxazines are bicyclic heterocycles generted by the Mannich-like condensation of a phenol, formaldehyde, and an amine[16,17]. They have long been recognized for their wide range of biological activity with uses as herbicides and agricultural microbiocides, as well as, bactericides, fungicides, and antitumor agents. On the other hand, polybenzoxazines, one of a series of phenolic-type polymer, which are generated upon thermal polymerization from various types of substituted 3,4 dihydro-2*H*-1,3-benzoxazines, offer excellent mechanical, physical, and thermal properties due to the phenolic groups, Mannich base linkages, and the existence of eztensive inter-and intramolecular hydrogen bonds.

The preferential conformation of a mono-oxazine ring containing benzoxazine is a destorted semichair structure, with the nitrogen and the carbon between the oxygen and nitrogen on the oxazine ring sitting, respectively, above and below the benzene ring plane. The resulting ring strain from this molecular conformation makes it possible for this type of six-membered ring containing molecule to undergo ring-opening polymerization under certain conditions. In addition, from the chemistry point of view, both the oxygen and the nitrogen on the oxazine ring can be potential cationic polymerization initiation sites due to their high basicity by Lewis definition. The electron charge calculation after energy minimization predicts, however, that oxygen might be the preferred polymerization site over nitrogen due to its high negative charge distribution (O, -0.311; N, -0.270), the oxygen on the oxazine ring will act as the initiation site.An alternative polymerization route which is similar to first mechanism but having nitrogen as the initiation and propagation sites. Furthermore, in a benzoxazine molecule, other than the electron-rich nitrogen and oxygen, the unobstructed ortho position of the benzene ring with respect to the phenoxy OR group is well-proven to possess high reactivity toward thermal polymerization of benzoxazines with or without catalysts. Therefore, it is logical to assume that upon initiation by a cationic initiator, the propagation can also proceed by insertion of the monomers through the reaction of the unobstructed benzene ortho position, producing a Mannich base phenolic-type polymer in Figure 2.13

In this latter case, the monomers propagate via reasonably stable carbocations, i.e., oxonium cations stabilized by intramolecular hydrogen bonding which could lead to high-molecular weight polymer formation

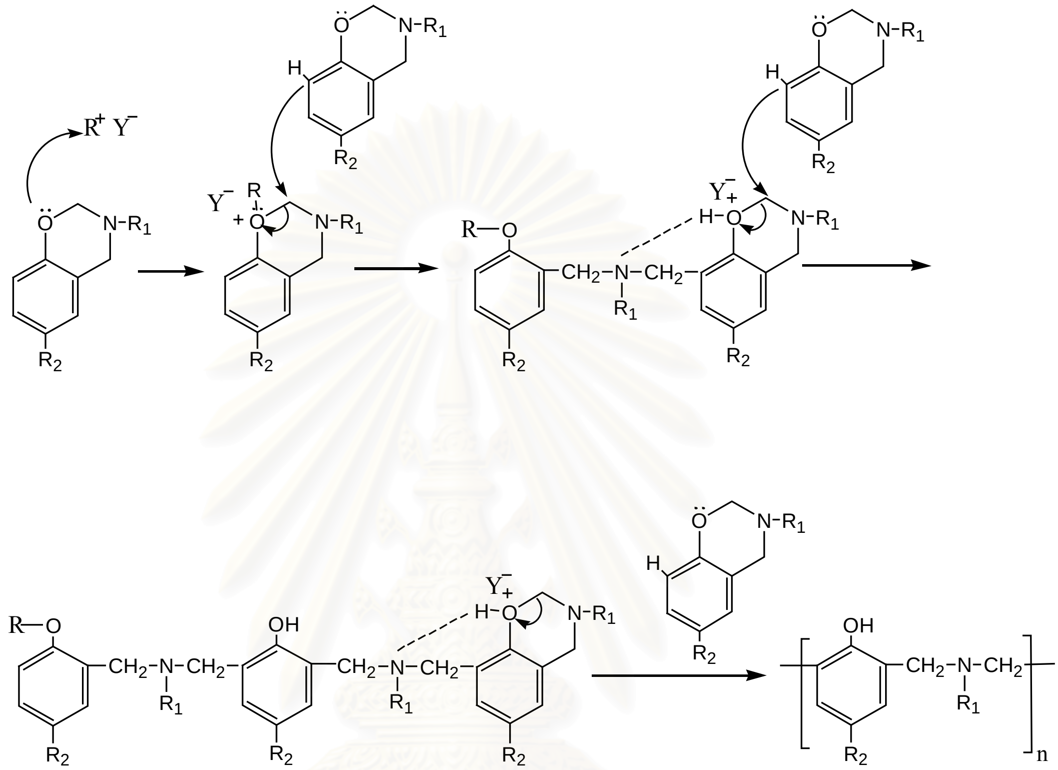


Figure 2.13 Polymerization mechanism of polybenzoxazine.

2.5.2 Properties of benzoxazine monomer.

- Appearance: Light yellow solid
- Softening point: 60 °C
- Starting point of polymerization: 150 ° C
- Solubility: Soluble in Aceton, THF, ethyl acetate and toluene. Slightly soluble in methanol. Insoluble in water.

2.5.3 Properties of polybenzoxazine[16]

Table 2.2 Properties of polybenzoxazine, phenolic and epoxy.

	(Unit)	Benzoxazine	Phenol	Epoxy
Physical properties				
Transparency	-	clear	-	unclear
Mold shrinkage	%	-0.31	-	-
Density	-	1.18	1.24-1.32	-
Water-absorption	%	0.13	0.1-0.36	-
Boiling water-absorption				
at 1 hour boiling	%	0.14	-	0.32
at 3 hours boiling	%	0.28	-	0.50
at 5 hours boiling	%	0.37	-	0.67
Thermal properties				
Heat distortion temperature	^{o}C	140	149-204	165
Coefficient of linear expension	x10^{-5}/^{o}C	4.5	6.8	6.6
Mechanical properties				
Tensile strength	Hgf/cm^{2}	660	350-630	-
Elongation at fracture point	%	4.2	1.5-2.0	-
Bending strength	Hgf/cm^{2}	1620	770-1200	810
Bending elasticity module	x10^{-4}	5.40	-	2.62
Impact strength	IZOD	1.5	1.3-2.2	-
Hardness	shore D	90	-	85
Electrical properties				
Volume resistivity	Ω·cm	4.34x10^{16}	-	8.2x10^{15}
at 1 hour boiling	Ω·cm	2.59x10^{16}	-	2.3x10^{15}
at 3 hours boiling	Ω·cm	2.43x10^{16}	-	1.1x10^{15}
at 5 hours boiling	Ω·cm	3.04x10^{16}	-	1.0x10^{15}
Permittivity	1 MHz	3.46	-	3.14
Dielectric tangent	%	0.48	-	2.98
Other properties				
Burning resistance	-	self extinguish		flammable
Chemical resistance	-	excellent		excellent

2.6 Fire-retardant

Fire takes a steady toll of both human life and property. The results are often tragic and in many cases (at least potentially) avoidable. The problem has many components which can be summarized as follows.

1. A wide range of commonly used materials is flammable.
2. A range of situations, in theatres, restaurants and aircraft, can cause heavy loss of life in the event of fire.
3. Use of particular materials, garments and upholstery structures can lead to sharply increased personal hazard.

Use of reduced flammability materials, testing of both materials and complete products, regulations and legislation have been applied to the problem. Each has contributed to reducing the risk of accidental injury, death or loss.

2.6.1 The combustion process

In order to understand how flammability hazards can be reduced, it is necessary to study the nature of the combustion process. Combustion can very easily develop into a runaway self-feeding event producing enormous heat, suffocating and toxic fumes, and total destruction. Figure 2.14 shows the essential components: fuel, an oxidant (usually air) and an ignition source.

Heat and fumes feed back readily burned gases and give increased ignition. The rate of combustion increases, and can reach explosive violence in so called ‘flashover’ events. A major contribution to saving life is to ‘retard’ the combustion process. By slowing down the developing situation, crowds can escape, fires can be extinguished, and garments removed. Time is available to formulate and execute the necessary measures.

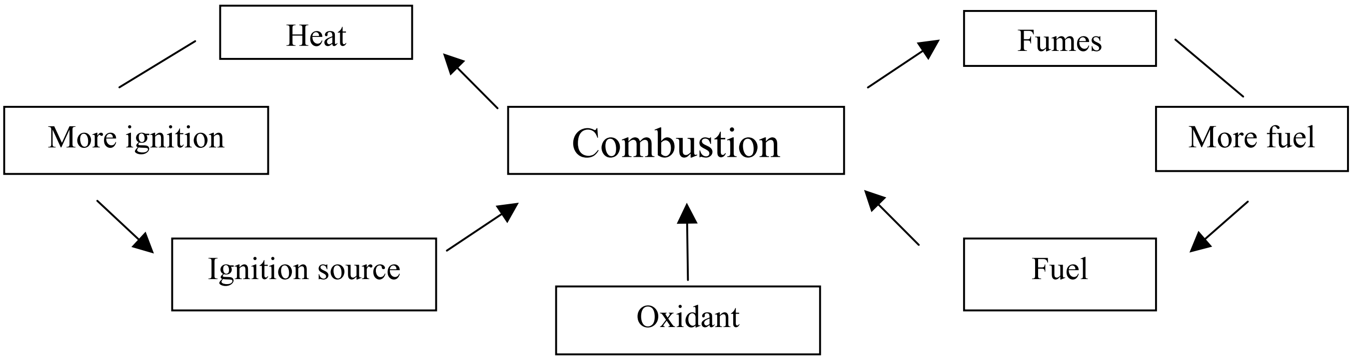


Figure 2.14 The combustion process.

2.6.2 Developing a fire-retarding solution[29]

- Design for fire retardancy and escape. It has resulted in fire fighters' uniforms capable of protecting against 2000°C exposure for 30s. Buildings are designed to prevent spread of fire and smoke.

- Legislate to eliminate known risks. The UK Children's Nightwear (Safety) Regulations, SI 616 (HMSO, 1959), prohibit the sale of nightwear which does not pass appropriate flammability tests.

- Develop adequate test methods. It is often not clear precisely what the nature of the hazard is, until similar events can be reproduced in a laboratory. Modern testing often involves complete structures, furniture, etc., tested in carefully designed settings

- Develop fire-retardant materials. It is probably true to say that fire retardant materials have been developed to meet every concelvable hazard. In theory nobody should be injured if the best available fire-retardant material were always used, however, also equally ture that only space programmes and the like can afford the really exotic materials. Many cheaper solutions give reduced comfort, colour, or aesthetic properties. There are no solutions at all which do not add significantly to the cost of products.

2.6.3 Limiting oxygen index

The atmosphere contains about 21 % oxygen. The rest (nitrogen, CO_2, water, ect.) does not support combustion. It has been found by experiment that increasing the ratio of oxygen to nitrogen makes some materials burn that are self-extinguishing in air. Conversely, materials which burn readily in the air are self-extinguishing in nitrogen-rich atmospheres.

This leads to a useful and general test for classifying flammability. The limiting oxygen index (LOI) test seeks to cstablish the minimum oxygen content atmosphere in which a material will continue to burn.

Those materials with a LOI greater than 25 are generally self-extinguishing in air. Those with the lowest LOI values burn most readily. Very few materials indeed refuse to burn in atmospheres approaching 100% oxygen.

A full description and discussion of the LOI test is given elswewhere[29], and Table 2.3 lists a range of materials and their LOI values.

Table 2.3 Limiting oxygen indices (LOI): minimum percentage oxygen contents for sustained combustion.

Substance	LOI
Polyethylene oxide	15.0
Poly(methyl methacrylate) (Perspex)	17.0
Polyethylene	18.0
Polypropylene	18.6
Cellulose	19.0
Nylon 6.6	23.0
Wool	25.2
Nomex (Aramid)	28.5
Phenol-formaldehyde resin	**35.0**
Neoprene	40.0
Carbon	60.0
Polytetrafluoroethylene	95.0

2.6.4 Insulation and retardancy

An important feature of fire retardancy is heat insulation. Any structure or material which prevents heat reaching further combustible material, or the human body, is valuable. Several types of material achieve this:

1. Non-thermoplastic materials. (wool, carbon fiber)
2. Carbonaceous char.
3. Silica and silicon-based polymers.

2.6.5 The role of char in thermal degradation: fire retardancy

Char, which is formed in the process of thermal degradation, can play several roles in fire retardancy. The formation of char in and of itself has a significant effect on the degradation because char formation must occur at the expense of other reactions that may form volatiles; thus, char formation may limit the amount of fuel available. An example of this occurs in cellulose, which may degrade either by a series of dehydration reactions that yield water, carbon dioxide, and char, or by a process in which levoglucosan is produced, which eventually leads to the formation of volatiles this is shown as

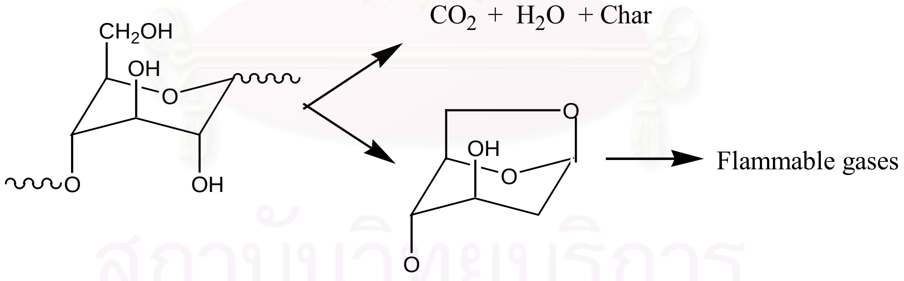


Figure 2.15 Thermal degradation of cellulose to char or flammable gases.

The second role that must be considered is that once char is formed, it can influence further degradation. When an adherent and insulating layer of char is built up on the surface of a polymer, this layer may insulate the underiying polymer from the flame and, thus, make further degradation more difficult. This assumes that the combustion of char is a difficult process and there will be some dependence on the composition of the char layer. The typical char layer consists of an amorphous carbon along the way to graphitization; the extent of graphitization will influence the combustibility of the char layer. Enhanced thermal stability may result if the char layer contains an inorganic component in addition to carbon.

2.6.5.1 Correlation between cross-linking and char formation

A cursory review of the literature would lead one to believe that any cross-linked polymer will be inherently less burnable than a non-cross-linked polymer. In fact this is not the case. The resistance to combustion of a polymer is in some way connected to both the number of cross-links and to the strength of the bonds that make up the cross-linked structure. In recent work from these laboratories, it has been observed that cross-linked methyl methacrylates, copolymers prepared by the radical polymerization of various dimethacrylates with methyl methacrylate, degrade at essentially the same temperature as does the homopolymer poly (methyl methacrylate). The most likely explanation is that the cross-linked structure is produced by very weak bonds that may be relatively easily cleaved thermally. Upon heating, the cross-linked structure is lost and the resulting polymer is now no different from that of methyl methacrylate and its degradation proceeds in the same way.

2.6.5.2 Formation of char.

It is believed that the temperature at the surface of a burning polymer is close to the temperature at which extensive thermal degradation occurs (usually 300 - 600° C). The bottom layer of char, near the polymer surface, is at the same temperature, whereas the upper surface, exposed to the flame, can be as hot as 1500°C. Therefore, fire-retardancy chemistry is concerned with chars, which may be produced at temperatures between 300 and 1500°C[28].

A polymer passes through several steps in the formation of char. These include (a) cross-linking, (b) aromatization, (c) fusion of aromatics, (d) turbostratic char formation, and (e) graphitization. Turbostratic char refers to an incomplete process of graphitization, when solid spheroids (precursors of graphite) appear in the molten carbonaceous material, typically at 500 - 700°C. At this point, the graphite layers are arranged in a parallel fashion, yet they are random in translation and rotation. The char formed during the combustion of polymeric materials is similar to the turbostratic char.

In fire-retardant terminology, all polymers are usually classified as noncharable or charable, depending on whether or not they produce char under pyrolytic conditions. In terms of the chemical processes governing thermal degradation, polymers may be divided into three classes:

(a) Polymers that undergo chain scission and volatilize with, at most, a negligible amount of the char formation [e.g., polyethylene (PE), polypropylene (PP)]

(b) Polymers that undergo chain stripping reactions, producing unsaturation in the main chain with loss of hydrogen atoms and the pendant groups and give a moderate amount of char [e.g., poly(vinyl chloride) (PVC), poly(vinyl alcohol) (PVA)]

(c) polymers that contain aromatic rings that can cross-link simultaneously with chain scission reactions and produce moderate to high amounts of char [e.g., aromatic polyamides (PA), polyesters (PS), polycarbonates (PC), polyimides (PI)]. Different authors may categorize each polymer in one or another category, depending on the emphasis they wish to place on a particular reaction.

2.7 Thermogravimetry

Thermogravimetry (TG) is the branch of thermal analysis which examines the mass change of a sample as a function of temperature in the scanning mode or as a function of time in the isothermal mode. Not all thermal events bring about a change in the mass of the sample (for example melting, crystallization or glass transition), but there are some very important exceptions which include desorption, absorption, sublimation, vaporization, oxidation, reduction and decomposition. TG is used to characterize the decomposition and thermal stability of materials under a variety of conditions and to examine the kinetics of the physicochemical process occurring in the sample. The mass change characteristics of the material are strongly dependent on the experimental conditions employed. Factors such as sample mass, volume and physical form, the shape and nature of the sample holder, the nature and pressure of the atmosphere in the sample chamber and the scanning rate all have important influences on the characteristics of the recorded TG curve.

TG curves are normally plotted with the mass change expressed as a percentage on the vertical axis and temperature or time on the horizontal axis. A schematic representation of a one-stage reaction process observed in the scanning mode is shown in Figure 2.16 The reaction is characterized by two temperatures, T_i and T_f , which are called the procedural decomposition temperature and the final temperature, respectively. T_i merely represents the lowest temperature at which the onset of a mass change can be detected for a given set of experimental conditions. Similarly, T_f represents the lowest temperature by which the process responsible for the mass change has been completed. The values of T_i and T_f have no absolute significance as both the reaction temperature and the reaction interval (T_i - T_f) have no definitive value but depend on the experimental conditions.

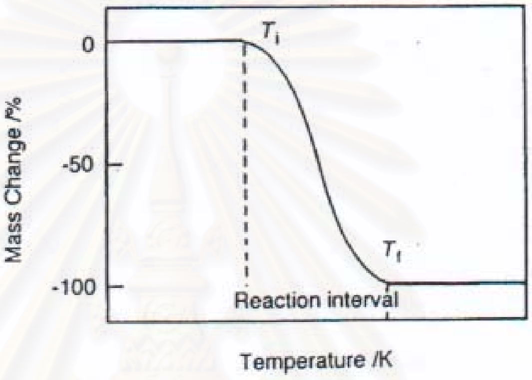


Figure 2.16 Schematic single-stage TG curve.

TG curves are recorded using a thermobalance. The principal elements of a thermobalance are an electronic microbabalance, a furnace, a temperature programmer and an instrument for simultaneously recording the outputs from these devices. A thermobalance is illustrated schematically in Figure 2.17

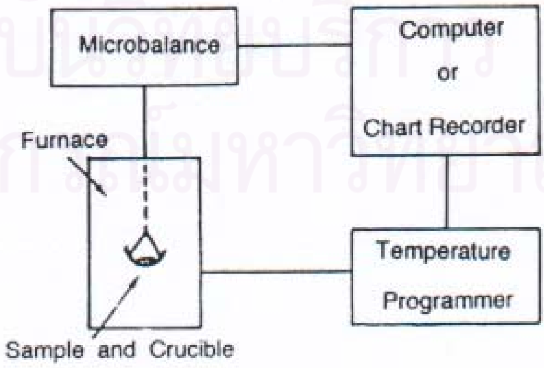


Figure 2.17 Block diagram of a thermobalance.

A scheme for classifying TG curves has been proposed where the curves are classified according to their shape into one of seven categories. Each category is schematically represented in figure 2.18

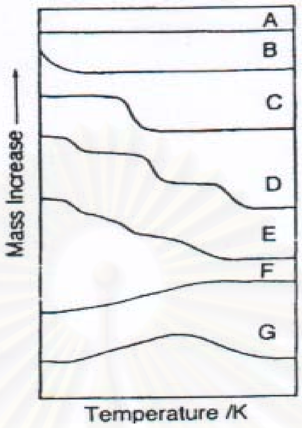


Figure 2.18 Classification scheme for TG curves.

Type A curves show no mass change over the entire temperature range of the experiment and the only information gleaned from the curve is that the decomposition temperature of the material is greater than the maximum temperature**,** under the experimental conditions. Other TA techniques such as DSC can be used to investigate whether nonmass-changing processes have occurred. A large initial mass loss followed by a mass plateau characterize type B curves. Evaporation of volatile components used during polymerization, drying and desorption processes give rise to such curves. Type C, is a single-stage decomposition reaction where the procedural decomposition temperatures (T_i and T_f) are used to characterized the curve. Multi-stage decomposition processes where the reaction steps are clearly resolved comprise type D curves. This is in contrast to type E where the individual reaction steps are not well resolved. In the case of type E the DTG curve is often preferred as the characteristic temperatures may be determined more accurately. In the presence of an interacting atmosphere a mass increase may be observed, giving rise to a type F curve. Surface oxidation reactions belong to this category. The final category, type G, is not frequently encountered and could be caused, for example, by surface oxidation followed by decomposition of the reaction products.

2.8 Differential scanning calorimetry (DSC)

2.8.1 The scope of thermal analysis

Thermal analysis is the name applied to a group of techniques having a common operating principle: as a sample is heated or cooled according to a predetermined programme, some physical property of the sample is recorded as a function of the temperature on a *thermal analysis curve*. Three further considerations have to be satisfied in thermal analysis as it is normally practised:

i. The physical property and the sample temperature should be measured continuously rather than intermittently.

ii. Both these parameters should be recorded automatically.

iii. The temperature of the sample should increase or decrease at a uniform rate.

The main purpose of making thermal analysis measurements is seldom merely the evaluation of the measured property itself as a function of the temperature, but rather the use of the thermal analysis curve to study both physical and chemical change occurring in the sample on heating. The "interpretation" of a thermal analysis curve therefore consisting in relating the features of the property-temperature curve (peaks, discontinuities, changes of slope, etc…) to possible *thermal events* in the sample, i.e. chemical reactions or physical transitions resulting from the change in the sample temperature.

Although in theory the measurement of any physical property can provide basis for a thermal analysis technique, only a few techniques have found widespread application.

In DSC the energy difference (heat enthalpy) between the sample and the reference is measured. In TGA the sample weight is measured.

Figure 2.19 shows a typical DSC run (thermogram) for a semicrystalline polymer. The vertical axis is proportional to the heat capacity of the sample and thus a glass transition is observed as a distinction step. In the figure, the sample has been heated up at a constant temperature rate, and the melting of the crystalline phase will appear 2 as an endothermic process. The area of the endothermic peak corresponds to the heat of fusion, and the peak temperature to the melting point.

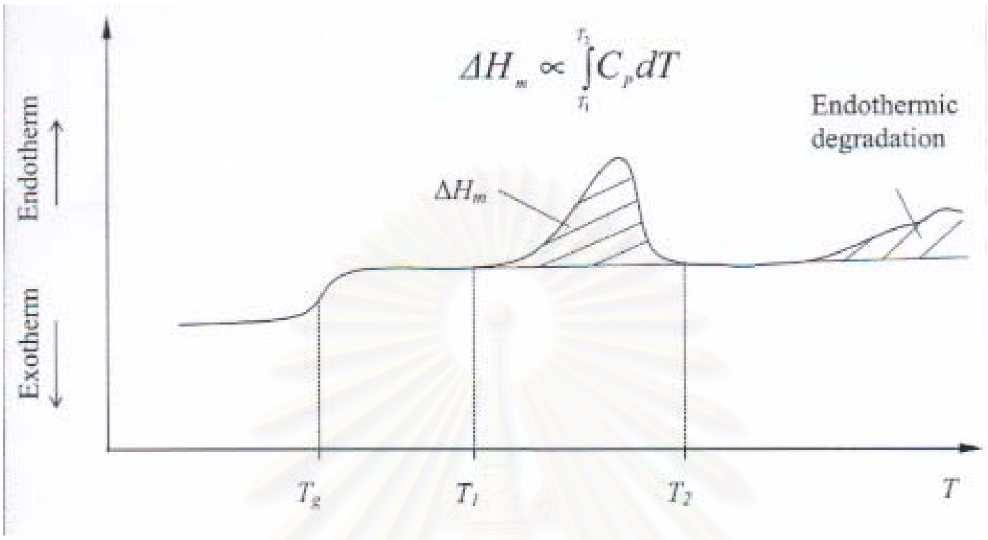


Figure 2.19 Typical thermogram of a semicrystalline polymer.

The sample is very small (3-20 mg) and is placed in a small aluminium vessel (pan). An empty pan is always used as a reference. When the sample is heated up at a constant rate, any kind of change in its calorimetric properties will cause a temperature difference between the sample and the reference. In the DSC apparatus the measured temperature difference is controlling the electrical power to the sample and the reference in order to keep them at the same temperature. In this technique the difference in power supply to the sample and reference is recorded. This means that a peak area from the output recording directly corresponds to the heat consumed or produced by the sample.

In differential thermal analysis (DTA), the temperature difference between the sample and reference is measured. Today, in many DTA instruments the technique has been improved. Instead of measuring the temperatures in the specimen and the reference, the temperatures are measured in thin plates in contact with those, thereby measuring the difference in heat flow from them. This gives a signal proportional to the difference in heat capacities between the sample and the reference and thus the instrument will rather work as a DSC. In fact such instruments are called DSC instruments, or to be more specific, "heat flow DSC". There is an instrument at our laboratory of that kind. However we have also a "power compensated DSC". The most distinguishing feature of the latter is that the sample and the reference have individual heaters and sensors and the measured variable is the difference in power that is supplied to keep the temperature of sample and reference the same during heating, cooling or even isothermal programmes.

2.8.2 Typical applications for DSC

- Determine important transition temperatures like T_m and T_g and study their nature.
- Determine the heat of fusion of a crystalline phase, .H_m, and the degree of crystallisation.
- Studies of crystallisation kinetics.
- Determine heat capacity, C_p.
- Determine the rate of cross-linking reactions, degradation reactions etc.
- Determine miscibility in polymer blends.
- Determine structural relaxation, like enthalpy relaxation during physical aging.

2.9 Infrared spectroscopy

Infrared (IR) radiation refers broadly to that part of the electromagnetic spectrum between the visible and microwave regions. Of greatest practical use to the organic chemist is the limited portion between 4000 and 400 cm^{-1}. There has been some interest in the near-IR (14,290 - 4000 cm^{-1}) and the far-IR regions, 700-200 cm^{-1}

From the brief theoretical discussion that follows, it is clear that even a very simple molecule can give an extremely complex spectrum. The organic chemist takes advantage of this complexity when matching the spectrum of an unknown compound against that of an authentic sample. A peak-by-peak correlation is excellent evidence for identity. Any two compounds, except enantiomers, are unlikely to give exactly the same IR spectrum.

Although the IR spectrum is characteristic of the entire molecule, it is true that certain groups of atoms give rise to bands at or near the same frequency regardless of the structure of the rest of the molecule. It is the persistence of these characteristic bands that permits the chemist to obtain useful structural information by simple inspection and reference to generalized charts of characteristic group frequencies. We shall rely heavily on these characteristic group frequencies.

Since we are not solely dependent on IR spectra for identification, a detailed analysis of the spectrum will not be required. Following our general plan, we shall present only sufficient theory to accomplish our purpose: utilization of IR spectra in conjunction with other spectral data in order to determine molecular structure.

The importance of IR spectrometry as a tool of the practicing organic chemist is readily apparent from the number of books devoted wholly or in part to discussions of applications of IR spectrometry. There are many compilations of spectra as well as indexes to spectral collections and to the literature.

Fourier Transform Infrared (FT-IR) Spectroscopy has been extensively developed over the past decade and provides a number of advantages. Radiation containing all IR wavelengths (e.g., 5000-400 cm^{-1}) is split into two beams (Figure 2.20). One beam is of fixed length, the other of variable length (movable mirror).

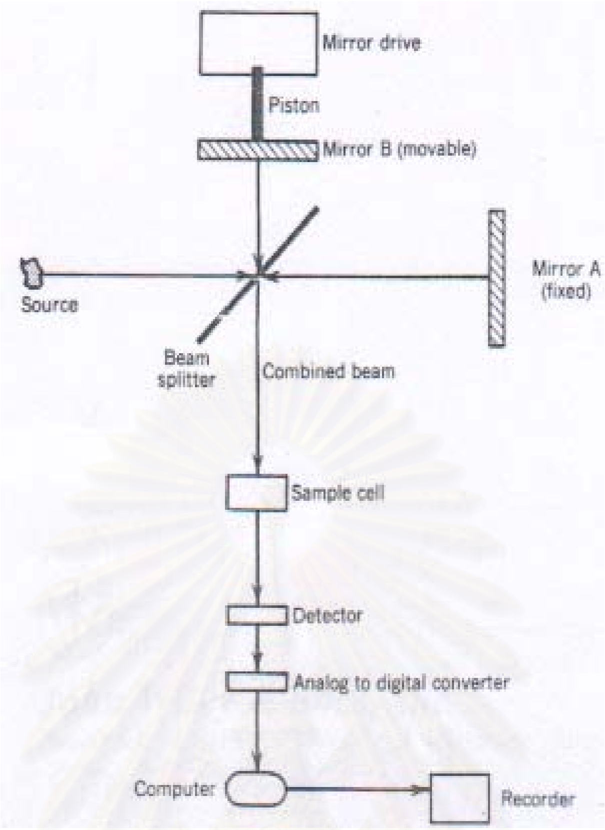


Figure 2.20 Schematic of an FT-IR spectrometer.

The varying distances between two pathlengths result in a sequence of constructive intreferences and hence variations in intensities: an interferogram. Fourier transformation converts this interferogram from the time domain into one spectral point on the more familiar form of the frequency domain. Smooth and continuous variation of the length of the piston adjusts the position of mirror B and varies the length of beam B; Fourier transformation at successive points througthout this variation gives rise to a complete IR spectrum.

There are a number of advantages to FT-IR methods. Since a monochromator is not used, the entire radiation range is passed through the sample simultaneously and much time is saved (Felgett's advantage);

FT-IR instruments can have very high resolution ($\leq$ 0.001 cm^{-1}). Moreover since the data undergo analog-to-digital conversion, IR results are easily manipulated: Results of several scans are combined to average out random absorption artifacts, and excellent spectra from very small samples can be obtained. An FT IR unit can therefore be used in conjunction with HPLC or GC. As with any computer-aided spectrometer, spectra of pure samples or solvents (stored in the computer) can be subtracted from mixtures. Flexibility in spectral printout is also available: for example, spectra linear in either wavenumber or wavelength can be obtained from the same data set.

2.10 Literature survey

Tada-Aki Yamagishi, Masahiro Nomoto, Shingo Ito[12] synthesized the high molecular weight novolac resins were prepared from phenol and formaldehyde in organic solvent , e.g., 2-propanol, ethyl propionate, 2- methoxyethanol, 4-methyl-2-pentanone, dioxane and acetic acid.And it was found that the resin obtained in organic solvent was a random novolac with higher molecular weight than a conventional novolac.

J.E. Shafizadeh, S. Guionnet, M.S.Tillman, J.C. Seferis[2] Studied the phenol-formaldehyde resins catalyzed with sodium hydroxide, triethylamine, and ammonium hydroxide were investigated and characterized in terms of their degradation dehavior, flammability, mechanical properties, and chemical structure. All three resins displayed similar degradative mechanisms, and their degradation behavior was broken down into three distinct stages. These stages were attributed to the evolution of water, the volatilization of species loosely bound to the phenolic backbone, and bulk degradation of the phenolic matrix. The sodium-hydroxide and ammonium-hydroxide-catalyzed resins were found relatively inflammable, while the triethylamine- catalyzed resins burned readily.The mechanical properties of the resins were found to be similar or higher than the mechanical properties of other untoughened epoxies or thermosetting resins.

Marie-Florence Grenier-loustalot, Stephane larroque, Daniel Granda[4-5] investigated the influence of the type of basic catalyst on the mechanisms and kinetics of phenol- formaldehyde reactions in perfectly controlled condition of synthesis (temperature, stoichiometry and pH).The results indicate that the nature of the basic catalyst affects the mechanisms and kinetics of condensation and thus the composition of the reaction medium. The results show that the valence and ionic radius of hydrated cations affect the changes of species in the reaction medium.

M.J. Sumner, M. Sankarapandian, J.E. McGrath, J.S. Riffle, U.Sorathia[11] investigated thermoset networks prepared from phenolic novolacs cured with bisphthalonitrile (BPh) reagents display attractive mechanical, thermal, and fire characteristics. The network properties depend strongly on the novolac-BPh composition. Networks containing 15 wt% BPh or greater had T_gs above 180 ^{o}C and good fracture toughness. Results for an 80:20 (wt/wt) novolac /BPh network, at an incident heat flux of 50 kW/m^2, demonstrated a peak heat release rate of 137 kW/m^2 and char yields > 50 %.These excellent flame properties are similar to those of phenolic resole networks, which are brittle but known to be flame retardant.

H.-T. Chiu , S.-H. Chiu, R.-E. Jeng, J.-S. Chung [10] The thermal degradation and combustion behaviour of an interpenetrating network (IPN) structure of unsaturated polyester UP resin and a resole type of phenolic resin was studied. Thermal gravimetric analysis (TGA) was used to monitor the degree of thermal decomposition for the UP/phenol IPN structure and the change of the oxygen index (OI) was used to describe the variation of the combustion behaviour. The results show that modication of the essentially flammable UP resin by the phenol structure to form an IPN system cannot only remarkably improve the heat resistance but also help to suppress the smoke, toxic gas and heat release during the combustion process.

Benzoxazine was first synthesized by Holly and Cope[13] from phenolic derivatives, primary amine and formaldehyde. Bruke et al.[15, 16] found that benzoxazine rings react preferentially with the ortho positions of the free phenolic compounds to form a dimer with a Mannich bridge structure.

Ning and Ishida[14] synthesized the bifunctional benzoxazine precursors to yield high molecular weight polymers. The physical and mechanical properties of polybenzoxazines had been reported.[17] Ishida and Rodriguez[18] studied them polymerization kinetics of benzoxazine precusor is autocayalytic in nature and is very similar to that of a purified monomer.

Ishida and Low[19] investigated the effect of intramolecular hydrogen bonding on volumetric expansion of benzoxazines by systematically varying the types of the primary amines used in the synthesis. Intramolecular hydrogen bonding occurs in these materials between the phenolic OH and nitrogen of the Mannich base. The strength of this hydrogen bonding depends on the electronegativity of the amine group attached to the nitrogen.The stronger the hydrogen bonding, the greater the volumetric expansion. In addition the steric effect of the amine group also influences the volumetric change during a curing process. Sopa et al.[31] studied the temperature dependency of various hydrogen bonding in the phenolic novolac and polybenzoxazine resin. They found that the intermolecular hydrogen bonding is more sensitive to temperature than the intramolecular hydrogen bond.

Rimdusit and Ishida[20,21,22] synthesized the ternary systems base on benzoxazine, epoxy, and phenolic resins. The materials showed a wide range of desirable reliability and processability, which are highly dependent on the composition of the monomers in the ternary mixture. Intriguing physical, mechanical, and rheological properties of these systems had been reported.Phenolic novolac resin acts mainly as an initiator for these systems while low melt viscosity,flexibility and improved crosslink density of the materials are attributed to the epoxy fraction.Polybenzoxazine imparts thermal curability, mechanical properties as well as low water uptake to the ternary systems.

Wang and Ishida[35] studied the effect of various initiators on the benzoxazine polymerization. They found that the ring-opening polymerization of the benzoxazine family follows a cationic polymerization.

CHAPTER 3

EXPERIMENT

3.1 Materials

Phenol (98%, AR grade) was purchased from BHD Laboratory Supplies. Formaldehyde in a form of formalin solution (37% w/w, AR grade), NaOH (AR grade) and *p*-formaldehype (AR grade) were purchased from Merck Company. Bisphenol-A (commercial grade) was kindly donoted by Thai Polycarbonate Co., Ltd. (TPCC). Aniline (AR grade) was purchased from APS Finechem Company. Oxalic acid (AR grade) was purchased from Suchapanpanit Company. All chemicals were used without further purification.

3.2 Instruments and equipment

3.2.1 Thermogravimetric analysis (TGA)

Thermal decomposition temperatures were obtained using a TA Instument High Resolution TGA (model TGA/SDTA851^e) of Metler Toledo. Each sample (15-20 mg) was put in crucible and then heated under nitrogen with heating rate of 20^{o}C/min from room temperature to 900^{o}C.

3.2.2 Differential scanning calorimetry (DSC)

Curing behaviors and thermal transitions of the sample were measured using a TA Instument DSC 2910 differential scanning calorimeter. Each sample (5-10 mg.) was sealed in aluminum pans and heated under nitrogen with a heating rate of 10^{o}C/min from room temperature to 300^{o}C.

3.2.3 Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra of the samples were obtained using Nicolet Impact FT-IR spectrometer scans at a resolution of 4 cm^{-1}. A frequency range of 4000-400 cm^{-1} was observed.The spectrum of each sample was recorded in the solid state as a KBr pellet.

3.3 Methodology

3.3.1 Synthesis of benzoxazine monomer

The benzoxazine monomer was synthesized by the following procedure[16,17]. 0.2 mole of aniline in 20 ml of dioxane was slowly added to an aqueous solution of formaldehyde 0.4 mole in dioxane 80 ml. The temperature of mixture was kept below 10°C during the addition of aniline. The mixture was stirred for 10 min and then 0.1 mole of bisphenol-A in 100 ml of dioxane was added to the system. The temperature was raised to 90°C and the mixture was refluxed for 6 hours. A clear yellowish solid resin was obtained after solvent (dioxane) was removed. This resin was used without further purification. The benzoxazine monomer was solid at the room temperature. It was ground fine powder and kept in a refrigerator. The chemical structure of benzoxazine resin used in this work are shown in Figure 3.1. The IUPAC notation of this compounds is bis(3,4-dihydro-2H-3-phenyl-1,3-benzoxazinyl) isopropane (abbreviated as BA-a).

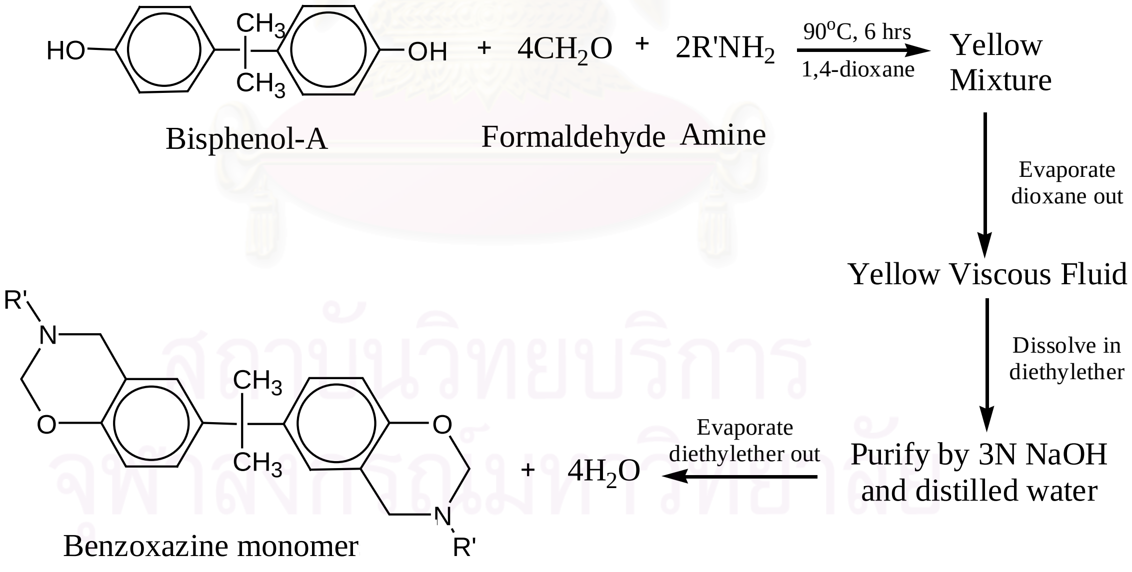


Figure 3.1 Synthesis of benzoxazine-based bisphenol-A (BA-a).

3.3.2 Synthesis of novolac resins

3.3.2.1 Part I: Effect of pH on % solid of product.

Novolac resins were prepared by polycondensation of phenol (P) and formaldehyde (F) using a molar ratio ([F]/[P]) of 0.8. The reaction mixture was heated under constant stirring for 4 hours at 100^{o}C. The pH of the mixture (2.4, 2.2, 2.0 and 1.8) was adjusted by adding aqueous solution of oxalic acid.Water was distilled out and the product was dried in vacuum at 70^{o}C for 6 hours.

3.3.2.2 Part II: Effect of [F]/[P] molar ratio on % solid of product.

The procedure used was the same as part I. But the pH of the mixture was adjusted to a suitable pH (from part I) while the molar ratios of [F]/[P] were varied from 0.6, 0.7, 0.8 to 0.9.

3.3.2.3 Part III: Effect of temperature on % solid of product.

The procedure used was the same as part I. But the pH of the mixture was adjusted to a suitable pH (from part I) and the molar ratio of [F]/[P] of the mixture was adjusted to a suitable molar ratio of [F]/[P] (from part II) while the temperature were varied from 80^{o}C, 90^{o}C, 100^{o}C to 110^{o}C.

3.3.3 Synthesis of resole resins

3.3.3.1 Part IV: Effect of [F]/[P] molar ratio on % solid of product.

Resole resins were prepared by polycondensation of phenol (P) and formaldehyde (F). The reaction mixture was heated under constant stirring for 60 min at 80^{o}C. The pH of the mixture was adjusted to 8.0 by adding aqueous solution of 37 % w/v of sodium hydroxide. While the molar ratios of [F]/[P] were varied from 1.4, 1.5, 1.6 and 1.7.Water was distilled out and the product was dried in vacuum at 50^{o}C for 8 hours.

3.3.3.2 Part V: Effect of pH on % solid of product.

The procedure used was the same as part I. But the molar ratio of [F]/[P] of the mixture was adjusted to a suitable molar ratio of [F]/[P] (from part IV) while the pH of the mixture were varied from 7.5, 7.8, 8.0, 8.2 to 8.4.

3.3.3.3 Part VI: Effect of temperature on % solid of product.

The procedure used was the same as part I. But the molar ratio of [F]/[P] of the mixture was adjusted to a suitable molar ratio of [F]/[P] (from part IV) and the pH of the mixture was adjusted to a suitable pH (from part V) while the temperature were varied from 70°C, 80°C, 90°C to 100°C.

3.3.4 Preparation of benzoxazine/phenolic alloys.

Each resin was first measured at desirable mass fraction. The mixture of benzoxazine and novolac resin was then heated to about 80°C in an aluminum pan and hand-mixed for a few minutes until the homogeneous mixture was obtained. Part of the mixture was then taken for differential scanning calorimetric analysis for determination of curing condition. On the other hand, the mixture of benzoxazine and resole resin was heated to about 70°C with aqueous solution of methanol and hand - mixed for a few minutes until the homogeneous mixture was obtained. Part of the mixture was then taken for differential scanning calorimetric analysis for determination of curing condition. All specimens were thermally cured at curing condition for a complete curing reaction in aluminum molds at various dimensions, depending upon the type of experiments.

3.4 Fire testing

3.4.1 Determination of limiting oxygen index

This is a parameter widely used for quality assurance although its use to indicate flammability has been seriously doubted.

BS 2782 (1978) Methods 141A to 141D cover the oxygen index of combustion determined on four different test pieces:(This study, the oxygen index of combustion determined on 141A)

141A A bar of 10 ✠ 4 mm nominal cross – section (right materials)
141B A bar of 6.5 ✠ 3 mm nominal cross – section (right materials)
141C A bar 10 mm wide cut from rigid sheet 1.2 6.5 mm thick
141D A bar of 6.5 ✠ 3 mm nominal cross – section of electric cable insulation or sheathing material

Basically, the test determines the minimum oxygen concentration necessary to support flaming combustion of the material under certain conditions. The test piece is clamped vertically at its base and supported in a glass chimney of specified dimensions. Arrangements are provided to ignite the top of the test piece with a propane flame and a mixture of nitrogen and oxygen (of known purity) is metered into the bottom of the chimney. Tests are then made to find the oxygen concentration in the gas mixture to cause the test piece, after ignition, to burn over a specified distance and time (at least 50 mm and at least 180 s). Fresh test pieces are used for each determination and the test is continued until the critical oxygen concentration for each burn is within 0 – 3 percent on total volume of gas. Three such determinations are carried out and the mean value is reported as the oxygen index of the material under test.

ASTM D 2863 (1977) (Figure 3.2) is similar to BS 2782 Method 141B.

NES 714 refers to BS 2782 Methods 141 A to D but is frequently used in conjunction with NES 715 which determines the temperature at which materials will just burn in air, i.e. at 21 percent oxygen. Two procedures are used, one in which the oxygen index is determined at various temperatures and the temperature at 21 percent LOI is read off. Alternatively, the temperature of the furnace is adjusted until the specimen just burns in air.

The OI then is defined as:

$$[OI]\% = \frac{[O_2]}{[O_2]+[N_2]} x100\%$$

$[O_2]$ = volumetric flow rate of O_2, cm^3/s;

$[N_2]$ = volumetric flow rate of N_2, cm^3/s.

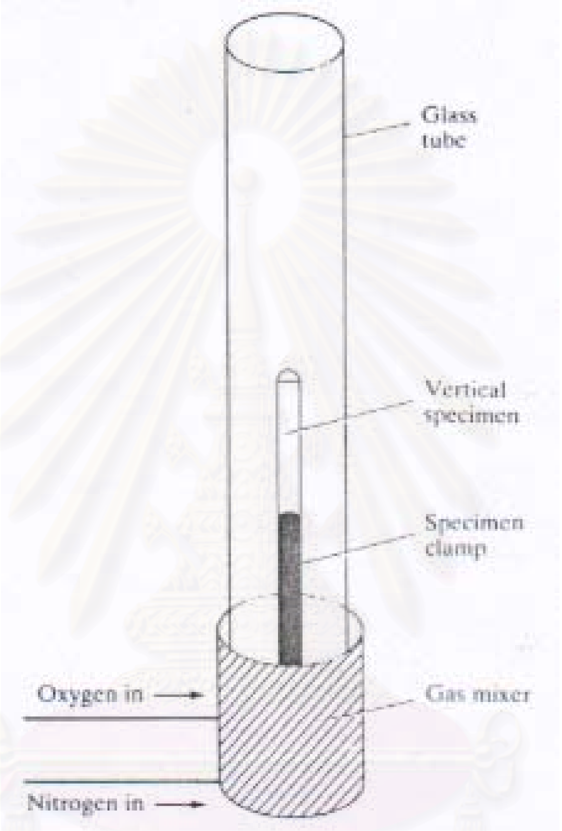


Figure 3.2 Schematic diagram of oxygen index test ASTM D2863.

3.4.2 Determination of burning rate (laboratory method)

BS 2782 1970 Method 508A (Figure 3.3). Burning Rate (laboratory method), currently under review, is similar to ASTM D635 (1981). A test piece in the form of a bar 150 mm long, 13 mm wide and 1.5 mm thick is scribed with reference lines across the test piece at 25 mm and 125 mm from one end. It is then clamped horizontally and with the plane of the width at an angle of 45°, and so mounted that the lower edge of the specimen is 6 mm above a sheet of metal gauze 130 mm square. A flame, from 13 to19 mm in height, is applied to the free end of the test piece for 10 s and the time taken for the edge of the flame of the burning test piece to travel the distance of 100 mm between the two reference line is measured with a stop-watch. At least three test pieces are used and the result (reported for each test piece) is expressed as: (a) The rate of burning (mm/min); or (b) that the flame does not reach the first mark; or (c) that the flame does not reach the second mark; or (d) for test pieces where the flame does not reach the first mark, the duration of flame or after flow after removal of the burner.

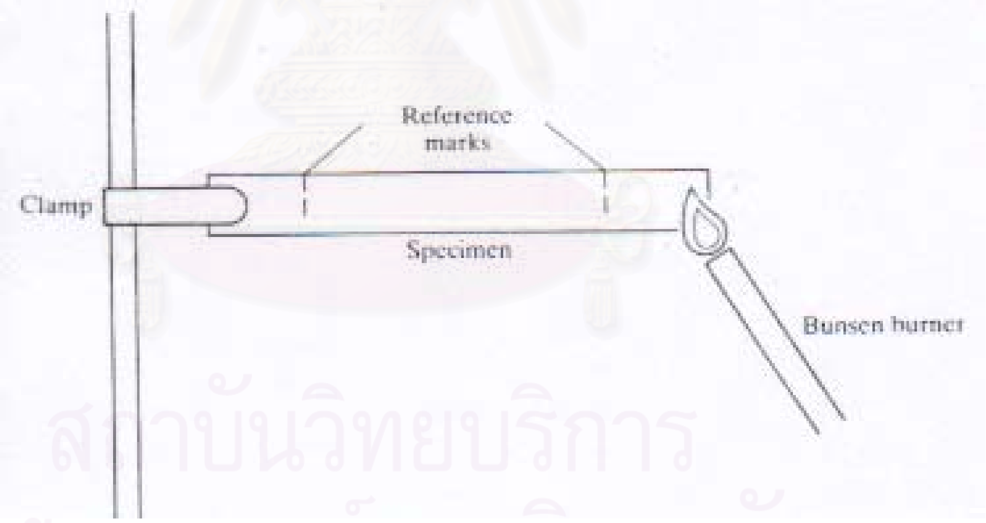


Figure 3.3 Typical arrangement of small flame ignitability/flame spread test with horizontal specimen of rigid material.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of alloy components.

4.1.1 Characterization of benzoxazine monomer.

The synthesized product was a light yellow solid at room temperature. It was soluble in acetone, THF, ethyl acetate, toluene and slightly soluble in methanol. FT-IR spectrum shown in Figure 4.1 with its peak assignments given in Table 4.1 confirms that the synthesize product is benzoxazine monomer.

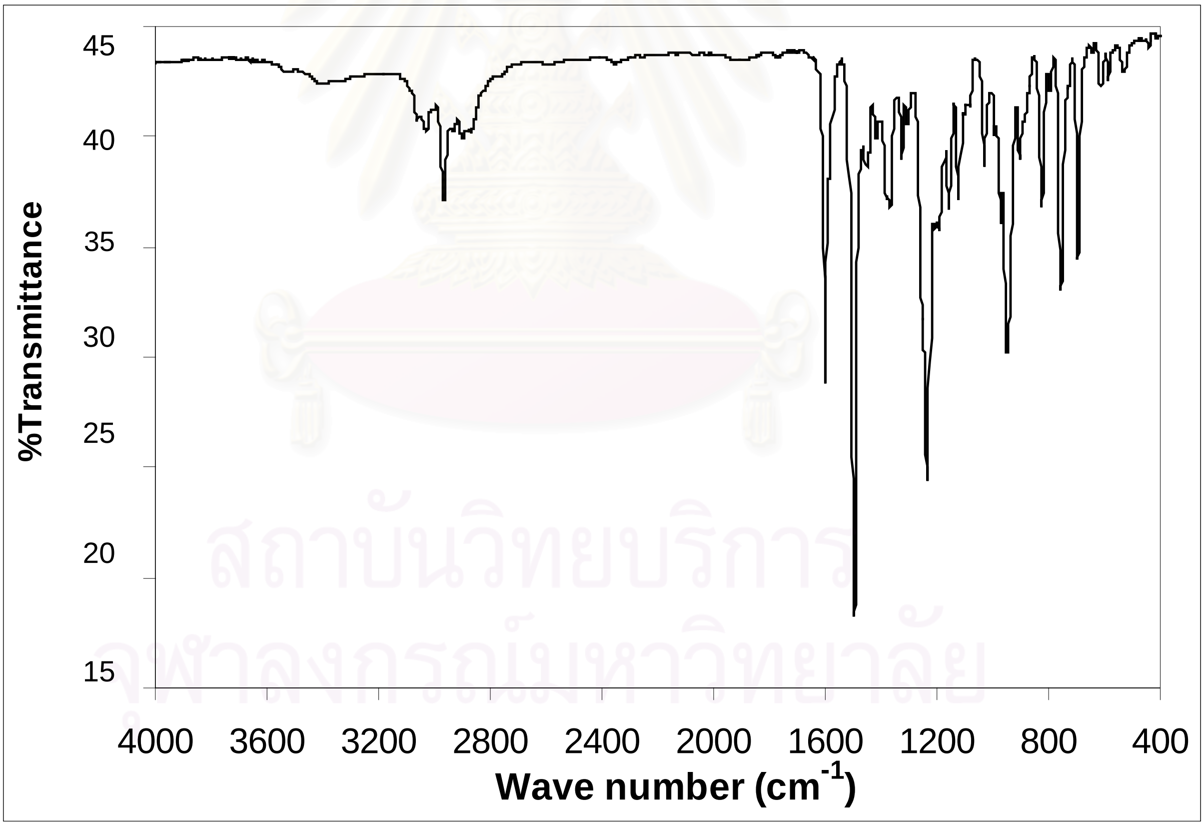


Figure 4.1 FT-IR spectrum of synthesized benzoxazine monomer.

Table 4.1 FT-IR peak assignments of synthesized benzoxazine monomer.

Peak position (cm^{-1})	**Assignment**
3059	C-H stretching of benzene ring
2965	C-H asymmetric stretching of methyl group
2899	C-H asymmetric stretching of methylene group
1608	C=C stretching of benzene ring
1500	C=C stretching of benzene ring
1450	C=C stretching of benzene ring
1381	C-H symmetric deformation of geminated methyl group of bisphenol-A
1366	C-N(-Ar) asymmetric stretching of aliphatic aromatic amine
1232	C-O(-Ar) asymmetric stretching of aliphatic aromatic ether
1121	C-H in plane deformation of 1,2,4-tri-substituted mode of oxazine ring
943	C-H out of plane deformation of 1,2,4-tri-substituted mode of oxazine ring
821	C-H out of plane deformation of 1,4-di-substituted mode of bisphenol-A
751	C-H out of plane deformation of mono-substituted mode of benzene ring
631	C-H out of plane deformation of mono-substituted mode of benzene ring

4.1.2 Characterization of novolac resin.

The synthesized product was an orange solid at room temperature. It was soluble in methanol, toluene but insoluble in water. FT-IR spectrum shown in Figure 4.2 with its peak assignments given in Table 4.2 confirms that the synthesize product is novolac resin.

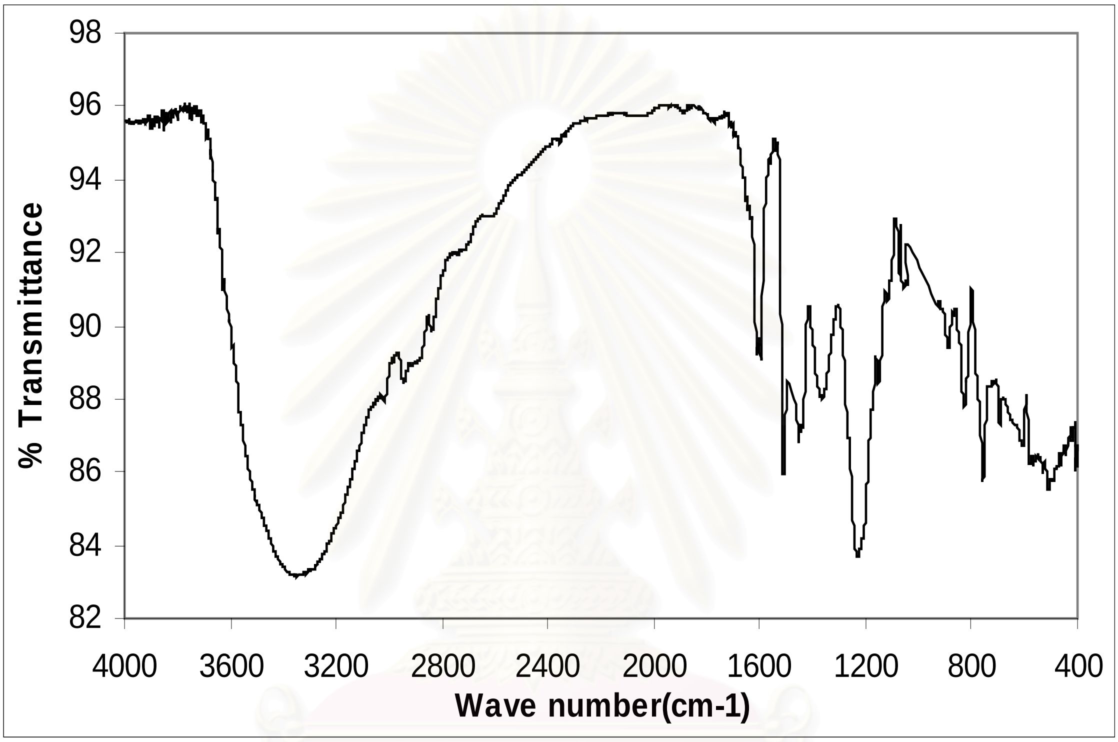


Figure 4.2 FT-IR spectrum of synthesized novolac resin

Table 4.2 FT-IR peak assignments of synthesized novolac resin.

Peak position (cm^{-1})	**Assignment**
3294	O-H stretching of phenol
3012	C-H stretching of benzene ring
2902	C-H asymmetric stretching of methyl group
2820	C-H symmetric stretching of methyl group
1615	C=C stretching of benzene ring
1508	C=C stretching of benzene ring
1427	C=C stretching of benzene ring
1240	C-O asymmetric stretching of phenol
1100	C-H in plane deformation of 1,2,3-tri-substituted mode of benzene ring
820	C-H out of plane deformation of 1,2,3-tri-substituted mode of benzene ring
758	C-H out of plane deformation of mono-substituted mode of benzene ring

4.1.3 Characterization of resole resin.

The synthesized product was a dark red solid at room temperature. It was soluble in methanol, toluene but insoluble in water. FT-IR spectrum shown in figure 4.3 with its peak assignments given in Table 4.3 confirms that the synthesize product is resole resin.

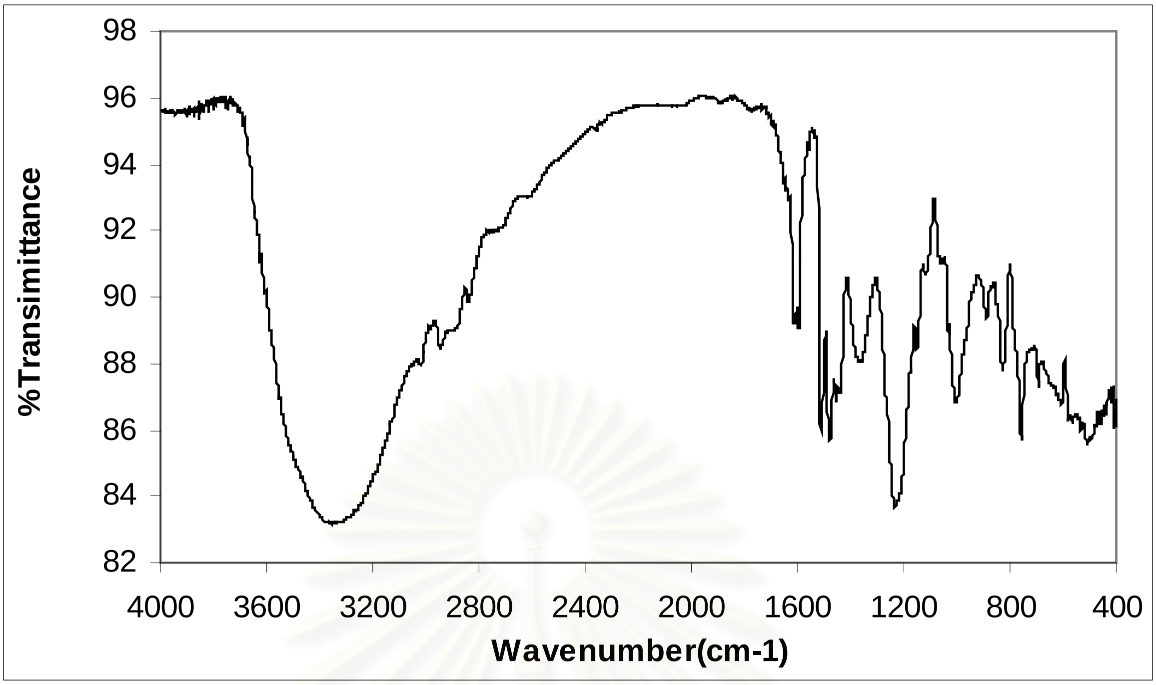


Figure 4.3 FT-IR spectrum of synthesized resole resin.

Table 4.3 FT-IR peak assignments of synthesized resole resin.

Peak position (cm^{-1})	**Assignment**
3408	O-H stretching of phenolic and methylol
3020	C-H stretching of benzene ring
2950	C-H asymmetric stretching of methyl group
1620	C=C stretching of benzene ring
1474	C-H deformation of aliphatic
1434	C=C stretching of benzene ring
1212	C-O in plane stretching of phenolic
1010	**C-O stretching of methylol (this peak no shows in IR of novolac resin)**
825	C-H out of plane deformation of 1,2,3-tri-substituted mode of benzene ring
766	C-H out of plane deformation of mono-substituted mode of benzene ring

4.2 Effect of reaction parameters on the polymerizations of phenolic resins.

4.2.1 Polymerization of novolac resins.

Table 4.4 % yield of novolac resins obtained from the polymerizations using different pH.

pH	Total mass of substance (g)	Total mass of product (g)	Total mass of product after 48 hours. (g)	Total mass of product after 72 hours. (g)	% yield
2.4	59.283	43.037	42.234	42.122	71.05
2.2	59.302	47.327	47.223	47.200	79.59
2.0	59.345	48.012	47.623	47.302	79.71
1.8	59.297	47.232	46.423	46.403	78.26

Table 4.4 shows the effect of pH on % yield of novolac resins. Novolac resins were synthesized via condensation polymerization of phenol (P) and formaldehyde (F) at 100^{o}C in a molar ratio of [F]/[P] 0.8 for 4 hours. This polymerization condition was proposed by Antony and Pillai[1]. In this experiment, pH of polymerization mixtures were adjusted to 2.4, 2.2, 2.0 and 1.8 using aqueous solution of oxalic acid. From Table 4.4, it can be seen that highest % yields were obtained when pH of the mixtures were 2.2 and 2.0. Since lower amount of oxalic acid solution was used when higher pH was desired; therefore, pH of 2.2 was selected in stead of pH 2.0 for further studies.

Table 4.5 % yield of novolac resins obtained from the polymerizations using different molar ratios of [F]/[P].

[F]/[P]	Total mass of substance (g)	Total mass of product (g)	Total mass of product after 48 hours. (g)	Total mass of product after 72 hours. (g)	% yield
0.6	56.132	41.315	38.212	38.192	68.04
0.7	57.565	45.215	43.266	43.124	74.91
0.8	59.293	50.533	47.212	47.180	79.57
0.9	60.675	52.283	48.625	48.492	79.92

Table 4.5 shows the effect of the molar ratios of [F]/[P] on % yield of novolac resins. Novolac resins were synthesized via condensation polymerization of phenol (P) and formaldehyde (F) at 100^{o}C, pH 2.2 using aqueous solution of oxalic acid (the results from table 4.4) for 4 hours. In this experiment, the molar ratios of [F]/[P] of polymerization mixtures were adjusted to 0.6, 0.7, 0.8 and 0.9. From these Table, it can be seen that highest % yields were obtained when the molar ratio of [F]/[P] of the mixture were 0.8 and 0.9. Since lower amount of formaldehyde was used when higher % yield was desired; therefore, the molar ratio [F]/[P] of 0.8 was selected in stead of the molar ratio [F]/[P] of 0.9 for further studies.

Table 4.6 % yield of novolac resins obtained from the polymerizations using different temperatures.

Temp.	Total mass of substance (g)	Total mass of product (g)	Total mass of product after 48 hours. (g)	Total mass of product after 72 hours. (g)	% yield
80	59.301	40.038	38.037	37.044	62.47
90	59.256	46.167	44.022	43.122	72.77
100	59.293	50.533	47.212	47.180	79.57
110	59.298	45.235	44.022	43.982	74.17

Table 4.6 shows the effect of temperature on % yield of novolac resins. Novolac resins were synthesized via condensation polymerization of phenol (P) and formaldehyde (F) in a molar ratio of [F]/[P] 0.8 (the results from table 4.5), pH 2.2 using aqueous solution of oxalic acid (the results from table 4.4) for 4 hours. In this experiment, temperature of polymerization mixtures were adjusted to 80^{o}C, 90^{o}C, 100^{o}C and 110^{o}C. From Table 4.6, it can be seen that highest % yields were obtained when temperature of the mixture were 100^{o}C. Therefore, temperature at 100^{o}C was selected for further studies.

4.2.2 Polymerization of resole resins.

Table 4.7 % yield of resole resins obtained from the polymerizations using different molar ratios of [F]/[P].

F/P	Total mass of substance (g)	Total mass of product (g)	Total mass of product after 48 hours (g)	Total mass of product after 72 hours (g)	% yield
1.7	72.623	59.102	56.403	56.311	77.54
1.6	71.124	58.326	56.183	56.023	78.77
1.5	69.525	56.329	54.703	54.623	78.57
1.4	66.603	44.502	43.269	43.233	64.91

Table 4.7 shows the effect of the molar ratio of [F]/[P] on % yield of resole resins. Resole resins were synthesized via condensation polymerization of phenol (P) and formaldehyde (F) at 80^{o}C, pH 8.0 using aqueous solution of 37 % w/v of sodium hydroxide for 60 min. This polymerization condition was proposed by Shafizadeh and Guionnet[2]. In this experiment, the molar ratio of [F]/[P] of polymerization mixtures were adjusted to 1.4, 1.5, 1.6 and 1.7. From Table 4.7, it can be seen that highest % yields were obtained when the molar ratio of [F]/[P] of the mixture were 1.5 and 1.6. Since lower amount of formaldehyde was used when higher % yield was desired; therefore, the molar ratio [F]/[P] of 1.5 was selected in stead of the molar ratio [F]/[P] of 1.6 for further studies.

Table 4.8 % yield of resole resins obtained from the polymerizations using different pH.

pH	Total mass of substance (g)	Total mass of product (g)	Total mass of product after 48 hours. (g)	Total mass of product after 72 hours. (g)	% yield
7.5	69.612	52.306	46.505	46.325	66.55
7.8	69.573	56.983	54.901	54.428	78.23
8.0	69.544	55.367	54.836	54.772	78.76
8.2	69.562	57.666	55.832	54.832	78.82
8.4	69.607	56.326	55.756	54.527	78.33

Table 4.8 shows the effect of pH on % yield of resole resins. Resole resins were synthesized via condensation polymerization of phenol (P) and formaldehyde (F) at 80°C in a molar ratio of [F]/[P] 1.5 (the result from table 4.7) for 60 min. In this experiment, pH of polymerization mixtures were adjusted to 7.5, 7.8, 8.0, 8.2 and 8.4 using aqueous solution of 37 % w/v of sodium hydroxide. From Table 4.8, it can be seen that highest % yields were obtained when pH of the mixture were 8.0 and 8.2. Since lower amount of sodium hydroxide was used when higher % yield was desired; therefore, pH of 8.0 was selected in stead of pH 8.2 for further studies.

Table 4.9 % yield of resole resins obtained from the polymerizations using different temperatures.

Temp.	Total mass of substance (g)	Total mass of product (g)	Total mass of product after 48 hours. (g)	Total mass of product after 72 hours. (g)	% yield
70	69.620	56.325	52.236	52.003	74.695
80	69.544	55.367	54.836	54.772	78.76
90	69.562	57.666	55.832	54.832	78.82
100	69.601	54.389	53.332	53.015	76.17

Table 4.9 shows the effect of on % yield of resole resins. Resole resins were synthesized via condensation polymerization of phenol (P) and formaldehyde (F) in a molar ratio of [F]/[P] 1.5 (the results from table 4.7) pH 8.0 using aqueous solution of 37 % w/v of sodium hydroxide (the results from table 4.8) for 60 min. In this experiment, temperature of polymerization mixtures were adjusted to 70^{o}C, 80^{o}C, 90^{o}C and 100^{o}C. From Table 4.9, it can be seen that highest % yields were obtained when temperature of the mixture were 80^{o}C and 90^{o}C. Since lower temperature was used when higher % yield was desired; therefore, temperature at 80^{o}C was selected in stead of 90^{o}C for further studies.

4.3 Curing conditions and thermal experiments of alloys and alloy components.

4.3.1 DSC analysis

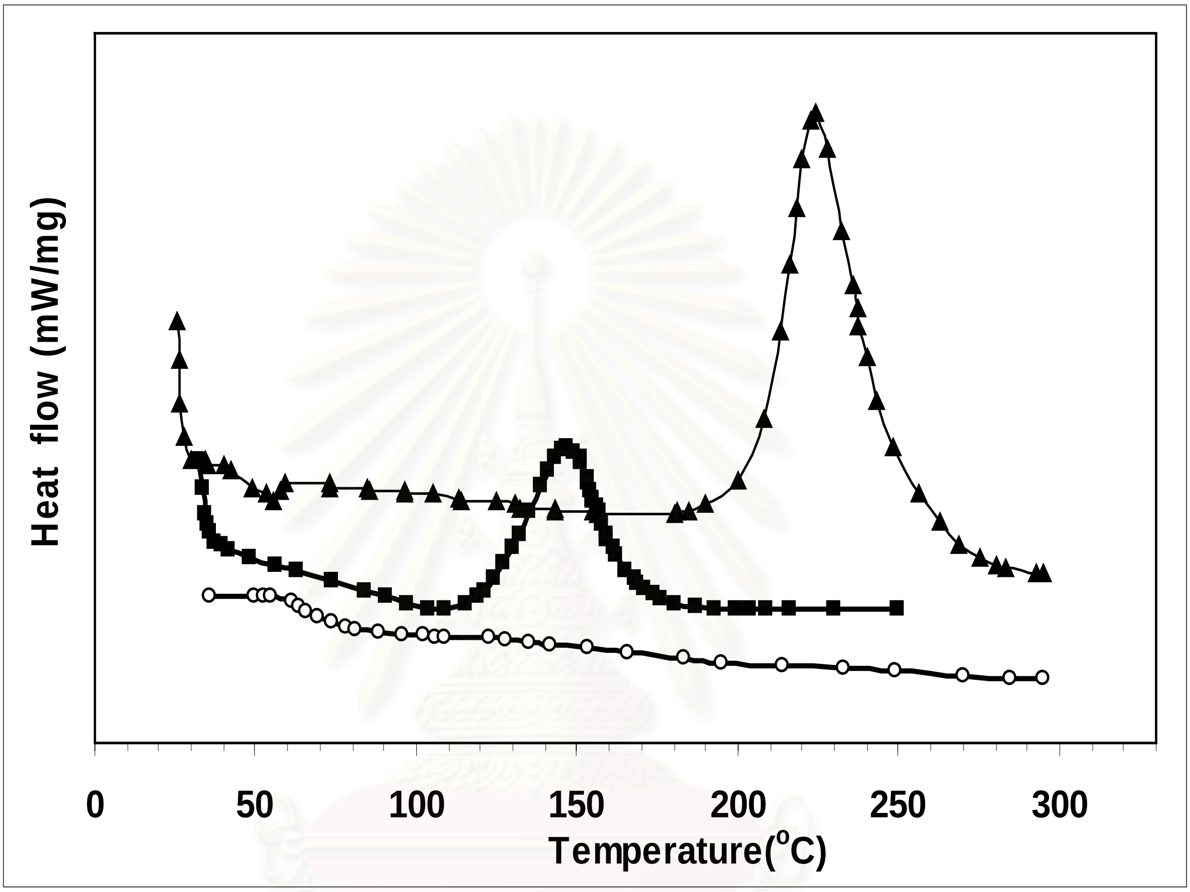


Figure 4.4 DSC thermograms of benzoxazine (▲); resole (■); novolac (○).

Figure 4.4 shows DSC thermograms in the temperature range of 30 – 300°C at the heating rate of 10°C/min of benzoxazine, resole, and novolac resins. It can be seen that the curing exotherms of the benzoxazine monomer and resole resin were at peak maxima of about 229°C and 149°C, respectively. This indicates characteristic of thermal curability of benzoxazine monomer and resole resin. On the contrary, the novolac resin show no sign of a curing behavior in this temperature range without adding curing agents.

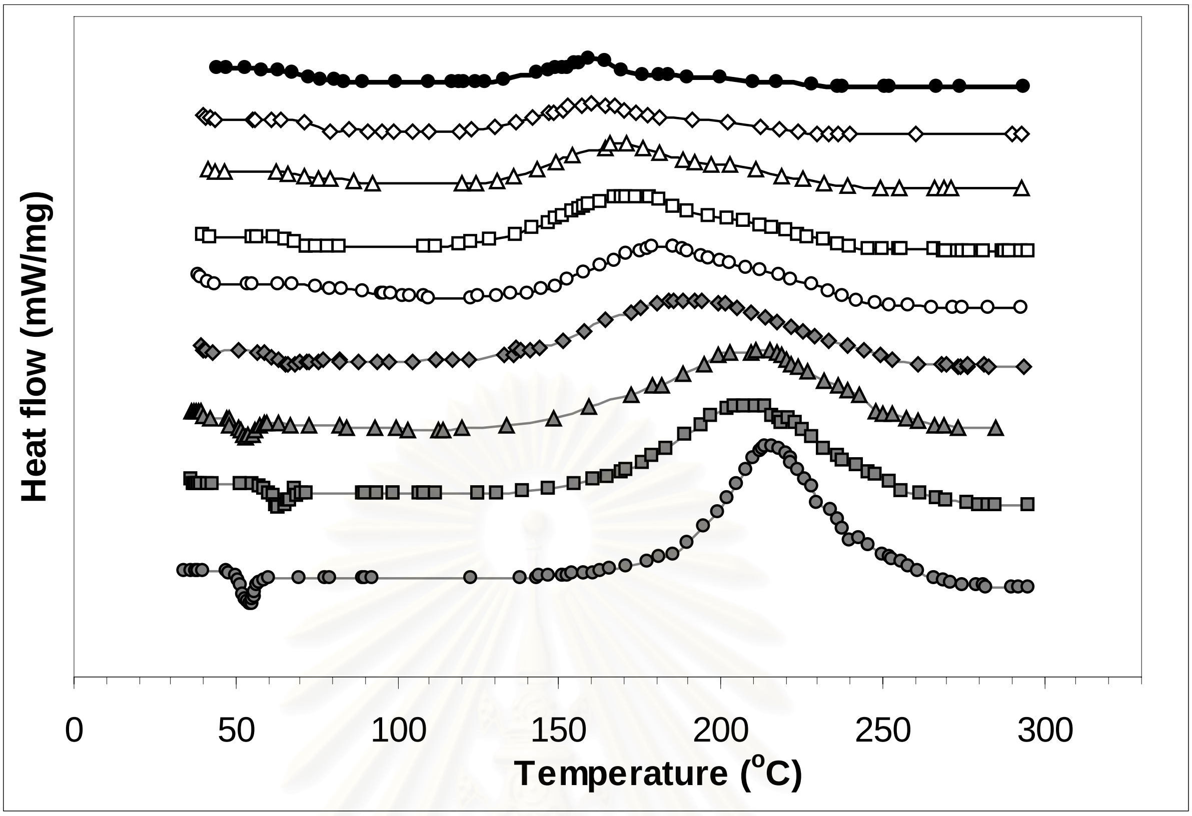


Figure 4.5 DSC thermograms presenting of the curing behavior of benzoxazine/novolac alloys: [(●) BN 91; (■) BN 82; (▲) BN 73; (◆) BN 64; (○) BN 55; (☐) BN 46; (Δ) BN 37; (◇) BN 28; (●) BN 19].

Figure 4.5 shows DSC thermograms presenting the curing behavior of benzoxazine/novolac alloys and the results are summarized in Table 4.10. From the thermograms, the curing acceleration is observed from the shift of the curing exotherm peaks to lower temperatures when the amount of novolac resin in the alloys increases. The relationship between the exotherm peaks and the amount of novolac resin in the alloys suggests that novolac resin acts as a curing accelerator for benzoxazine resin. This is in good agreement with the previous works reported by Ishida and Ning[14].

Table 4.10 Glass transition temperatures (T_g) and curing characteristics of benzoxazine/novolac alloys.

Sample	**DSC cure temperatures (^OC)^a**			**Quan. (J/g)**	**T_g (^OC)**
	T_i	**T_{max}**	**T_f**		
Benzoxazine	171	229	286	220.2	170
B/N 9/1	148	216.51	282	257.1	167.14
B/N 8/2	131	210.66	285	242.0	167.95
B/N 7/3	120	208.05	280	211.0	163.24
B/N 6/4	117	191.37	272	196.0	160.49
B/N 5/5	121	183.60	265	173.1	151.84
B/N 4/6	115	172.64	256	149.2	143.70
B/N 3/7	117	169.00	249	106.9	121.34
B/N 2/8	108	160.27	240	68.9	107.31
B/N 1/9	110	157.72	252	43.43	92.83
Novolac	-	-	-	-	74.56

a T_i, T_{max} and T_f refer to the cure initiation, maximum and cure end temperatures.

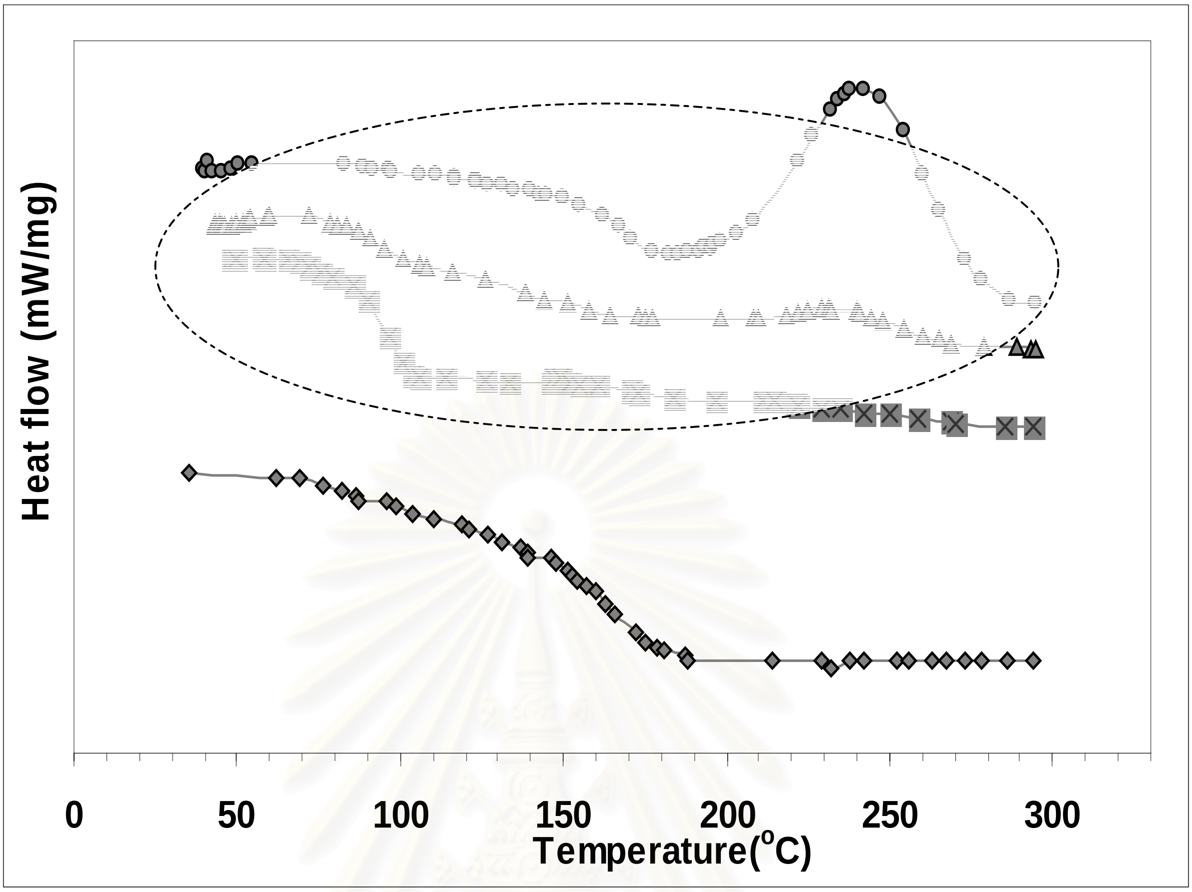


Figure 4.6 DSC thermograms of benzoxazine/novolac alloys at various curing conditions: [(●) BN 91, (▲) BN 55, (▣) BN 19 after cure at 150^{O}C/ 1 hour + 180^{O}C/ 1 hour: And (◆) BN 91 after cure at 150 ^{O}C/ 1 hour + 180 ^{O}C/2 hours].

Figure 4.6 exhibits the DSC thermograms of benzoxazine/novolac alloys at various curing conditions. At curing condition of 150°C/1 hour + 180°C/1 hour, the thermograms show no exotherm maxima within the temperature range of 30 – 300°C but the thermograms show the glass transition temperature (T_g) of these systems when the mass fraction of novolac resin is lower than 50% by weight in the alloys. For this reason, suitable curing condition for completing the curing reaction of the alloys when mass fraction of novolac resin is lower than 50% by weight is at 150°C/1 hour + 180°C/1 hour.

At curing condition of 150°C/1 hour + 180°C/2 hours the thermograms show no exotherm maxima within the temperature range of 30 – 300°C but the thermograms show the T_g of this system when the mass fraction of novolac resin is higher than 50% by weight in the alloys. This suggests that this curing condition is suitable for completing the curing reaction of the alloys when mass fraction of novolac resin is higher than 50% by weight.

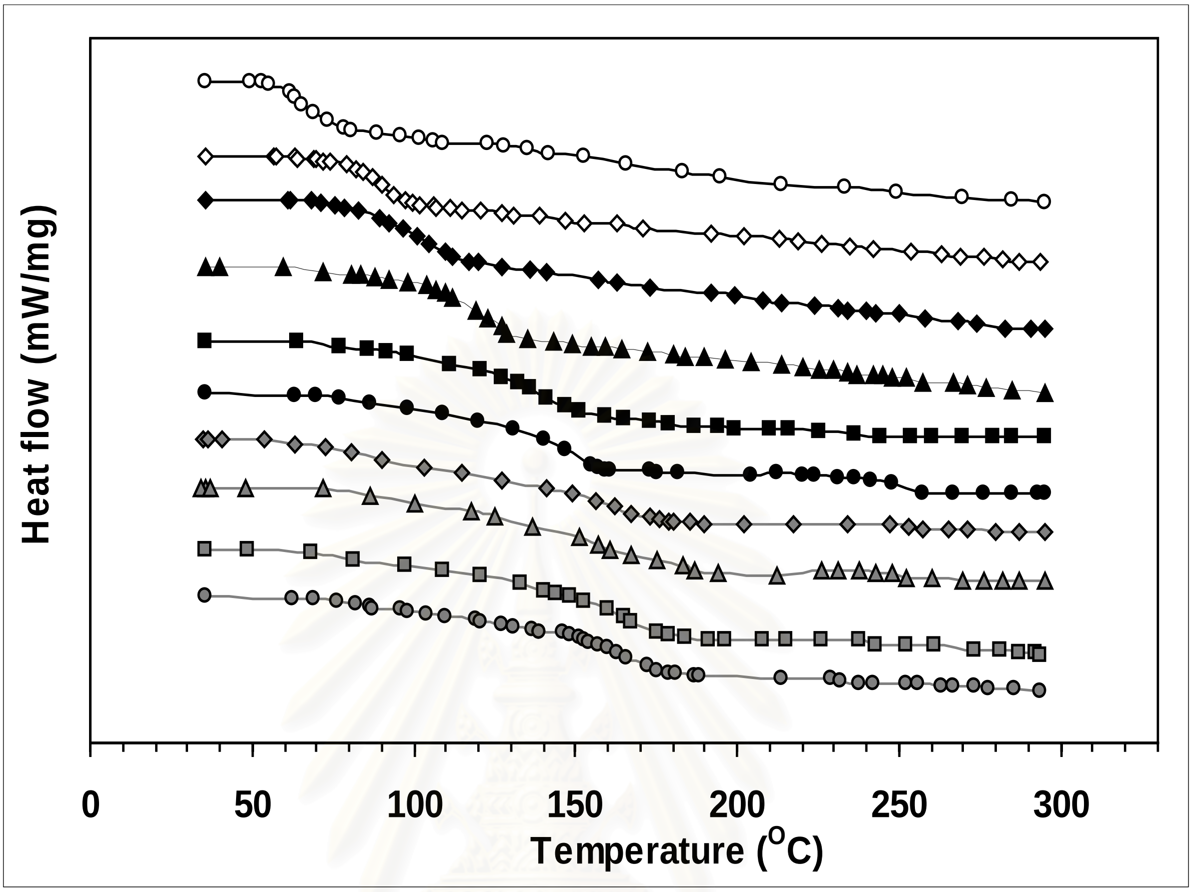


Figure 4.7 DSC thermograms showing T_gs of benzoxazine/novolac alloys :[(●) BN 91; (■) BN 82; (▲) BN 73; (◆) BN 64; (●) BN 55; (■) BN 46; (▲) BN 37; (◆) BN 28; (◇) BN 19; (○) Novolac].

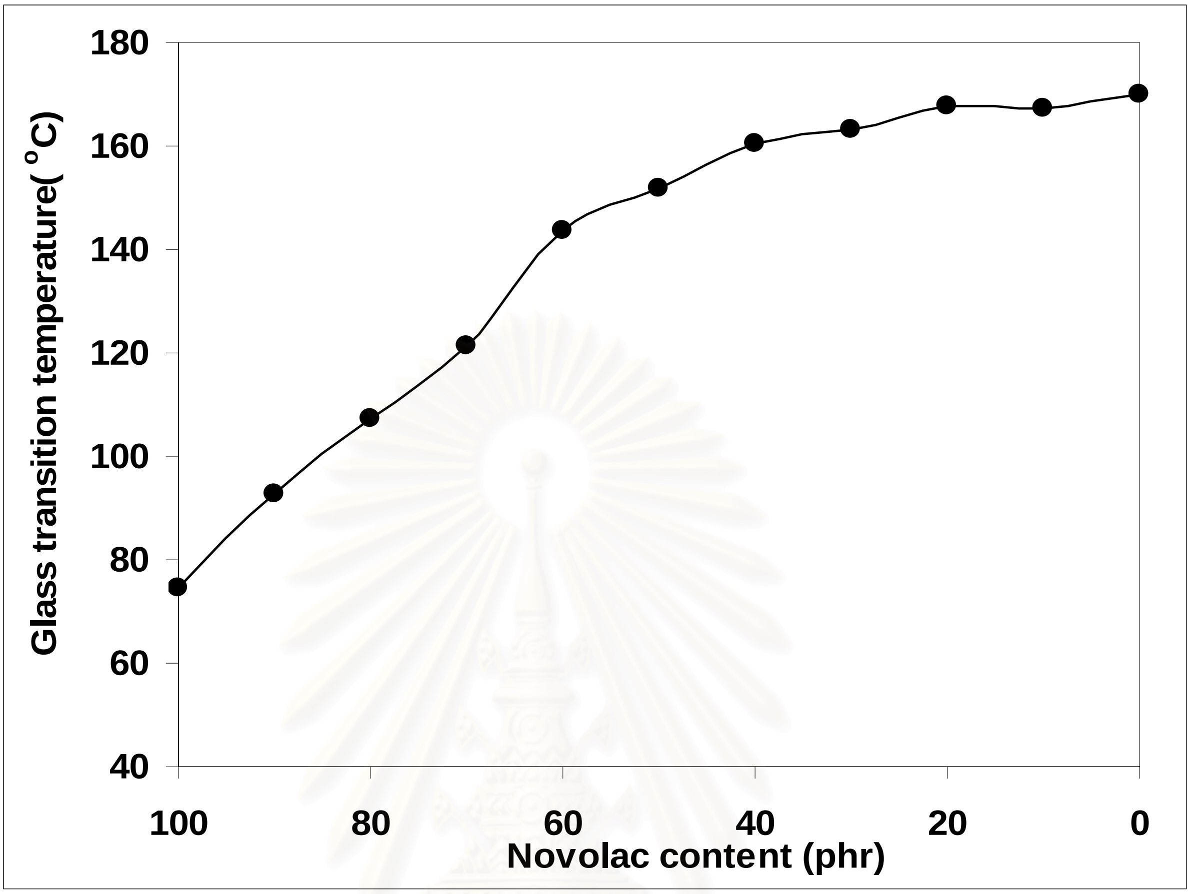


Figure 4.8 Relationship between T_g and novolac contents of benzoxazine/novolac alloys.

Glass transition temperatures of benzoxazine/novolac alloys increase as the amouts of benzoxazine in the alloys increase as shown in Figures 4.7, 4.8 and Table 4.10. The enhancement of T_g is due to an increase in crosslinking and molecular rigidity of the alloy which are believed to contribute to this synergestic behavior of alloys and source of the behavior should come from the contribution of benzoxazine resin. On the contrary, pure novolac resin without curing agents exhibit lowest T_g. This suggests that benzoxazine can possible act as a curing agent for novolac resin.

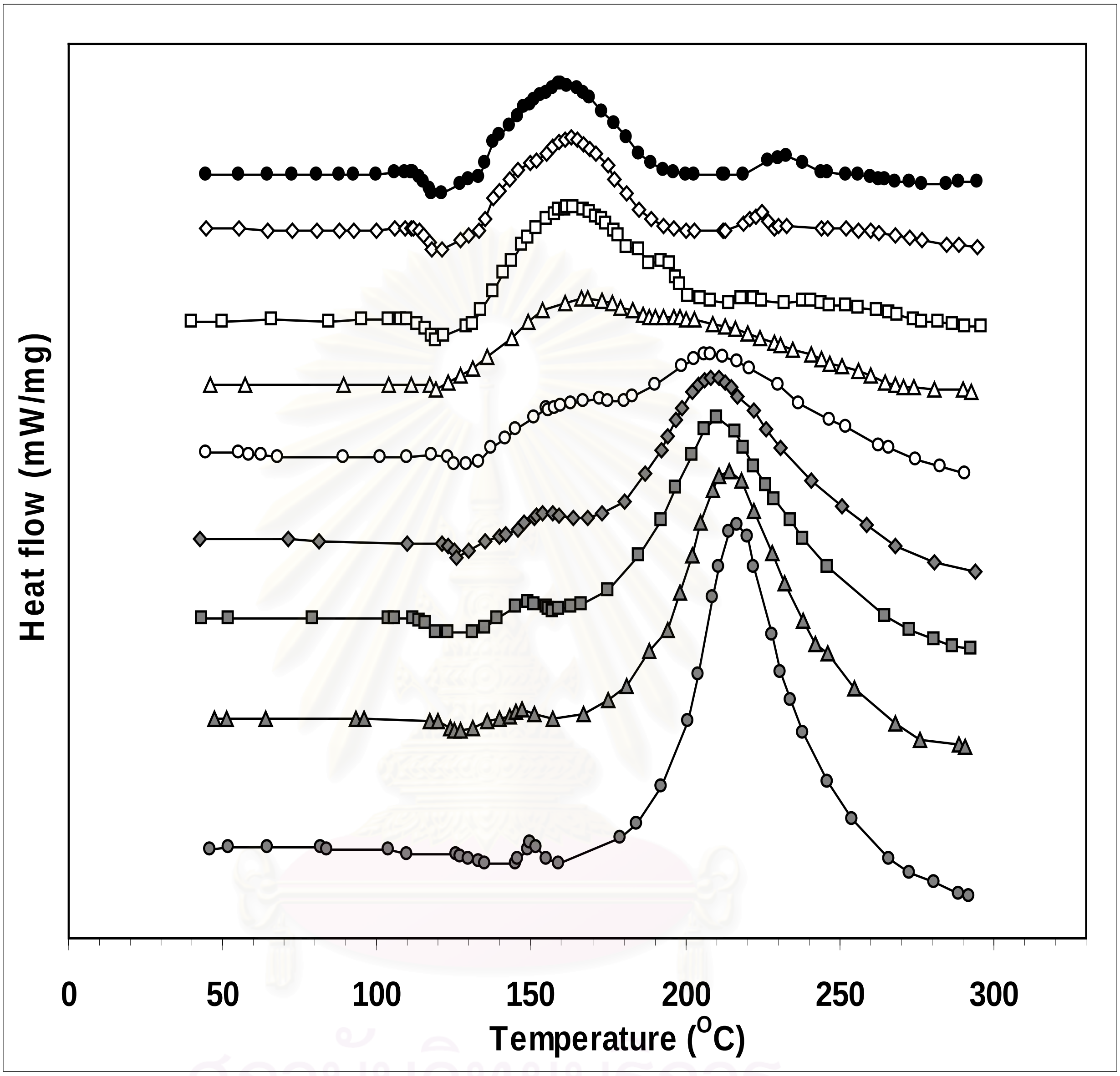


Figure 4.9 DSC thermograms presenting the curing behavior of benzoxazine/resole alloys: [(●) BR 91; (▲) BR 82; (■) BR 73; (◆) BR 64; (O) BR 55; (Δ) BR 46 ; (☐) BR 37; (◇) BR28; (●) BR 19].

Figure 4.9 is the DSC thermograms presenting curing behavior of benzoxazine/resole alloys. From the thermograms, it can be seen that the curing behavior of these alloys shows two exothermic peaks. It observed the first peak positioned at about 150°C, whereas the second peak at higher temperature. The position of the second peak ranges from about 229°C. The position of the first peak at lower temperature is about that of the exothermic peak of pure resole resin, which is characteristic of the thermal curability of phenolic resole resin. As well as, the second peak at higher temperature is about that the exothermic peak of thermal curability of benzoxazine resin. This is in good agreement that when the area under the first peak increases with increasing amount of resole. On the contracy, when increase resole resin the area under the second peak decreases i.e. with decreasing benzoxazine fraction.

Table 4.11 Glass transition temperatures (T_g) and curing characteristics of benzoxazine/resole alloys.

Sample	Exothermic Band			T_g (^{O}C)
	$T_{max\ 1}$ (^{O}C)	$T_{max\ 2}$ (^{O}C)	T_f (^{O}C)	
Benzoxazine	229	-	286	170
B/R 9/1	152	219	290	172
B/R 8/2	147	214	276	171
B/R 7/3	149	210	287	178
B/R 6/4	157	211	291	169
B/R 5/5	174	208	287	168
B/R 4/6	168	198	281	166
B/R 3/7	167	195	282	165
B/R 2/8	165	225	263	162
B/R 1/9	160	223	265	158
Resole	149	-	193	145

T_{max1}, T_{max2} and T_f refer to the first maximum, second maximum and cure end temperatures.

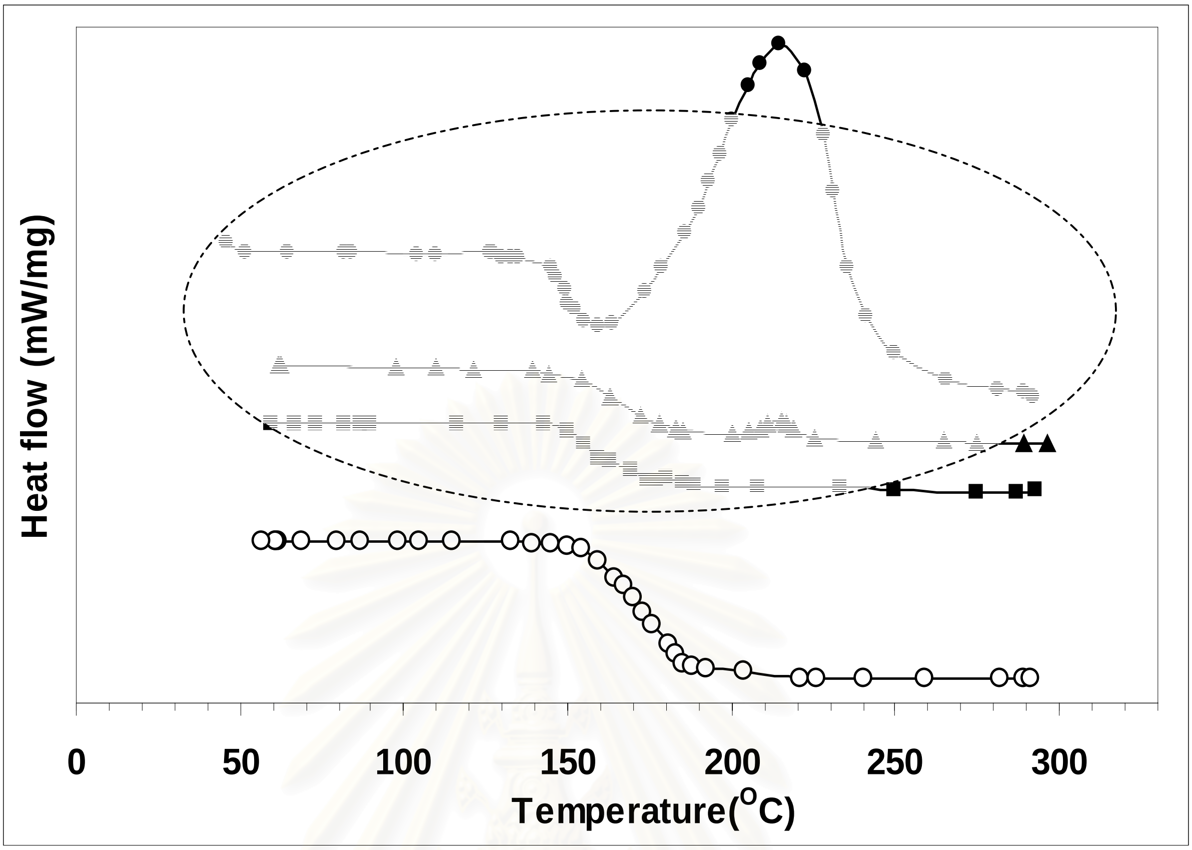


Figure 4.10 DSC thermograms of benzoxazine/resole alloys at various curing conditions: [(●) BR 91; (▲) BR 55; (■) BR 19 after cure at 100^{O}C/2 hours+180^{O}C/1.5 hours and (○) BR 91 after cure at 100^{O}C/2 hours+180^{O}C/2 hours]

Figure 4.10 exhibits the DSC thermograms of benzoxazine/resole alloys at various curing conditions. At curing condition of 100°C/2 hours + 180°C/1.5 hours the thermograms show no exotherm maxima within the temperature range of 30 – 300°C but the thermograms shows the glass transition temperature (T_g) of these systems when the mass fraction of resole resin is lower than 50% by weight in the alloys. For this reason, curing condition for a complete curing reaction of alloys when mass fraction of phenolic resole resin is lower than 50% by weight is at 100°C/2 hours + 180°C/1.5 hours.

At curing condition of 100°C/2 hours + 180°C/2 hours the thermograms show no exotherm maxima within the temperature range of 30 – 300°C but the thermograms shows the T_g of this systems when the mass fraction of phenolic resole resin is higher than 50% by weight in the alloys. This suggests that this curing condition is suitable for completing the curing reaction of the alloys when mass fraction of resole resin is higher than 50% by weight.

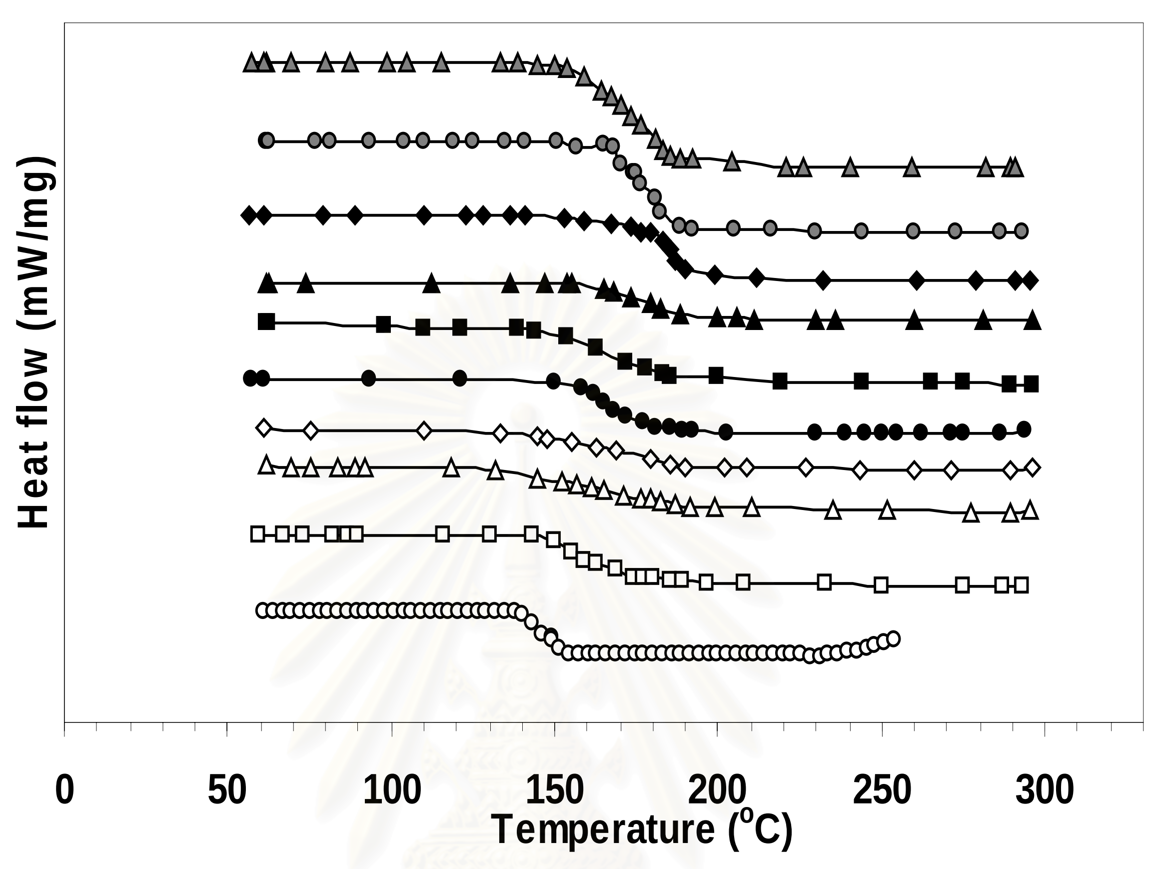


Figure 4.11 DSC thermograms showing T_gs of benzoxazine/resole alloys: [(▲) BR 91; (●) BR 82; (◆) BR 73; (▲) BR 64; (■) BR 55; (●) BR 46; (◇) BR 37; (Δ) BR 28; (□) BR 19; (○) Resole].

Glass transition temperatures of benzoxazine/resole alloys increase as the amouts of benzoxazine in the alloys increase as shown in Figures 4.11, 4.12 and Table 4.11. The enhancement of T_g is due to an increase in crosslinking and molecular rigidity of the alloy which are believed to contribute to this synergestic behavior of alloys and source of the behavior should come from the contribution of benzoxazine resin. On the contrary, pure resole exhibit lowest T_g.

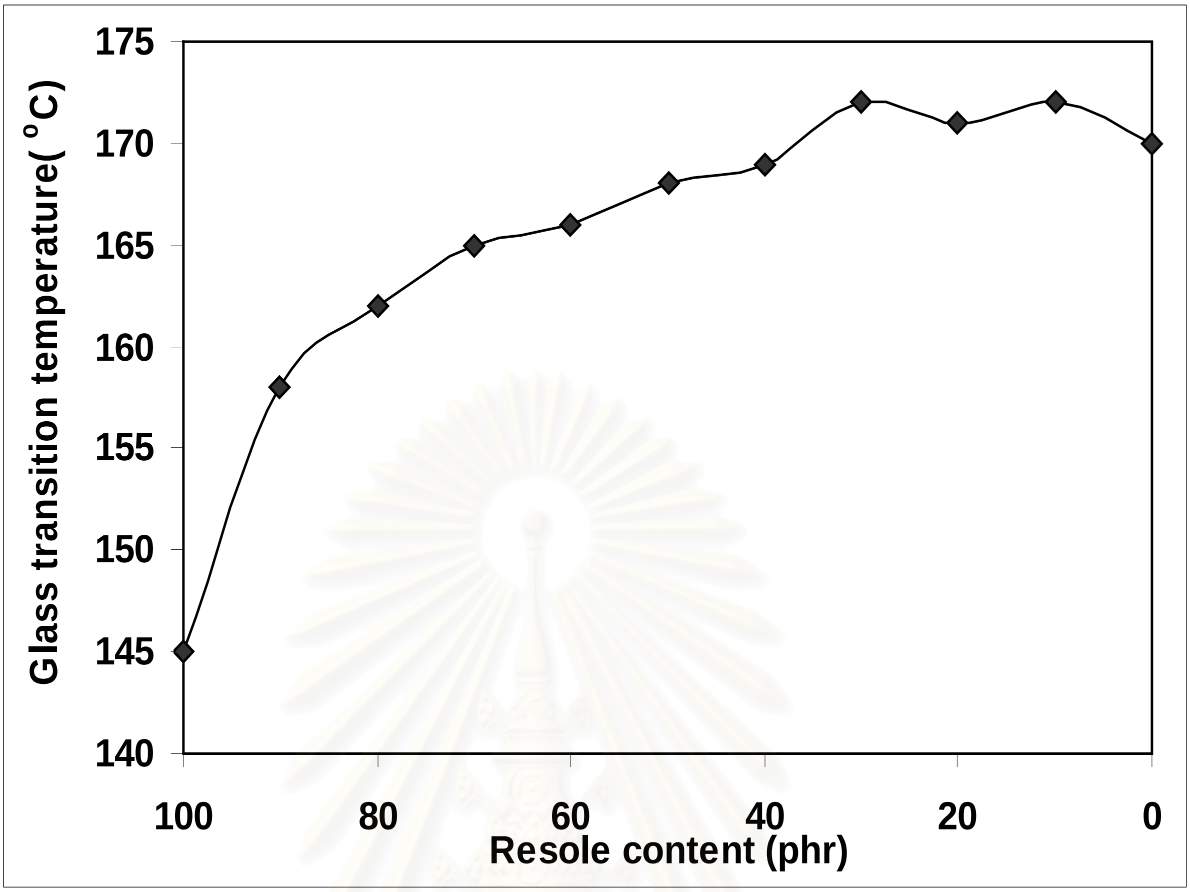


Figure 4.12 Relationship between T_g and resole content of benzoxazine/resole alloys.

4.3.2 TGA analysis.

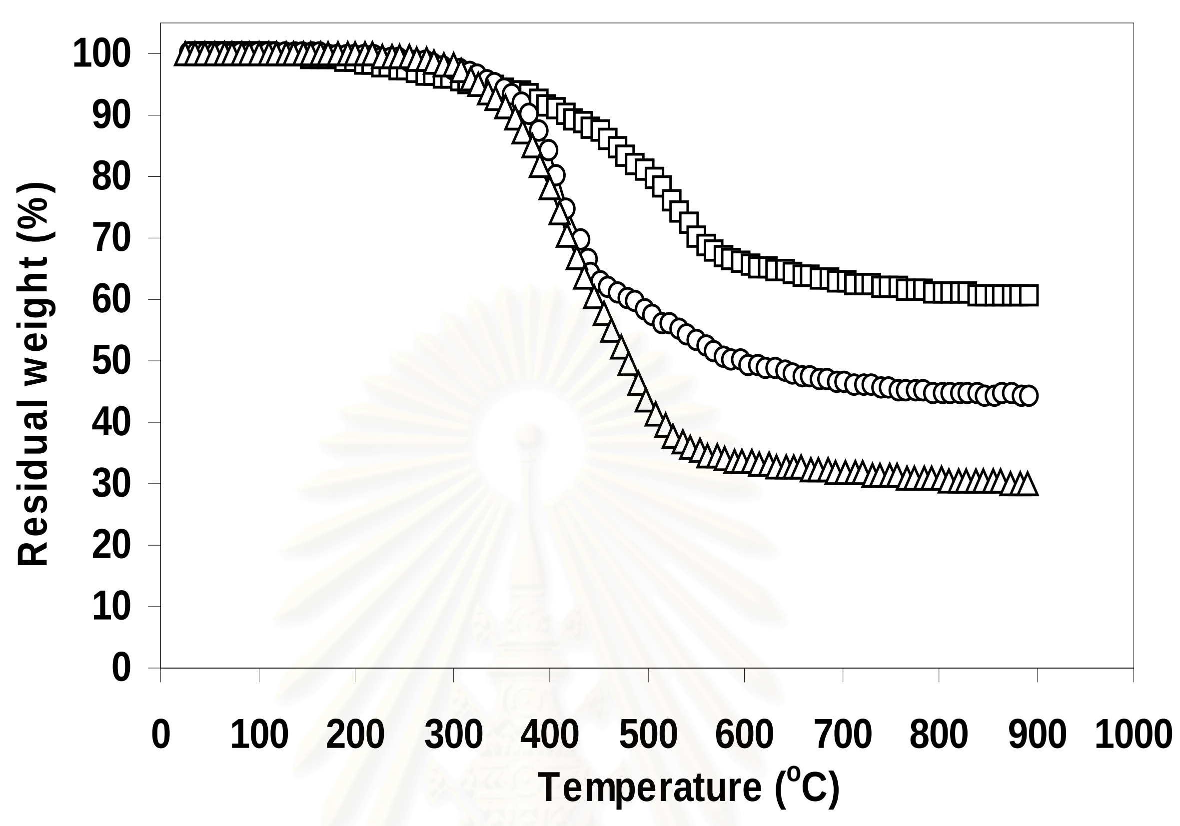


Figure 4.13 TGA thermograms of benzoxazine (Δ); novolac (○); resole (☐).

The TGA thermograms of benzoxazine, novolac and resole resins under nitrogen atmosphere are shown in Figure 4.13. It is cleary seen from the figure that both novolac and resole resins possess better thermal stability than benzoxazine resin. Significant improvement is observed in the lowest initial decomposition temperature for benzoxazine. TGA curves also indicate that benzoxazine has the lowest char yield while resole resin has the highest char yield.

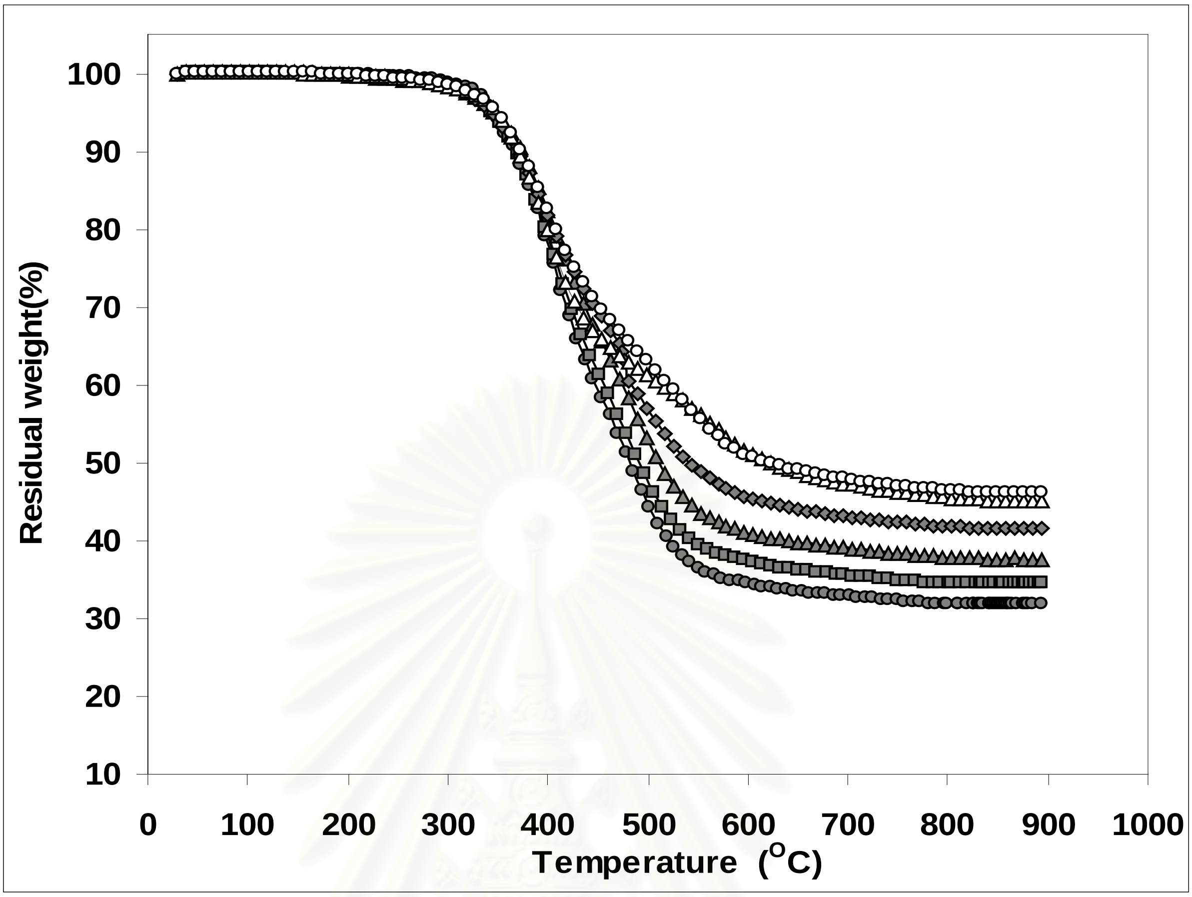


Figure 4.14 TGA thermograms of benzoxazine/novolac alloys: [(●) BN 91; (■) BN 82; (▲) BN 73; (◆) BN 55; (Δ) BN 37; (O) BN 19].

Table 4.12 TGA results of benzoxazine/novolac alloys.

Sample	Weight loss temperature (^{O}C)		Char yield (%)
	5 wt %	10 wt %	
Benzoxazine	325.60	361.27	30.71
B/N 9/1	335.23	367.48	31.82
B/N 8/2	344.82	369.04	34.03
B/N 7/3	346.02	373.35	37.56
B/N 6/4	347.12	371.76	38.60
B/N 5/5	347.16	370.45	41.52
B/N 4/6	348.53	371.05	43.58
B/N 3/7	348.13	374.32	45.08
B/N 2/8	348.53	376.06	46.09
B/N 1/9	345.46	375.32	46.48
Novolac	343.56	380.48	44.26

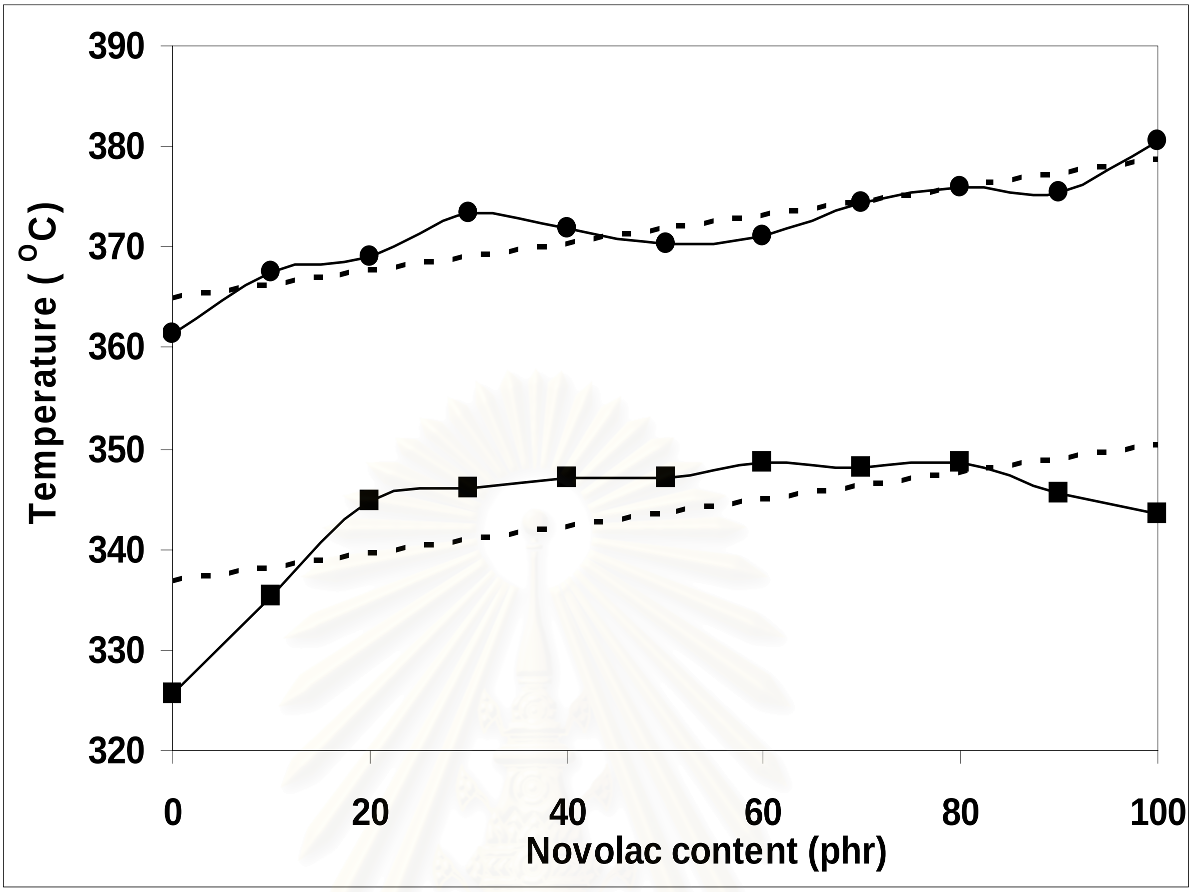


Figure 4.15 Comparison of weight loss temperatures at 5 wt % and 10 wt % of benzoxazine/novolac alloys: [(■) 5 wt%; (●) 10 wt %].

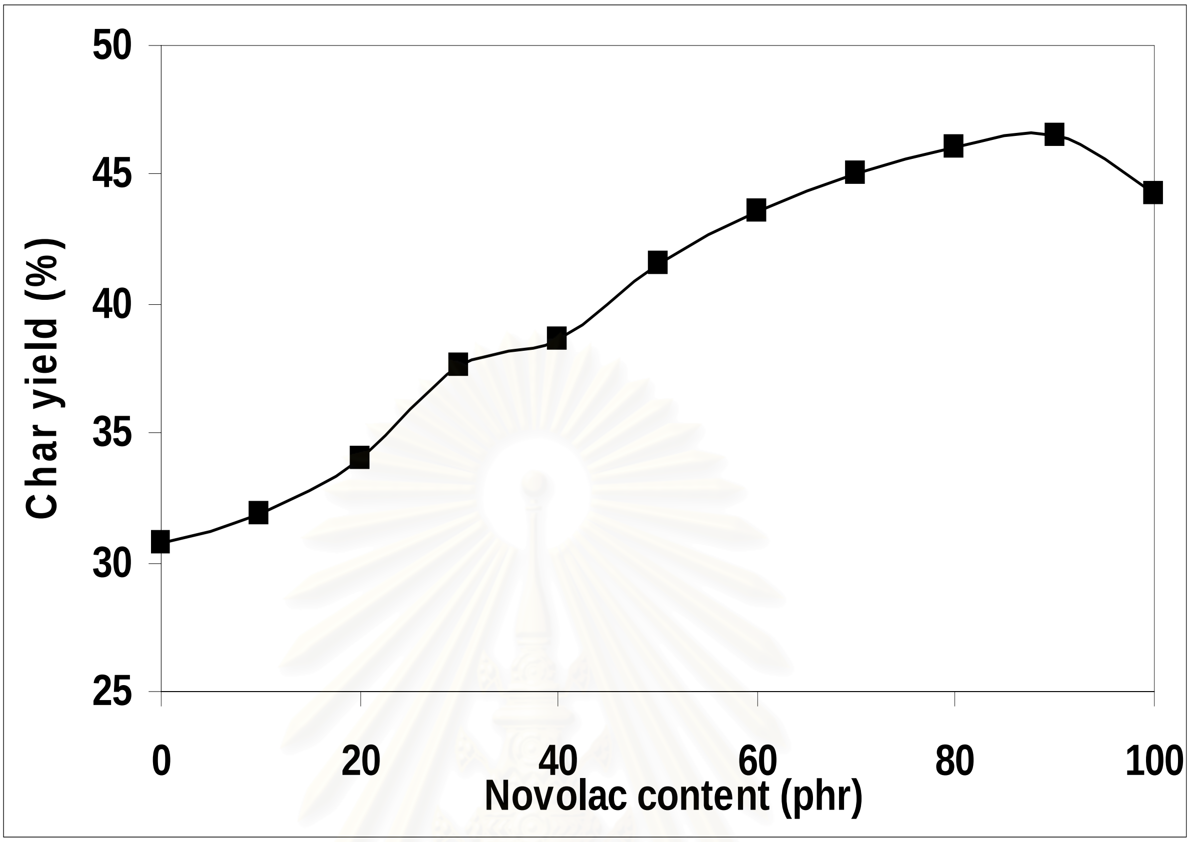


Figure 4.16 Relationship between char yield and novolac content of benzoxazine/novolac alloys.

TGA thermograms of benzoxazine/novolac alloys are shown in the figure 4.14 and their results are summarized in Figure 4.15, 4.16 and Table 4.12. It can be seen that all materials show relatively high decomposition temperatures when increasing the amount of novolac resin, i.e. up to 348°C for 5 % weight loss of B/N 4/6 comparing with 325°C for 5% weight loss of pure benzoxazine resin. This indicates that thermal stability of the alloys are improved with increasing mass fraction of novolac resin in the system. This maybe attributed to the higher thermal stability of novolac resin than benzoxazine resin as previously mentioned. Furthermore, the char yield of the alloys also significantly increases when compared to that of pure benzoxazine resin. It is cleary seen that as novolac content in the alloys increases, the amount of the char yield increases. This is due to the fact that novolac resin gives higher char yield than benzoxazine resin as shown in Figure 4.9.

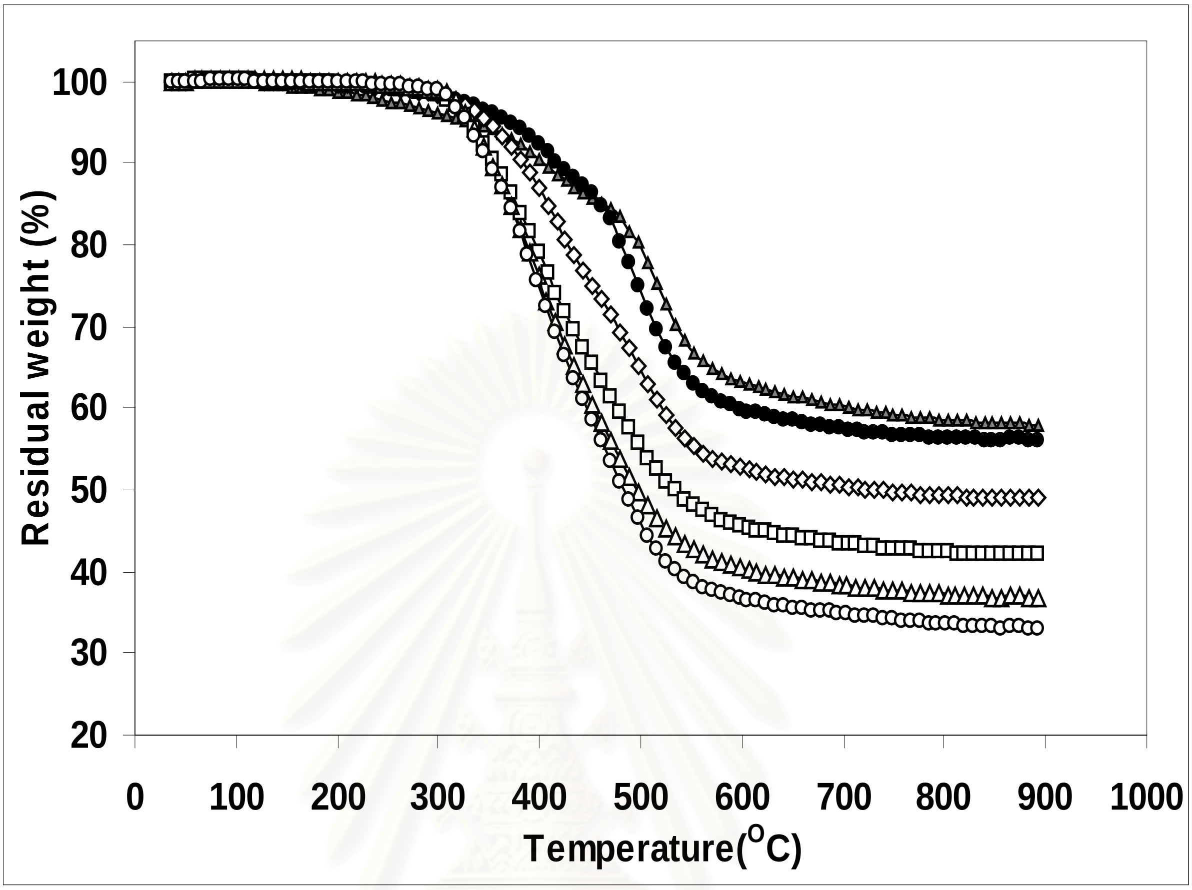


Figure 4.17 TGA thermograms of benzoxazine/resole alloys: [(○) BR 91; (Δ) BR 82; (□) BR 73; (◇) BR 55; (●) BR 37; (▲) BR 19].

TGA thermograms of benzoxazine/resole alloys are shown in the Figure 4.17 and their results are summarized in Table 4.13. From Figures 4.17, 4.18 and Table 4.13, it can be seen that at 5% weight loss, thermal decomposition temperatures of the alloys and the alloy components are comparable while at 10% weight loss, they increases as resole content in the alloys increases. This indicates that thermal stability of the alloys are improved with increasing mass fraction of resole resin in the system. This maybe attributed to the higher thermal stability of resole resin than benzoxazine resin as previously mentioned. Furthermore, the char yield of the alloys also significantly increases when compared to that of pure benzoxazine resin. It is cleary seen that as resole content in the alloys increases, the amount of the char yield increases. This is due to the fact that resole resin gives higher char yield than benzoxazine resin as shown in Figure 4.9. When char yield between benzoxazine/novolac systems and benzoxazine/resole systems are compared as shown in Figure 4.20, it can be seen that char yield of benzoxazine/resole alloys are higher than that of benzoxazine/novolac alloys. This is because resole resin has higher char yield than novolac resin.

Table 4.13 TGA results of benzoxazine/resole alloys.

Sample	Weight loss temperature (^{O}C)		Char yield (%)
	5 wt %	10 wt %	
Benzoxazine	325.60	361.28	30.71
B/R 9/1	327.62	360.28	32.98
B/R 8/2	331.28	362.37	36.81
B/R 7/3	327.08	365.47	41.99
B/R 6/4	326.03	372.14	45.16
B/R 5/5	325.02	379.64	49.05
B/R 4/6	328.82	398.39	52.72
B/R 3/7	330.82	417.12	56.10
B/R 2/8	329.82	408.84	57.95
B/R 1/9	326.33	409.89	58.63
Resole	325.15	415.62	61.06

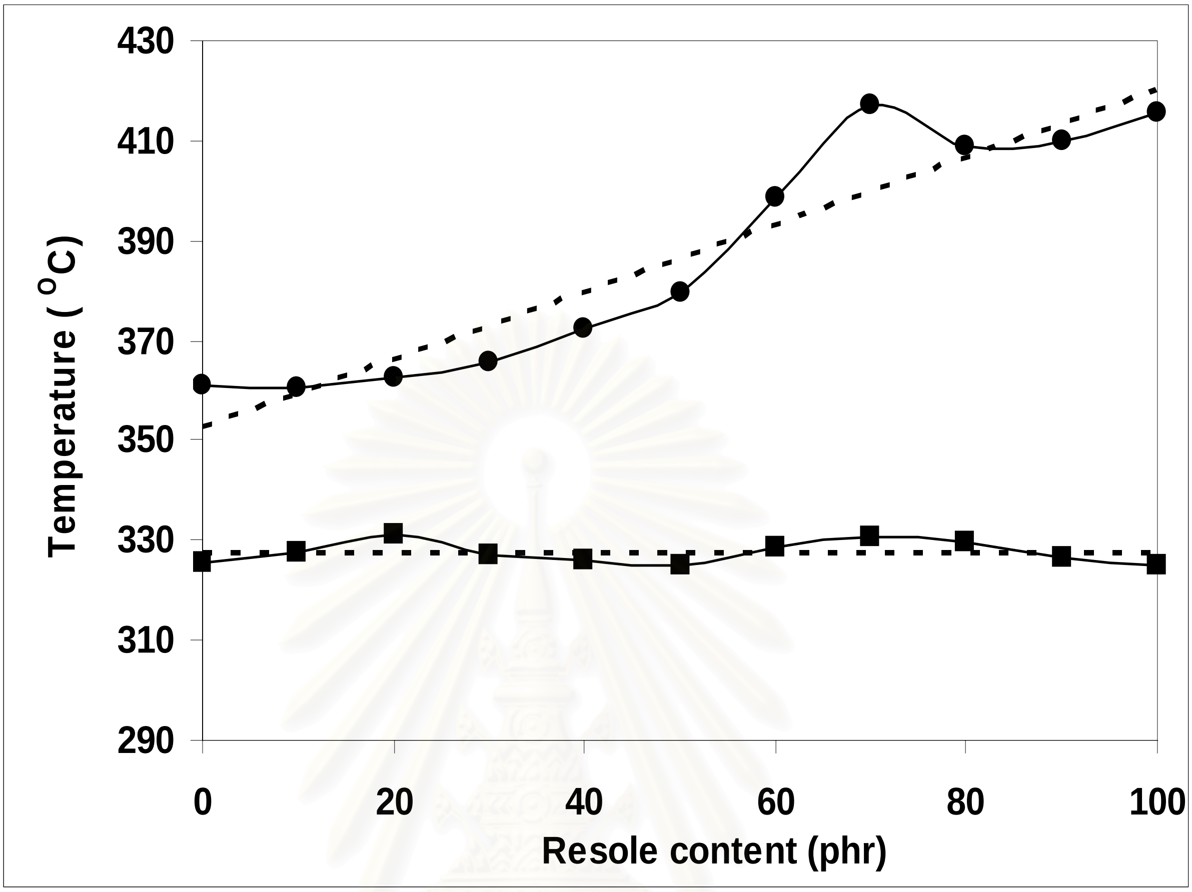


Figure 4.18 Comparison of weight loss temperatures at 5 wt% and 10 wt% of benzoxazine/resole alloys: [(■) 5 wt%; (●)10 wt %].

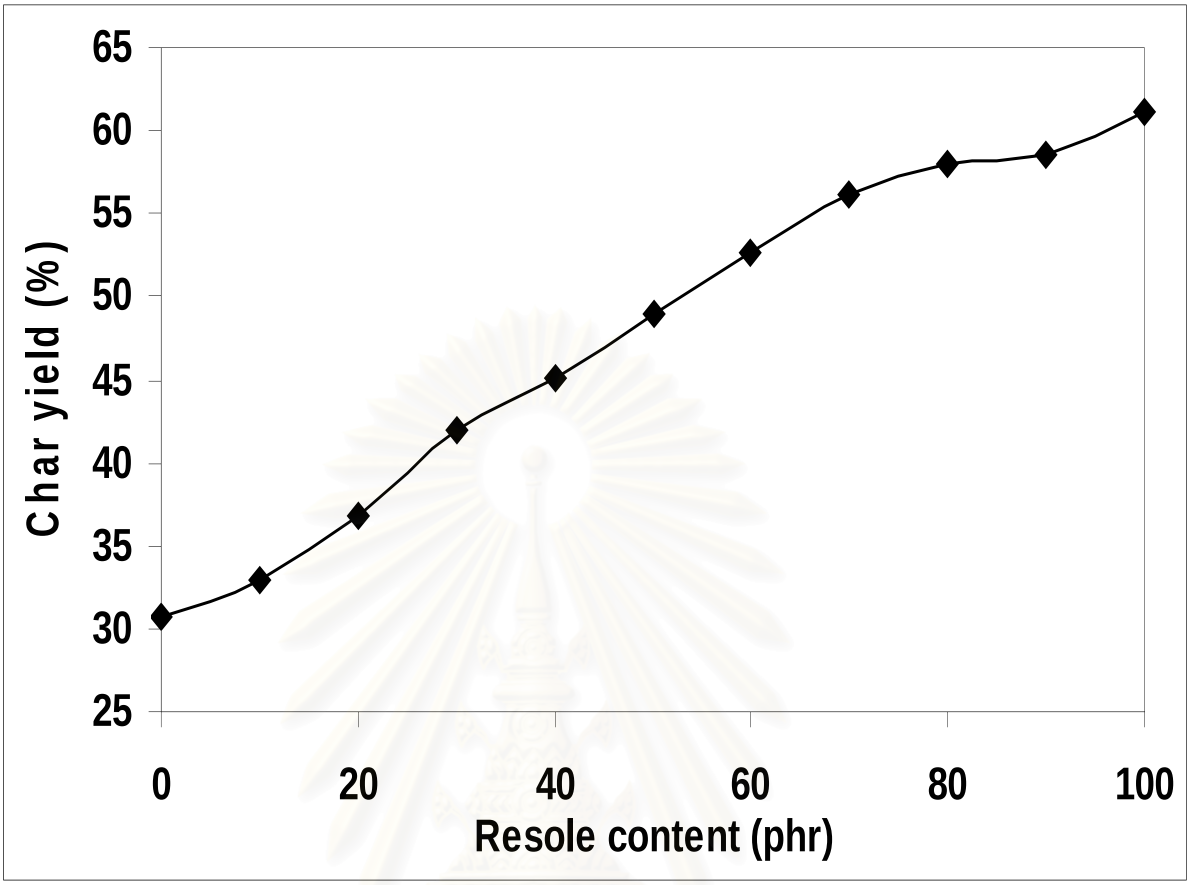


Figure 4.19 Relationship between char yield and resole content of benzoxazine/resole alloys.

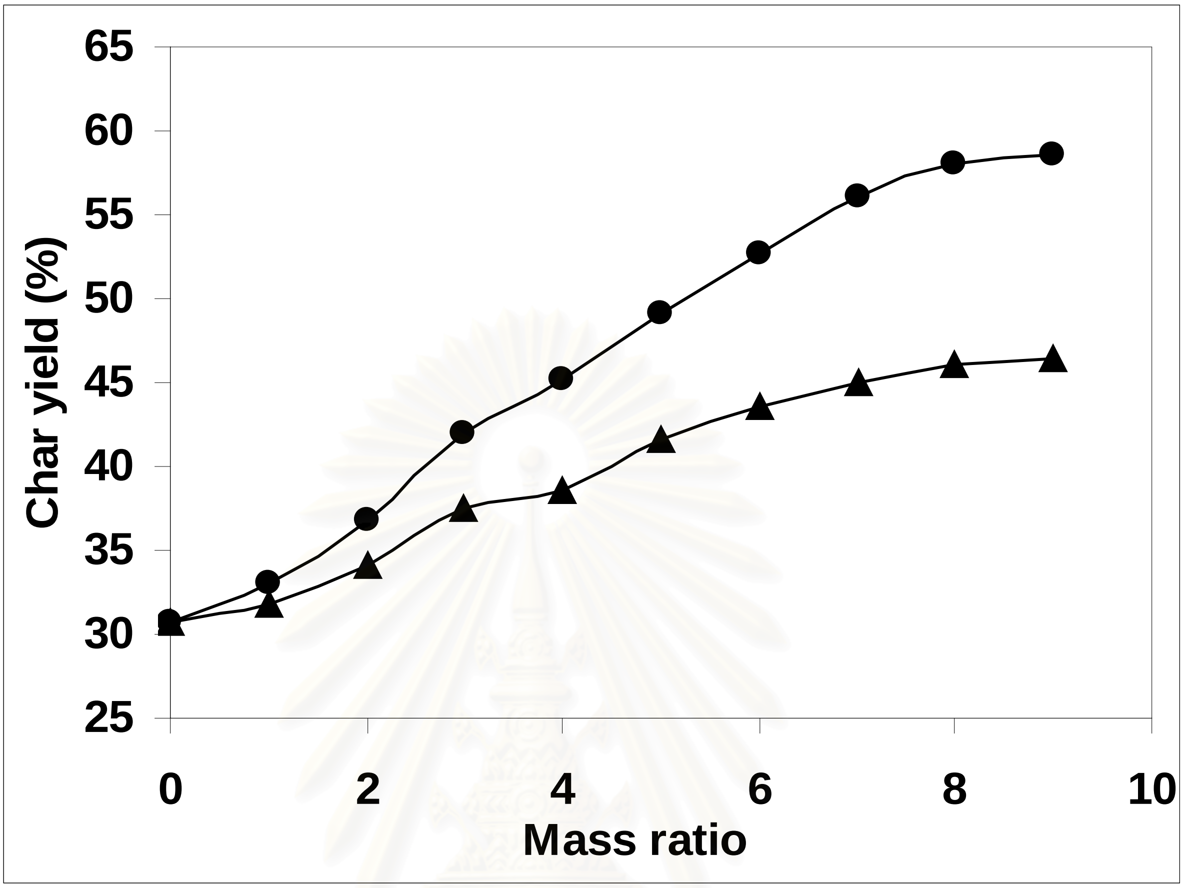


Figure 4.20 Comparison of all position’s char yield between benzoxazine/novolac systems and benzoxazine/resole systems: [(▲) B/N systems; (●) B/R systems].

4.4 Ignition behavior of alloys

4.4.1 Limiting oxygen index (LOI) tests.

For evaluation of the flame retardation of a material, temperature of thermal decomposition (T_d) is usually a reference index that can be determined from the inflection point of the TGA curve. However, for the realistic applications, limiting oxygen index (LOI) is used. The larger value of LOI, the harder it is for the material to catch fire and to burn. Generally speaking, for the case of LOI below 21, the material is considered as “flammable"; for LOI = 22-125, the material is “self extinguishable”; and for the case of LOI is above 26, thematerial is ``hard to burn."[25].

Table 4.14 LOI values of benzoxazine/novolac alloys.

Sample	**LOI**			**Average of LOI**
	1	**2**	**3**	
Benzoxazine	26.9	26.8	26.8	26.8
B/N 9/1	27.5	27.4	27.4	27.4
B/N 8/2	27.5	27.4	27.8	27.6
B/N 7/3	27.9	27.9	28.0	27.9
B/N 6/4	28.4	28.3	28.3	28.3
B/N 5/5	29.3	29.4	29.5	29.4
B/N 4/6	30.8	30.5	30.6	30.6
B/N 3/7	31.8	32.0	32.0	31.9
B/N 2/8	-	-	-	-
B/N 1/9	-	-	-	-
Novolac	-	-	-	-

(LOI of phenolic resin = 35.0[29])

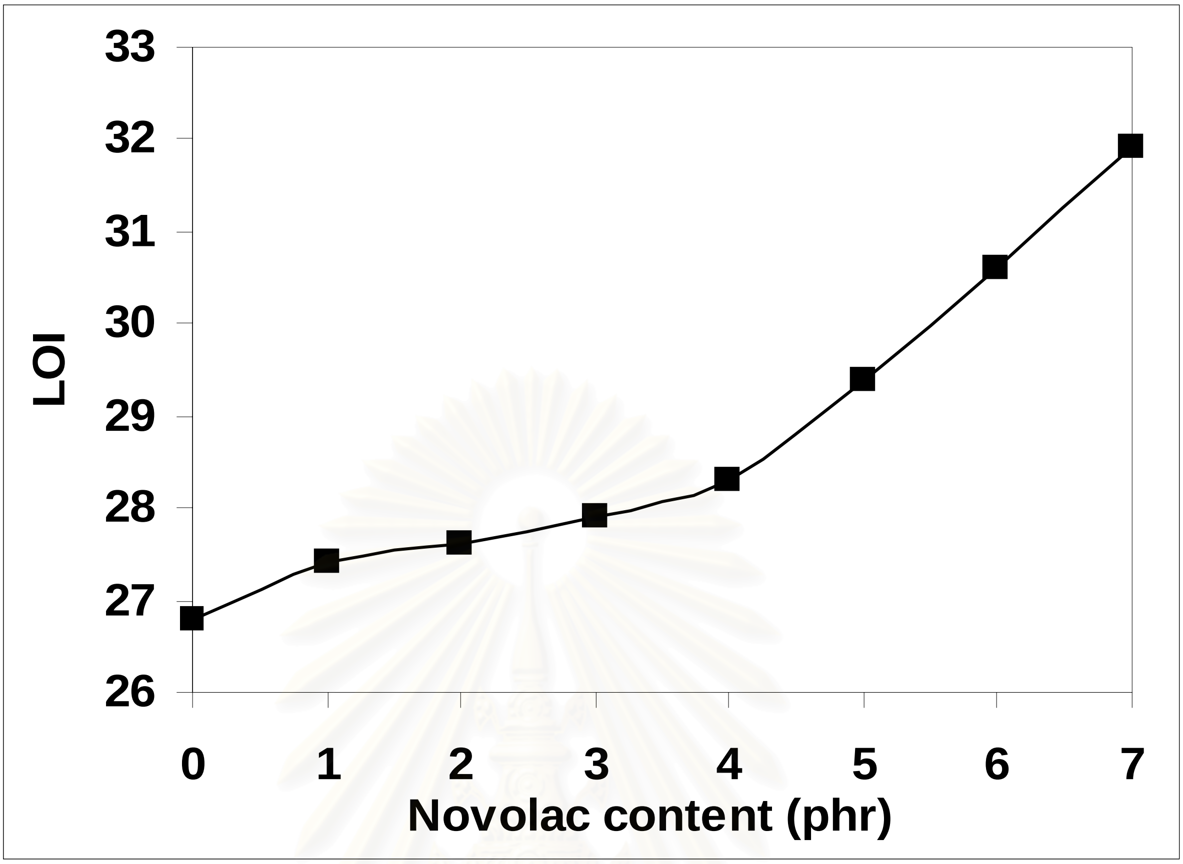


Figure 4.21 Relationship between LOI value and novolac content of benzoxazine/novolac alloys.

The table 4.14 demonstrates that both benzoxazine and novolac resins have LOI above 26 indicating both the materials are hard to burn. Since novolac resin has LOI value higher than benzoxazine resin; therefore, the LOI value of this system increases with increasing, the amount of novolac resin in the alloys as shown in Figure 4.21. In the case of alloys prepared from low amount of benzoxazine, the specimen for LOI Test could not formed. This is because the amount of benzoxazine was not enough for the alloys to completely cured.

Table 4.15 LOI values of benzoxazine/resole alloys.

Sample	**LOI**			**Average of LOI**
	1	**2**	**3**	
Benzoxazine	26.9	26.8	26.8	26.8
B/R 9/1	27.7	27.8	27.7	27.7
B/R 8/2	28.0	27.9	28.0	28.0
B/R 7/3	28.4	28.4	28.5	28.4
B/R 6/4	28.7	28.9	28.7	28.8
B/R 5/5	30.9	30.9	31.1	30.9
B/R 4/6	-	-	-	-
B/R 3/7	-	-	-	-
B/R 2/8	-	-	-	-
B/R 1/9	-	-	-	-
Resole	-	-	-	-

(LOI of phenolic resin = 35.0[29])

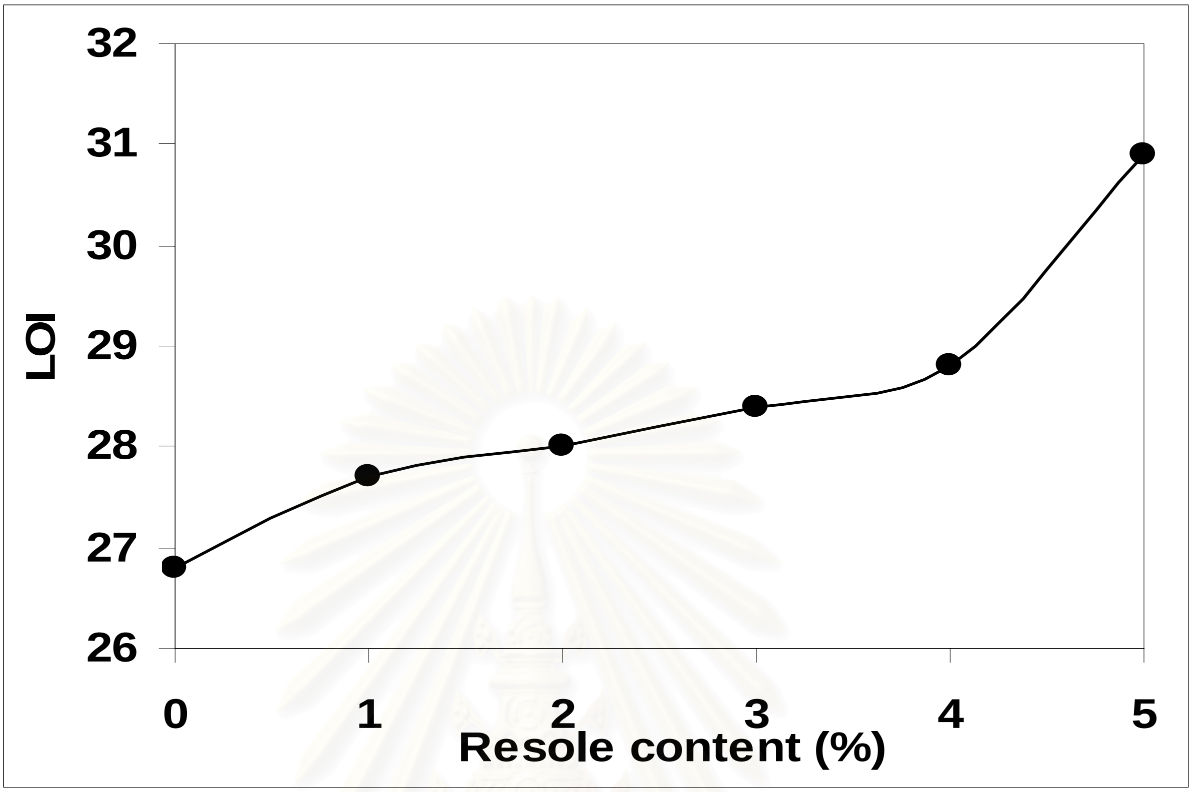


Figure 4.22 Relationship between LOI value and resole content of benzoxazine/resole alloys.

Figure 4.22 is the LOI value of benzoxazine/resole alloys, and the results are summarized Table 4.15. The table demonstrates that resole had LOI above 26 indicating resole resin is thematerial is hard to burn[25]. Since resole resin has LOI value higher than benzoxazine resin; therefore, the LOI value of this system increases with increasing, the amount of resole resin in the alloys as shown in Figure 4.22. However, it was observed that as resole content in the alloys increased, the voids in the specimens increased. This may be caused by the releasing of by products during curing reaction. Therefore, when resole content in the alloys was higher than 50% by weight, the specimens were not used for LOI Test because too many voids present.

4.4.2 Burning rate tests.

Table 4.16 Burning rates of benzoxazine/novolac alloys.

Sample	**Burning rate (mm/min)**			**Average of burning rate (mm/min)**
	1	**2**	**3**	
Benzoxazine	25.17	27.02	23.04	25.08
B/N 9/1	17.52	20.12	16.67	18.10
B/N 8/2	11.37	15.04	13.22	13.21
B/N 7/3	7.29	7.02	6.89	7.07
B/N 6/4	7.95	6.87	5.95	6.91
B/N 5/5	5.23	6.01	5.13	5.46
B/N 4/6	5.01	5.20	4.97	5.08
B/N 3/7	3.16	4.07	3.26	3.50
B/N 2/8	-	-	-	-
B/N 1/9	-	-	-	-
Novolac	-	-	-	-

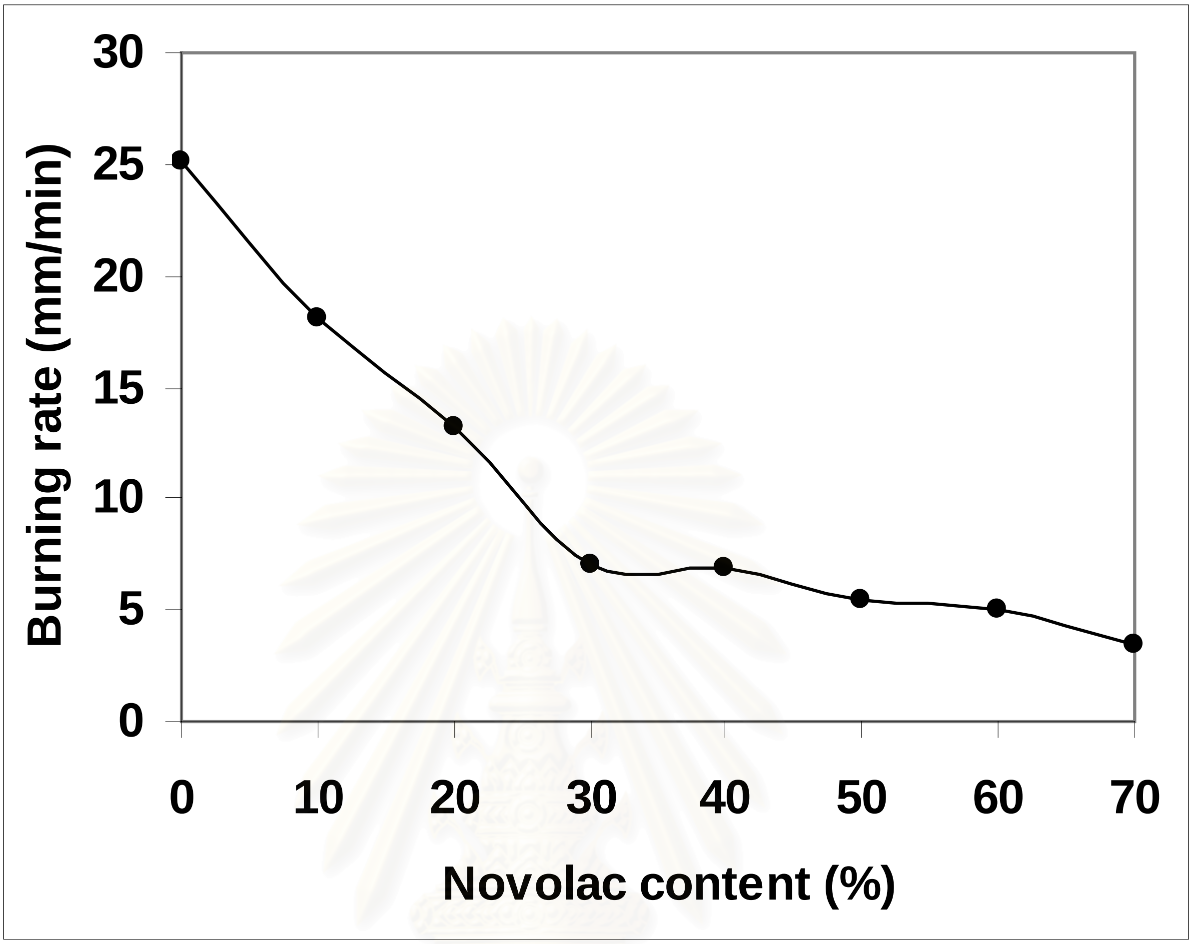


Figure 4.23 Relationship between burning rate and novolac content of benzoxazine/novolac alloys.

The results given in Table 4.16 and Figure 4.23 indicate that the burning rate of this system decreases with increasing the amount of novolac resin in the alloy. The burning rate of benzoxazine/novolac resin alloys are much lower than that of benzoxazine resin. This is because the novolac resin has a high layer of char on the surface of the resin alloy, which can inhibit the flammable gases and oxygen to go through further mixing and burning. The heat release during the combustion is reduced and the heat radiated to the surroundings is retarded as well. It can also be confirmed from the TGA curve of the alloys between benzoxazine and novolac resin.

Table 4.17 Burning rates of benzoxazine/resole alloys.

Sample	**Burning rate (mm/min)**			**Average of burning rate (mm/min)**
	1	**2**	**3**	
Benzoxazine	25.17	27.02	23.04	25.08
B/R 9/1	12.12	13.01	11.53	12.22
B/R 8/2	12.13	11.56	10.83	11.51
B/R 7/3	7.14	7.02	8.01	7.39
B/R 6/4	7.02	6.49	6.59	6.70
B/R 5/5	5.20	5.11	5.27	5.19
B/R 4/6	-	-	-	-
B/R 3/7	-	-	-	-
B/R 2/8	-	-	-	-
B/R 1/9	-	-	-	-
Resole	-	-	-	-

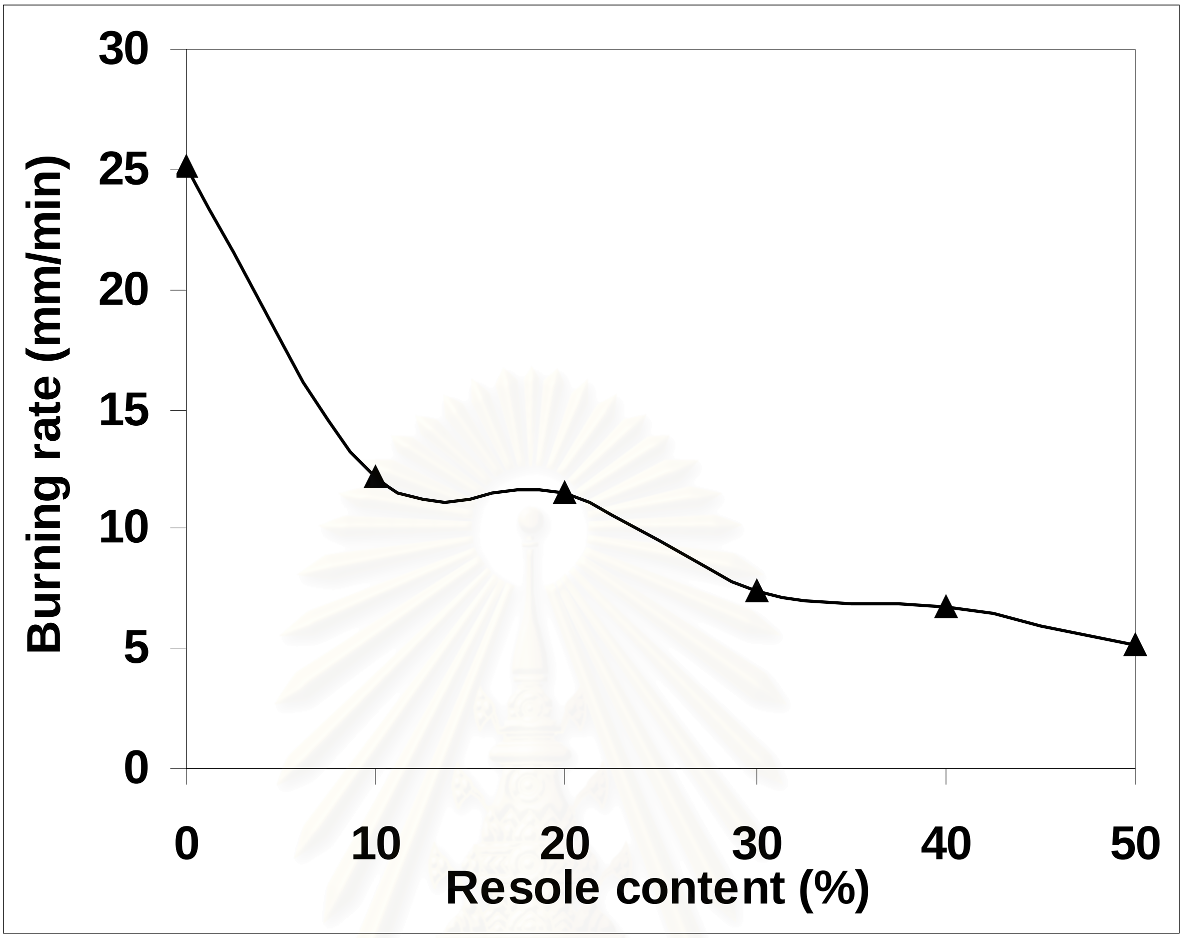


Figure 4.24 Relationship between burning rate and resole content of benzoxazine/resole alloys.

The results given in Table 4.17 and Figure 4.24 indicate that the burning rate of this system decreases with increasing the amount of resole resin in the alloys. The burning rate of benzoxazine/resole alloys are much lower than that of benzoxazine resin same results of benzoxazine/novolac alloys. This is because resole resin has a high layer of char on the surface of the resin alloy, which can inhibit the flammable gases and oxygen to go through further mixing and burning. The heat release during the combustion is reduced and the heat radiated to the surroundings is retarded as well. It can also be confirmed from the TGA curve of the alloys between benzoxazine and resole resin.

CHAPTER 5

CONCLUSIONS

The aim of this work was initially to find the suitable conditions for synthesis two types of phenolic resins. For novolac phenolic, the suitable condition was a molar ratio of formaldehyde/phenol ([F]/[P]) of 0.8, a temperature of 100^{o}C, a pH of 2.2 and a reaction time of 4 hours. Suitable condition for resole synthesis was a molar ratio of [F]/[P] of 1.5, a temperature of 80^{o}C, a pH of 8.0 and a reaction time of 1 hour. Benzoxazine monomer was synthesized based on the patented synthesis method.

Two binary mixture of benzoxazine/novolac resin and benzoxazine/resole resin were developed. The alloys rendered homogeneous and showed a wide range of desirable reliability and processability, which were highly dependent on the composition of the resins in the mixture. Polymer alloys between benzoxazine and phenolic resins were prepared by mixing these two components followed by heating until the alloys were completely cured. From DSC studies, it was found that the suitable curing condition for benzoxazine /novolac phenolic alloys was 150°C/1 hour and 180°C/1 hour when the amount of novolac resin is lower than 50% by weight and the suitable curing condition was 150°C/1 hour and 180°C/2 hours when the amount of novolac resin is higher than 50% by weight. On the other hand, the suitable curing condition for benzoxazine/ resole phenolic alloys was 100°C/2 hours and 180°C/1.5 hours when the amount of resole resin is lower than 50% by weight and the suitable curing condition was 100°C/2 hours and 180°C/2 hours when the amount of resole resin is higher than 50% by weight. The results suggested that novolac resin acted mainly as a curing accelerator for benzoxazine systems while polybenzoxazine and resole resin imparted thermal curability. Furthermore, it can be seen that benzoxazine improved T_g of the alloy and gave low viscous resin rendering void-free specimens. Both phenolic resins improved thermal stability and increased flame retardation of benzoxazine resin. However, it is clearly seen that at the same blending ratio, benzoxazine/resole alloys gave higher char yield than benzoxazine/novolac alloys. This indicates that the former has better flame retardation than the latter.

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APPENDICES

APPENDICES

I. Preparation of benzoxazine/phonolic alloys.

Table I Amounts of alloy components in benzoxazine/phenolic alloys for DSC and TGA experiments

B/N	B/R	B (g)	N (g)	R (g)
9/1	9/1	3.6	0.4	0.4
8/2	8/2	3.2	0.8	0.8
7/3	7/3	2.8	1.2	1.2
6/4	6/4	2.4	1.6	1.6
5/5	5/5	2	2	2
4/6	4/6	1.6	2.4	2.4
3/7	3/7	1.2	2.8	2.8
2/8	2/8	0.8	3.2	3.2
1/9	1/9	0.4	3.6	3.6

Table II Amounts of alloy components in benzoxazine/phenolic alloys for LOI experiments.

B/N	B/R	B (g)	N (g)	R (g)
9/1	9/1	5.4	0.6	0.6
8/2	8/2	4.8	1.2	1.2
7/3	7/3	4.2	1.8	1.8
6/4	6/4	3.6	2.4	2.4
5/5	5/5	3	3	3
4/6	4/6	2.4	3.6	3.6
3/7	3/7	1.8	4.2	4.2
2/8	2/8	1.2	4.8	4.8
1/9	1/9	0.6	5.4	5.4

Table III Amounts of alloy components in benzoxazine/phenolic alloys for burning rate experiments.

B/N	B/R	B (g)	N (g)	R (g)
9/1	9/1	18	2	2
8/2	8/2	16	4	4
7/3	7/3	14	6	6
6/4	6/4	12	8	8
5/5	5/5	10	10	10
4/6	4/6	8	12	12
3/7	3/7	6	14	14
2/8	2/8	4	16	16
1/9	1/9	2	18	18

II Pictures of instrument and accessories used in this research.

a.) Thermogravimetric Analyzer (TGA)

b.) Differential scanning calorimeter (DSC)

c.) Fourier transform infrared spectrometer (FT-IR)

d.) Limiting oxygen index analyzer (LOI)

VITA

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