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# COMPARATIVE STUDY ON FLEXIBILITY ENHANCEMENT OF POLYBENZOXAZINE USING EPOXY AND URETHANE PREPOLYMER

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การเพิ่มสมบัติด้านความยืดหยุ่นของพอลิเบนซอกซาซีนสามารถทำได้โดย นำมาทำพอลิเมอร์อัลลอยกับยูรีเทนพรีพอลิเมอร์ชนิดไอโซเฟอโรนไดไอโซไซยาเนต หรืออีพอกซีชนิดยืดหยุ่น ผลจากการทดลองอย่างเป็นระบบในการทดสอบสมบัติด้านการดัดโค้งและการวิเคราะห์สมบัติทางกลแบบพลศาสตร์ แสดงให้เห็นว่าความยืดหยุ่นของพอลิเมอร์อัลลอยระหว่างพอลิเบนซอกซาซีนที่มีความแข็งเกร็งและยูรีเทนพรีพอลิเมอร์ หรืออีพอกซีชนิดยืดหยุ่น มีค่าสูงขึ้นเมื่อปริมาณสารที่เติมทั้งสองสูงขึ้น เนื่องจากการเติมโมเลกุลที่ยืดหยุ่นกว่าลงไปในระบบ อุณหภูมิการบ่มของเบนซอกซาซีนเรซินอยู่ที่ประมาณ 225 องศาเซลเซียส แต่จะมีค่าสูงขึ้นเมื่อสัดส่วนของเบนซอกซาซีนลดลงในทั้งสองระบบ สิ่งที่น่าสนใจคือ เราสามารถสังเกตเห็นสมบัติการส่งเสริมกันของอุณหภูมิเปลี่ยนสถานะคล้ายแก้วในระบบเบนซอกซาซีน/ยูรีเทนพรีพอลิเมอร์ซึ่งพิจารณาได้จากจุดสูงสุดของกราฟ loss modulus ในการวิเคราะห์สมบัติทางกลแบบพลศาสตร์ นั่นคือ อุณหภูมิสถานะเปลี่ยนคล้ายแก้วของระบบเบนซอกซาซีน/ยูรีเทน (มากกว่า 200 องศาเซลเซียส) มีค่าสูงกว่า ของเบนซอกซาซีน (165 องศาเซลเซียส) และ ยูรีเทนพรีพอลิเมอร์ (-70 องศาเซลเซียส) อย่างไรก็ตาม เราจะไม่พบสมบัติการส่งเสริมกันในระบบเบนซอกซาซีน/อีพอกซี โดยที่สมบัติการส่งเสริมกันของอุณหภูมิเปลี่ยนสถานะคล้ายแก้วในระบบเบนซอกซาซีน/ยูรีเทนพรีพอลิเมอร์ที่อัตราส่วนโดยมวลเป็น 70/30 มีค่า 221 องศาเซลเซียส ในขณะที่ระบบเบนซอกซาซีน/อีพอกซีที่อัตราส่วนโดยมวลเดียวกันจะมีค่าอุณหภูมิเปลี่ยนสถานะคล้ายแก้วเพียง 95 องศาเซลเซียสเท่านั้น และลดลงตามอัตราส่วนของอีพอกซีที่เพิ่มขึ้น ปรากฏการณ์ดังกล่าวสามารถอธิบายได้ว่า ยูรีเทนพรีพอลิเมอร์สามารถเพิ่มความหนาแน่นในการเชื่อมโยงโครงสร้างตาข่ายของพอลิเมอร์อัลลอย ในทางตรงกันข้าม อีพอกซีนอกจากจะไม่สามารถเพิ่มความหนาแน่นในการเชื่อมโยงได้แล้ว ยังลดความหนาแน่นในการเชื่อมโยงโครงสร้างตาข่ายอีกด้วย เมื่อมีสัดส่วนในระบบมากกว่า 50% โดยมวล นอกจากนี้จากการวิเคราะห์ผล TGA อุณหภูมิการสลายตัวที่มวลลด 5% ของระบบเบนซอกซาซีน/ยูรีเทนพรีพอลิเมอร์ พบว่ามีค่าสูงขึ้นเมื่อเทียบกับพอลิเบนซอกซาซีน ในขณะที่ระบบเบนซอกซาซีน/อีพอกซี จะแสดงผลตรงกันข้าม โดยที่ปริมาณเถ้าของทั้งสองระบบจะสูงขึ้นตามสัดส่วนของเบนซอกซาซีนซึ่งเป็นผลเนื่องมาจาก ปริมาณเถ้าของเบนซอกซาซีนมีค่าสูงเมื่อเทียบกับสารเพิ่มความยืดหยุ่นทั้งสองดังกล่าว ระบบที่เหมาะสมสำหรับเพิ่มความยืดหยุ่นและเป็นพอลิเมอร์โครงข่ายที่มีเสถียรภาพทางความร้อนสูงสำหรับขึ้นรูปและทำเป็นคอมโพสิท คือ ระบบพอลิเบนซอกซาซีนที่ใช้ยูรีเทนพรีพอลิเมอร์ชนิดไอโซเฟอโรนไดไอโซไซยาเนตเป็นตัวเพิ่มความยืดหยุ่น ในอัตราส่วนโดยมวลของเบนซอกซาซีน/ยูรีเทนพรีพอลิเมอร์เป็น 70/30

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## 4470617221: MAJOR CHEMICAL ENGINEERING

KEYWORD: POLYBENZOXAZINE / SYNERGY/ POLYMER ALLOY.

SURASAK PIRSTPINDVONG: COMPARATIVE STUDY ON FLEXIBILITY ENHANCEMENT OF POLYBENZOXAZINE USING EPOXY AND URETHANE PREPOLYMERS. THESIS ADVISOR: ASSIST. PROF. DR. SARAWUT RIMDUSIT, THESIS CO-ADVISOR: ASSIST. PROF. DR. SIRIPORN DAMRONGSAKKUL, 114 pp. ISBN 974-17-4302-5

The flexibility of polybenzoxazine (BA) can substantially be improved by alloying with IPDI-based urethane prepolymers (PU) or with flexible epoxy (EPO732). The experimental results, i.e. flexural testing and dynamic mechanical analysis, reveal that flexibility of the rigid polybenzoxazine and the PU or the EPO732 alloys systematically increases with the amount of both tougheners due to the added flexible molecular segments in the polymer hybrids. The curing temperature of the benzoxazine resin at about 225 degree celcius shifts to a higher value when the fraction of BA in both resin mixtures decreases. Interestingly, the synergism in glass transition temperature (Tg) obtained from the peak of loss modulus in the dynamic mechanical analysis of BA/PU alloys is clearly observed, i.e. Tg of the BA/PU alloys are significantly greater (Tg beyond 200 degree celcius) than those of the parent resins, i.e. BA (Tg = 165 degree celcius) and PU (Tg = -70 degree celcius). However, this synergistic characteristic is not observed in the BA/EPO732 alloy systems. The synergistic Tg of BA/PU alloy at 70/30 mass ratio is found to be 221 degree celcius while that of BA/EPO732 at the same mass ratio is reported to be of only 95 degree celcius and further decreases with the amount of epoxy fraction. The phenomenon is explained by the ability of the PU fraction to substantially enhance the crosslinked density of the polymer alloys thus create the more connected network structure of the resulting alloys whereas the EPO732 shows almost negligible effects on the alloys crosslinked density or even reduce the alloy's crosslinked density when the amount of this flexible epoxy is greater than 50wt%. Furthermore, the degradation temperature based on the 5% weight loss of the TGA thermograms of BA/PU alloys is found to be improved with the presence of the PU while the opposite trend is observed in BA/EPO732 systems. Finally, the char yield of both alloy systems is steadily enhanced with increasing the amount of the benzoxazine fraction due to the inherent high char yield of the benzoxazine resin comparing with the other two tougheners. The toughened polybenzoxazine using IPDI-based urethane prepolymer, e.g. 70/30 BA/PU, is thus the promising system for a tough and high thermal stability polymeric network for bulk or composite matrix applications.

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# CHAPTER 1

# INTRODUCTION

## 1.1 Background

Thermoset are plastics that are based on chemically cross-linked polymers with high glass-transition temperatures of relatively short network chains. They are made from monomers or oligomers (prepolymers) that are also designated as reaction polymers and ought to be called thermosetting. Thermosetting raw materials can be liquid or solid. Powdery raw materials must have glass-transition temperatures of at least (40-50) $^{o}$C in order to avoid agglomeration on storage [1].

The density of junctions or cross-linkages in elastomeric networks is generally low, typically 0.05-0.2 mol/kg. Yet, the degree of interlinking places them far beyond the gel point. It follows that imperfections in the form of chain attached to the network at one end are usually of minor consequence. To characterize the constitution of the network in a way that comprehends network imperfections, the cycle rank of the network defined below turns out to be the appropriate measure of connectivity. A feature of networks, second in importance only to the degree of connectivity, is the copious interpenetration of the chain comprising them. Chains emanating from a given junction of the network are embedded in a maze of other chains and junctions. Most of the latter are only remotely topologically related to the junction considered. This fact, often overlooked, has an important bearing on the properties of elastomeric networks. It precludes their treatment in terms of a lattice, albeit a disordered one, consisting of junctions related to their spatial neighbors by connecting chains [2].

## 1.2 Benzoxazine Resins

Polybenzoxazine, a new thermoset plastic, possess various good properties, i.e. high thermal stability, easy processability, low water sorption, near zero shrinkage after processing with excellent mechanical properties. It can be synthesized from inexpensive raw material and do not release by-products during polymerization, thus being high potential in many applications. However, one shortcoming of this resin is the high rigidity. Alloying, blending or composite materials can improve the mechanical properties or thermal stability of polybenzoxazine [3-8]. The epoxy and urethane elastomer were used to alloy with benzoaxine resin to improve the thermal stability and mechanical properties [3, 4, 6-8].

## 1.3 Epoxy Resins

Epoxy resins belong to the thermosetting class of plastics and bear similarities to materials such as the phenolics and polyester. The most of epoxy resin was synthesized by using bisphenol A or bisphenol F with epichlorohydrin. The advantages of this resin are low viscosity, low shrinkage, high adhesive strength, good chemical resistance, easy cure and high mechanical properties. Because of their versatility, the epoxy resins are used in numerous industrial applications. Epoxy resins are also used in coating, adhesives for aircraft honeycomb structures, paintbrush bristles, encapsulation compounds and sealant compounds for electronic packages.

## 1.4 Polyurethane

Polyurethane constitutes a group of polymers with highly versatile properties and a wide range of commercial applications. Polyurethane plastics were materialized by Bayer in 1974 [9]. They are usually produced by the reaction of a polyfunctional isocyanate, most often with hydroxyl compounds. Since the functionality of the hydroxyl-containing reactant on the isocyanate can be varied, a wide variety of branched or cross-linked polymers can be formed. Hydroxyl-containing components cover a wide range of molecular weights and types, including polyester and polyether polyols. The polyfunctional isocyanates can be aromatics, aliphatic, cycloaliphatic, or polycyclic in structure and can be used directly as produced or modified. This flexibility in the selection of reactants leads to the wide range of physical properties that allows polyurethanes to play an important role in the world market for quality products from synthetic polymers. Polyurethane elastomers have found wide application in virtually every industry because of their very special properties. The most important of urethane elastomer are high elasticity over the entire hardness range, flexibility over a wide temperature range, good weather resistance and good resistance against many solvent. Polyurethane elastomers are also used in exterior auto body parts, rollers, damping elements, drive components, sport and track surface.

The purpose of this work is to investigate the flexibility enhancement of polybenzoxazine based on alloying with more flexible network i.e. flexible epoxy or urethane elastomer. We investigated the effect of benzoxazine mass fraction on the curing behavior temperature and time of the alloys. The effect of benzoxazine mass ratio on the flexural modulus and thermal stability (Tg, Td) to optimize the suitable composition for high performance alloys were also be studied.

## 1.5 **Objectives**

1. To study the interaction of benzoxazine resin with urethane elastomer and flexible epoxy.
2. To compare the improvement in flexibility of polybenzoxazine using urethane elastomer and flexible epoxy.
3. To find optimum composition of the obtained polymer alloys which maintain overall good properties of polybenzoxazine

## 1.6 **Scope of Research**

1. To synthesize benzoaxine monomer using solventless synthesis technology [9].
2. To study the curing behaviors in both benzoxazine resin/epoxy and benzoxazine resin/urethane prepolymer using differntial scanning calorimetry (DSC).

3. To study the effect of composition of benzoaxine resin on glass transition temperature by using dynamic mechanical analyzer (DMA) and on degradation temperature using thermogravimetric analyzer (TGA).
4. To study the effect of composition on the flexibility using universal testing machine (LLOYD).
5. To study the effect of molecular weight of urethane prepolymer on glass transition temperature, degradation temperature and flexibility of the resulting benzoxazine/urethane polymer alloys.

# CHAPTER 2

# THEORY

## 2.1 Benzoxazine Resin

Polybenzoxazine is a phenolic polymer in which generated by the Mannich-like condensation of phenol, formaldehyde and amine. It can be prepared by using solventless synthesis technology [10]. The general pattern for this process is:

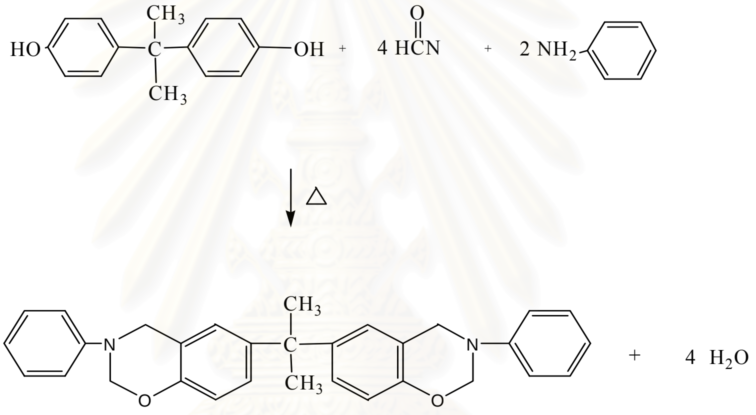
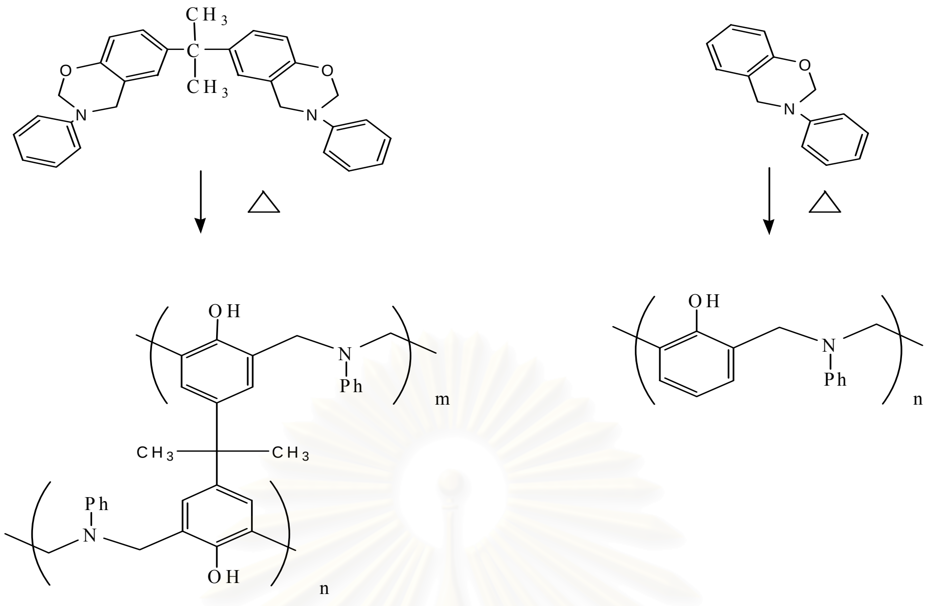


**Figure 2.1** The reaction of benzoxazine formation

The molecular of the polybenzoxazine often superb designs flexibility that allows the properties of the cured materials to be controlled for the specific requirements of a wide variety of individual applications. This is because polybenzoxazine can be synthesized from a wide selection of raw materials consisting of phenolic derivatives and primary amines. Figure 2.2 shows two major types of polybenzoxazine:



a. bifunctional b. monofunctional

**Figure 2.2** Two types of benzoxazine resin

Benzoxazine resin can be polymerized by heating and do not need catalyst or curing agent. These two kinds of polybenzoxazine are different in reactant. The benzoxazine bifunctional monomer use bi-phenol and the benzoxazine monofunctional monomer use phenol to synthesize. Their properties are also different. The benzoxazine bifunctional monomer can be polymerized to yield network structure and the later can be polymerized to yielde linear structure.

Ishida, et al. [11] proposed mechanism of polybenzoxazine formation. A single-crystal X-ray crystallographic study shows that the preferential conformation of a mono-oxazine ring containing benzoxazine is a distorted semichair structure, with the 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). In light of this knowledge, we propose that the oxygen on the oxazine ring will act as the initiation site, upon attack of a cationic initiator, to form a cyclic tertiary oxonium ion. The polymerization will then proceed by insertion of the monomers through the reaction of the oxygen on the oxazine ring, thereby leading to a Mannich base phenoxy-type (Type I) polybenzoxazine structure. This mechanism is illustrated as mechanism A in Figure 2.3

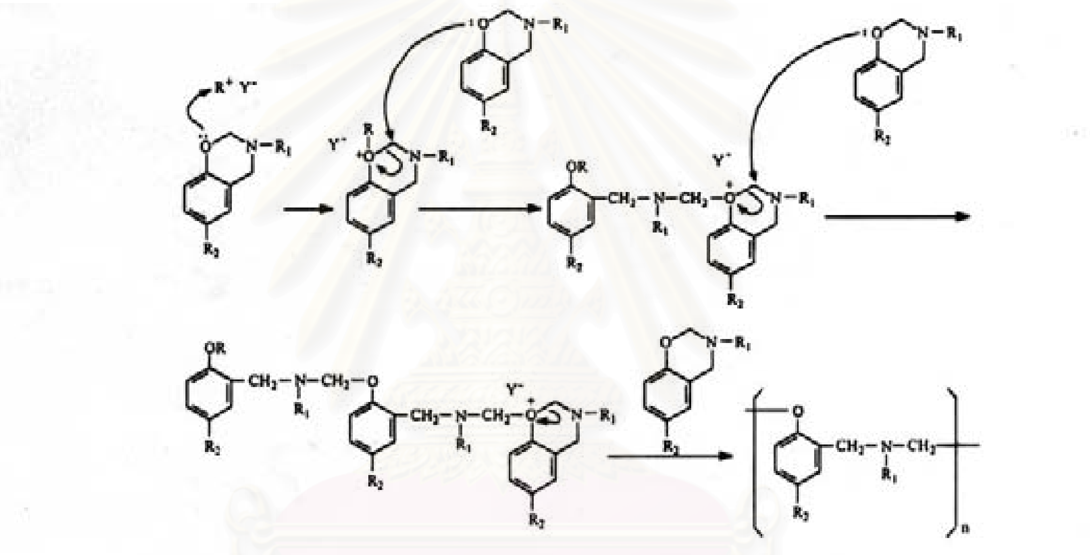


**Figure 2.3** The mechanism of polybenzoxazine monofunctional formation (mechanism A ,Type I) [11]

Also, an alternative polymerization route which is similar to mechanism A but having N as the initiation and propagation sites can be proposed (Figure 2.4). This mechanism could also lead to the formation fo a Manich base phenoxy-type (Type I) polybeenzoxazine structure.

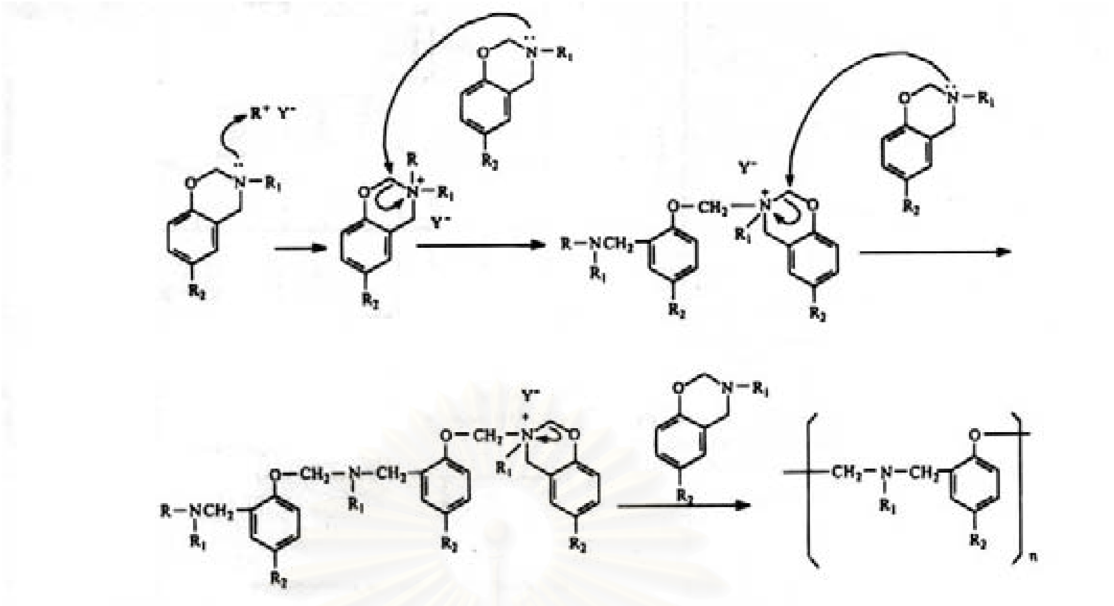


**Figure 2.4** The mechanism of polybenzoxazine monofunctional formation (mechanism B ,Type I) [11]

Futhermore, 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 catalyts.

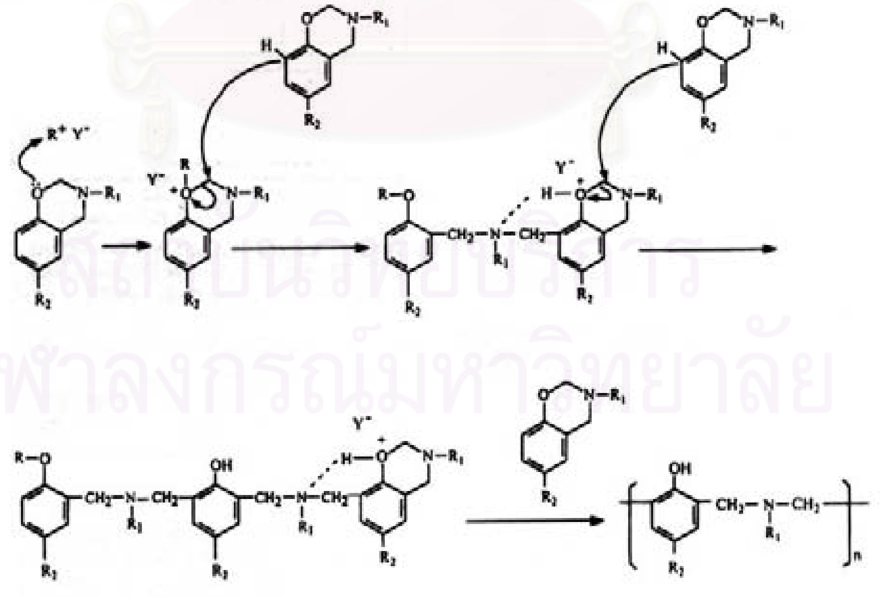


**Figure 2.5** The mechanism of polybenzoxazine monofunctional formation (Type II) [11]

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 (Type II) polymer. This proposed mechanism is illustrated as mechanism B in Figure 2.5. Moreover, in this latter case, the monomers propagate via reasonably stable carbocations, i.e., oxonium cations stabilized by intramolecular hydrogen bonding (as shown in Figure 2.5), which could lead to high-molecular weight polymer formation.

In this research, we used polybenzoxazine bifunctional monomer which was synthesized from inexpensive raw materials. The polymerization occurred by a simple ring-opening addition reaction and did not yield any reaction by-products. Benzoxazine resins were cured without the aid of the strong acid catalysts required by the other phenolic materials. The gained thermoset plastic, polybenzoxazine, have excellent mechanical properties and thermal properties such as near-zero volumetric shrinkage upon polymerization, low water sorption despite high concentration of hydrophilic groups, glass-transition temperature much higher than polymerization temperature, fast mechnical and physical properties development as a function of the degree of polymerization and excellent electrical properties. A fill-polybenzoxazine pending with maximum occupation around 88 % by weight and thermal conductivity up to 32 W/m.k [12].

The other advantages of polybenzoxazine include easy to processs, lack of volatile formation, and high mechanical properties, all attractive for composite material manufacturing. In the literature reported that the mixture of the benzoxazine resin with epoxy resin and benzoxazine resin with urethane prepolymer can be alloyed.

In the binary system, benzoxazine resin with epoxy resin can be polymerized to obtain a high crosslink density and glass transition temperature than the polybenzoxazine homopolymer [6]. In the binary system, benzoxazine resin with urethane prepolymer based on toluene diisocyanate had greater elongation than the polybenzoxazine homopolymer [4].

## 2.2 Epoxy Resin

Epoxy resin refers to a chemical group consisting of an oxygen atom bonded with two carbon atoms already united in some other way. The simplest epoxy is a three-member ring, to which the term α-epoxy or 1,2-epoxy is applied. In Figure 2.6, ethylene oxide (I) is an example of this type and the term 1,3 and 1,4-epoxy are applied to trimethylene oxide (II) and tetrahydrofurane (III).

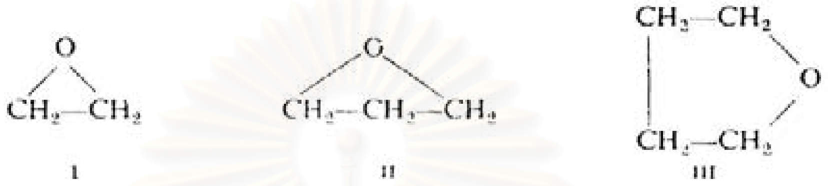


**Figure 2.6** The examples of epoxide ring [13]

Epoxy resins are prepared commercially by dehydrohalogenation of the chlorohydrin prepared by the reaction of epichlorohydrin with suitable di- or polyhydroxyl material or other active-hydrogen-containing molecule; by the reaction of olefins with oxygen-containing compounds such as peroxides or peracids, and by dehydrohalogenation of chlorohydrins.

Epoxy resins are the thermosetting class of plastics such as the phenolics and polyurethane. The basic characteristics of epoxy resin offer great versatility, low shrinkage, easy cure, high mechanical properties, good chemical resistance, high electrical insulation, and outstanding adhesion.

The structure determination from IR spectrum and the specification of felxible epoxy (DER.732) used in the study are shown in Figure 2.7 and Table 2.1, respectively.

**DER732**

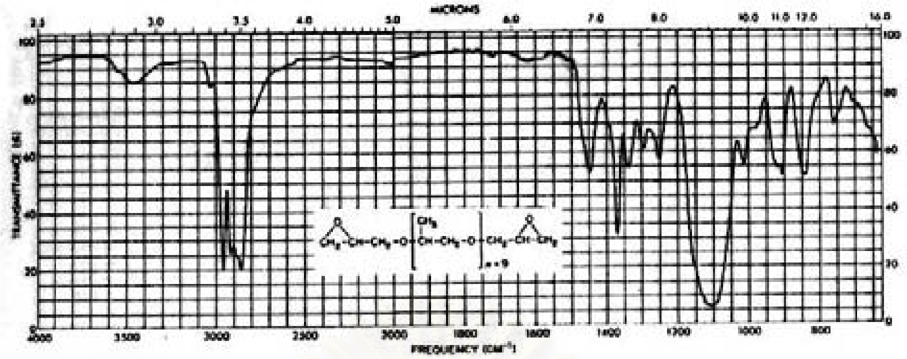


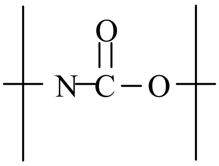
**Figure 2.7** Diglycidyl ether of polypropylene glycol [polypropylene glycol di (2,3-epoxy-propyl)ether] [13]

**Table 2.1** The specification of flexible epoxy DER.732

| properties | value | unit |
|---|---|---|
| Epoxide Eq. weight | 322 | - |
| Vapor pressure | 1.4 at 20$^{o}$C | mmHg |
| Boiling point | >200 | $^{o}$C |
| Solubility in water | 7.8 | wt % |
| Specfic gravity | 1.06 | - |
| viscosity | 62.8 at 25$^{o}$C | cps |

## 2.3 Polyurethane

Polyurethane is the polymer that contains urethane group. The urethane group results from the interaction of an isocyanate and a hydroxyl compound as shown in Figure 2.8. A diisocyanate and a diol react together. Then, a linear polyurethane is obtained whilst a diisocyanate and a polyhydric compound (polyol) lead to a cross-linked polymer. Thus diisocyanates and diols (and polyols) are the principal raw materials used in the manufacture of polyurethanes.



$$\left[ -N-\overset{\overset{\displaystyle O}{||}}{C}-O- \right]$$

**Figure 2.8** Urethane linkage [14]

The functionality of the hydroxyl-containing reactant or the isocyanate can be varied; a wide variety of linear, branched and crosslinked can be formed. The hydroxyl-containing components cover a wide range of molecular weights and types, including polyester and polyether polyols. The polyfunctional isocyanates can be aromatic, aliphatic, cycloaliphatic, or polycyclic in structure and can be used directly as produced or modified. This flexibility in the selection of reactants leads to the wide range properties.

Isocyanates

While the chemistry and technology of polyurethanes are of relatively recent origin, the chemistry of organic isocyanates dates back over hundred years. Wurtz, in 1849, was the first to synthesize aliphatic isocyanates by reacting organic sulfates with cyanates:

$$R_2SO_4 + 2KCNCO \longrightarrow 2RNCO + K_2SO_4 \qquad (2.1)$$

The structure of the isocyanates obtained by Wurtz was later confirmed by Gautier (1869), who oxidized aliphatic isocyanides with mercuric oxide to the corresponding isocyanates:

$$R\text{-}N{=}C + HgO \longrightarrow R\text{-}N{=}C{=}O + Hg \qquad (2.2)$$

The first aromatic isocyanate and phenyl isocyanate, was prepared by Hofmann (1850), by pyrolysis of symmetrical diphenyl oxide:

$$2C_6H_5\text{-}NH\text{-}C{=}O \longrightarrow 2C_6H_5NCO + H_2 \qquad (2.3)$$

Polyols

A wide range of polyols is used in polyurethane manufacturing. Most of the polyols used, however, fall into two classes: hydroxyl-terminated polyester and polyethers. 90% of polyols used in manufacturing polyurethanes are polyethers with terminal hydroxyl groups. Hydroxyl-terminated polyesters are also used to obtain polyurethanes with special properties.

The structure of polyol plays a large part in determining the properties of the final urethane prepolymer. The molecular weight and functionality of the polyol are the main factors, but the structure of polyol chains is also important.

*Polyether polyols*

The commercial polyether polyols used in the urethane field is relatively recent development. The first report of experiments with polyethers as intermediates for polyurethanes utilized polyethers derived from ethyloxide or propylene oxide. The first polyether designed specifically for use in preparing polyurethanes was a poly (oxytetra methylene) glycol derived from tetrahydrofuran. These are made by the addition of alkylene oxides usually propylene oxide, onto alcohols or amines which are usually called starter or ‘initiators’. The addition polymerization of propylene oxide occurs with either anionic (basic) cationic (acidic) catalysis although commercial polyol product is usually by base catalysis. The epoxide ring of propylene oxide may theoretically open at either of two positions on reaction but, in practice, the ring opens preferentially at the less sterically-hindered position with base catalysis. Polyethers based of propylene oxide thus contain predominantly secondary hydroxyl end-group. Secondary hydroxyl end-groups are several times less reactive with isocyanates than primary hydroxyl groups.

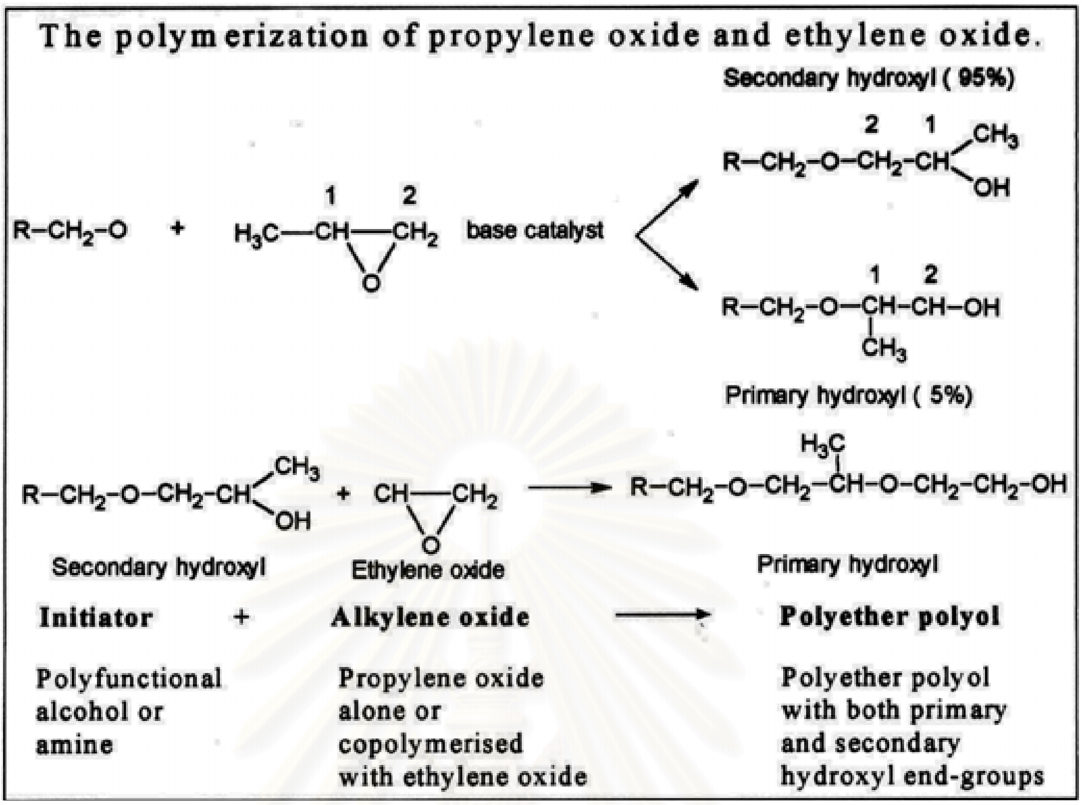


**Figure 2.9** The manufacture of polyether polyols [15]

Figure 2.9 shows the manufacture of polyether polyols is usually carried out in stainless steel of glass-lined reactors by essentially batch processes. The catalyst is usually sodium or potassium hydroxide in aqueous solution although sodium methoxide, potassium carbonate and sodium acetate are also used. A polymerization initiator is employed to control the type of polyether produced.

*Polyester polyols*

Polyester polyols tend to be more expensive than polyether polyols and they are usually more viscous and therefore more difficult to handle. They also yield polyurethane polymers which are more easily hydrolyzed, consequently they are only used to make polyurethanes for demanding applications where the particular physical properties abtainable from polyesters are important. Polyester-based polyurethane elastomers combine high levels of tensile properties with resistance to flexing and abrasion. They also have good resistance to many types of oil.

The polyesters are prepared by reaction of dibasic acids (usually adipic but other components such as sebasic or phatalic acid may be presented) with diol such as ethylene glycol, 1,2-propylene glycol, and diethylene glycol (where linear polymer segments are required).

For preparation of the polyesters, conventional methods of polyesterification, i.e. reaction between acid and diol or polyol, are used, the water of condensation being removed by distillation and the reaction assisted, if necessary, by use of vacuum or an azeotrope. Branching can be introduced by the adding of small amount of a triol to the reaction mixture.

One convenient preparation involves reaction of the components without solvents. The glycol and triol, if desired, are added to the reactor and heated with stirring to 60-90$^{o}$C. The acid component is added quickly and the mixture stirred and heated at such a rate the water distills out rapidly. The hydroxyl and acid components are used in such a ratio that nearly all acid groups react and the hydroxyl groups are in sufficient to control the molecular weight in the desired range.

The reactivity of isocyanates with different type of active hydrogen compound can be placed in the following order:

aliphatic $NH_2$ > aromaticNH2 >primary OH > water >
secondary OH >tertiary OH > phenolic OH> COOH

and

RNHCONHR > RCONHR > RNHCOOR

The excellent application properties of polyurethane account for the facts that their use is economically feasible and that their range of applications is constantly increasing. In some instance they are even irreplaceable. Among these properties are unique combination of a high elastic modulus, good flexibility, exceptional tear and abrasion resistance, resistance to mineral oils and lubricants, resistance to UV radiation and finally the fact that the products retain these properties, as well as providing fairly easy and efficient processing.

In this work, we synthesized urethane prepolymer in our laboratory. Raw materials Isophorone diisocyanate and diol are available from Degussa-huels and Mitsui Chemical. INC., respectively. The specifications of isophorone diisocyanate are shown in table 2.2

**Table 2.2** The specification of isophorone diisocyanate

| properties | value | unit |
|---|---|---|
| NCO content | 37.5-37.8 | wt% |
| Vapor pressure | $9*10^{-4}$ at 20°C | Hpa |
| Flash point | 155 | °C |
| Density | 1.058-1.064 at 20°C | $g/cm^3$ |
| Purity | >99.5 | wt% |
| Total chlorine | 80-200 | ppm |

## 2.4 Dynamic Mechanical Analyzer (DMA) [16]

Dynamic mechanical properties are the mechanical properties of materials as they are deformed under periodic forces. The dynamic modulus, the loss modulus, and a mechanical damping or internal friction expresses these properties. The dynamic modulus indicates the inherent stiffness of material under dynamic loading conditions. It may be a shear, a tensile, or a flexural modulus, depending upon the investigating technique. Dynamic modulus is especially important for engineering structural applications of plastics and composites since the variation of properties is easily determined as a function of temperature and frequency (or time). The polymeric materials under use conditions are often in the dynamic stress and strain field, such as parts of automobiles, aircraft, and aerospace structures. Knowledge of the dynamic moduli and properties of polymeric materials is indispensable for the design of these materials.

The mechanical damping or internal friction indicates the amount of energy dissipated as heat during the deformation of the material. The internal friction of material is important as a property index and for environmental and industrial applications. Since noise is radiated by vibration, especially of metallic materials with small internal friction (0.001-0.001), the application of damping materials to the vibrating surface converts the energy into heat, which is dissipated within the damping materials rather than being radiated as airborne noise. Many viscoelastic polymers are good damping materials with high internal friction (0.1-0.3). High damping or internal friction is essential in decreasing the effect of undesirable vibration and in reducing the amplitude of resonance vibrations to safe limits, as well as in playing a key role in all kinds of structures from airplanes to buildings.

The investigation of the dynamic modulus and internal friction over a wide range of temperatures and frequencies has proved to be very useful in studying the structure of high polymers and the variations of properties in relation to performance. These dynamic parameters have been used to determine the glass-transition region, relaxation spectra, degree of crystallinity, molecular orientation, cross-linking, phase separation, structural or morphological changes resulting from processing, and chemical composition of polymer blends, graft polymers, and copolymers. In addition to these structure-property relationships, dynamic mechanical studies have been extended to material composites and structural systems.

Dynamic mechanical properties, such as the dynamic modulus and internal friction, are the most basic of all mechanical properties. The dynamic modulus indicates stiffness of polymeric material under the dynamic stress and strain condition. It varies from 100 kPa to 100 GPa ($10^6$-$10^{12}$ dyn/cm$^2$) and depends upon the type of polymer, temperature, and frequency. This value is related to the Young's modulus of polymers. The dynamic loss modulus, or internal friction, is sensitive to many kinds of molecular motion, transitions, relaxation processes, structural heterogeneity and the morphology of multiphase systems (crystalline polymers, polymer blends, and copolymers). Therefore, interpretations of the dynamic mechanical properties at the molecular level are of great scientific and practical importance in understanding the mechanical behavior of polymers.

The effects of molecular parameters on the dynamic mechanical properties are based on internal structure. However, many polymeric materials are combined as structural units, e.g., laminated plastics, fiber-reinforced composites, tires, and fabrics. Dynamic mechanical properties are useful in determining the properties of these structural units and the effects of the structural geometry on dynamic properties. The ultimate performance of these structural assemblies is influenced by the inherent properties of the components and the external structural factors of the systems.

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

## 2.5 Differential Scanning Calorimetry (DSC) [17, 18]

Differential Scanning Calorimetry (DSC) is the dominant technique for the thermal analytical investigation of polymeric materials. It measures the difference in energy inputs into a substance and a reference material as they are subjected to a controlled temperature program. Practically all physical and chemical processes involve changes in enthalpy or specific heat, and the applicability of DSC to condensed-phase systems is almost universal. Its measurement process is quantitative and the change of enthalpy is usually a linear function of the reaction coordinate. A DSC endothermal or exothermal peak is shown in Figure 2.10 A DSC measurement gives the rate of change of enthalpy, so that the area between a DSC curve and its extrapolated baseline indicates the total heat of reaction. The fraction reacted is obtained from division of the fractional area by the total area. The amplitude between the baseline and the DSC curve measures the rate of reaction.

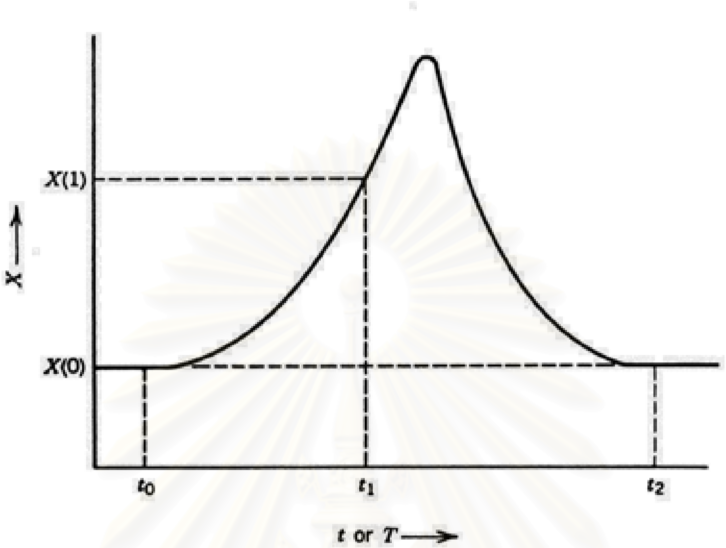


**Figure 2.10** First-order transition peak for DTA: $X = \Delta T$; for DSC: X = J/s, peak area = enthalpy of transition, fractional area/total area = fraction conversion, peak amplitude/total area = rate of conversion [17].

Differential Scanning Calorimetry (DSC) has almost completely superseded differential thermal analysis (DTA), except for some very high temperature or pressure applications. The latter technique measures the temperatue difference between temperature sensors, one in a specimen and the other in a reference material as they are subjected to the same programmed temperature change. This supersession is actually a result of the redefinition of DSC to include both power-compensated and heat-flux instruments. In effect, this classifies all quantitative dta instruments as DSC instruments.

DSC is used for research on and characterization of copolymers, blends and composites. It is used to study the properties of block copolymers such as the crystallizations and glass transitions of its components. For example, in the case of polyurethane, the glass-transition temperature can be determined for the domain containing polyether or polyester soft segments and the melting temperatures of the butanediol hard segment can be obtained. The hard segments are thought to act as macroscopic cross-links. The mechanical and rheological properties change during these transitions. The temperatures at which the transitions occur affect these proporties and the potential commercial applications of the material.

Differential scanning calorimetry is also widely used to investigate the properties of polymer blends. It is especially useful for distinguishing compatible and incompatible polymers; the former has a glass-transition temperature intermediate between those of the two components, whereas the latter exhibit the two individual glass transitions. Effects of varying component fraction on the melting temperatures of the blends are determined as well, so that phase diagrams can be developed showing regions of incompatibility, solution, and eutectic, and interaction parameters can be calculated.

## 2.6 Thermogravimetry Analysis (TGA) [19]

Thermogravimetry (TG) is the branch of thermal analysis that 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, absortion, 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 physico-chemical processes occurring in the sample. The mass change characteristics of a 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 cannot be considered as a black box technique where fingerprint curves are obtained irrespective of the experimental conditions. Establishing the optimum conditions for TG analysis frequently requires many preliminary tests. It is essential for accurate TG work that the experimental conditions be recorded and that within a given series of samples the optimum conditions be standardized and maintained throughout the course of the experiments. Only they can TG curves from different experiments be compared in a meaningful way.

TG curves are normally plotted with the mass change ($\Delta$m) expressed as a percentage on the vertical axis and temperature (T) or time (t) on the horizontal axis. A schematic representation of a one-stage reaction process observed in the scanning mode is shown in Figure 2.11. 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.

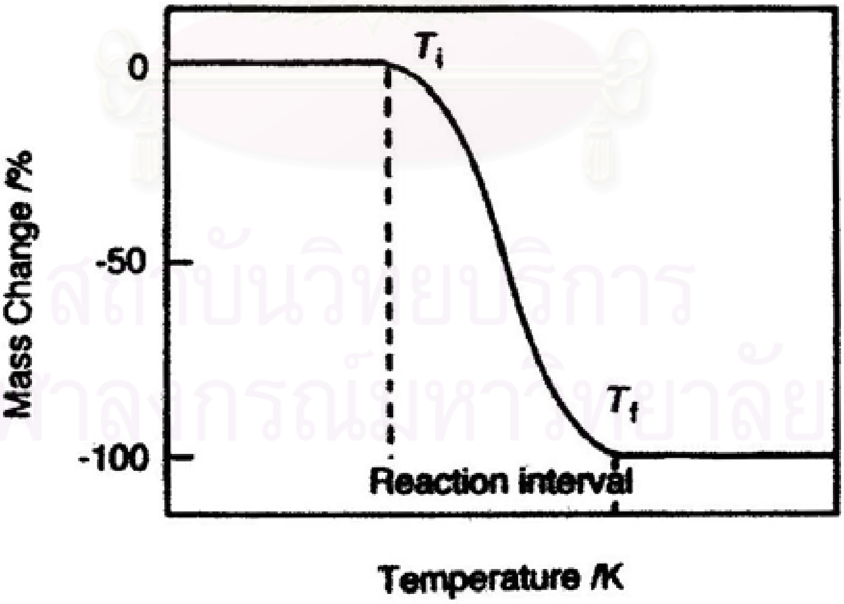


**Figure 2.11** Schematic single stage TG curve [19].

## **2.7 Flexural Testing** [ASTM D790]

Flexural properties are the ability of the material to withstand bending forces applied perpendicular to the beam. The stresses induced due to the flexural load are the combination of compressive and tensile stresses, as illustrated in figure 2.12. The results from this test give the flexural modulus and flexural strength. Explanation of the terminology used in flexural testing is as follows:

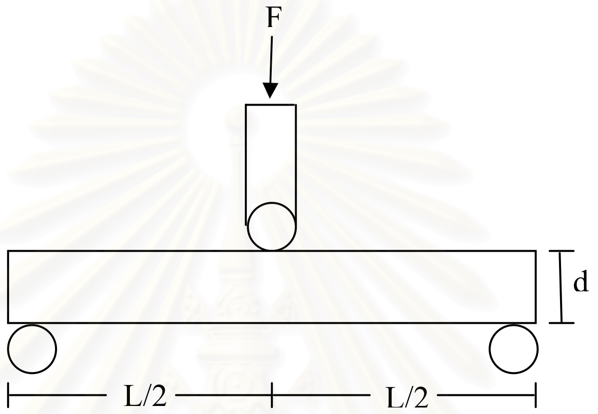


**Figure 2.12** Flexural testing (three point bending)

The flexural modulus is represented by the slope of the initial straight-line portion of the stress-strain curve. In addition, flexural modulus gives a good indication of the stiffness. It is calculated by drawing a tangent to the steepest initial straight-line portion of the load-deflection curve and using Eq. 2.4

$$E_B=L^3m/4bd^3 \qquad (2.4)$$

where

$E_B$ = modulus of elasticity bending, MPa,

L = support span, mm,

b = width of beam tested, mm,

d = depth of beam tested, mm,

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

The flexural strength is equal to the maximum stress in the outer fibers at the moment of break. However, many polymers do not break under the flexural test even after a large deflection. This stress may be calculated for any point on the load-deflection curve by the following equation:

$$S = 3PL/2bd^2 \tag{2.5}$$

where

S = stress in the outer fibers at midspan, MPa,

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

L = support span,mm,

b = width of beam tested, mm and

d = depth of beam tested, mm.

## **2.8 Fourier Transform Infrared Spectroscopy (FT-IR)** [20-23]

Infrared spectroscopy is the study of interactions of infrared light with a matter. It provides the specific information of molecular vibrations. When infrared light interacts with a matter, it can be absorbed and causing the vibrations of chemical bonds consisted in the material. There are two kinds of fundamental vibrations for a molecule: stretching and bending. Stretching is the movement along the bond axis (i.e., symmetric and untisymmetric) types. In the contrary, bending vibrations arise from changes in bond angle between two atoms and movement of an atomic group. It relates to the remainder of the molecule. As a result, molecule adsorbs a certain energy that is quantized to raise the vibrational energy level and additional exchange its electronic dipolemoment. These cause absorption peaks appearing on an infrared spectrum at the wave number of slight absorbed. Various stretching and bending vibrations occur at specific frequencies. Bending vibrations normally require less energy and occur at longer wavelength than those with stretching vibrations. Vibrational frequencies depend not only on the structures of specific atomic groups, but they are also affected by either greater or lesser degree by structures of the other parts of the molecule. Therefore, different molecules represent different vibration patterns due to different compositions in molecular structure.

Since molecular vibrations readily reflect chemical feature of molecule, such as a rearrangement of nuclei and chemical bonds within the molecule, infrared spectroscopy contributes considerably not only to molecular identification but also studies of the molecular structure. Futhermore an interaction with the surrounding environment causes changes in molecular vibrations. As a consequence, infrared spectroscopy has become a useful technique for study of molecular interactions. The infrared spectrum can be divided into three catagories: i.e., the far-infrared (<400 cm$^{-1}$), the mid-infrared (400-4000 cm$^{-1}$), and the near-infrared (4000-13000 cm$^{-1}$) regions. Most infrared applications employ the mid-infrared region since it contains fundamental mode of vibration of molecules. It is used to establish the idenity of a compound. However the near- and far-infrared regions can also provide specific information about materials. The near-infrared regions consist mostly of overtone or combination bands of fundamental modes appearing in the mid-infrared region. The far-infrared region can provide such information regarding lattice vibrations.

According to basic of FT-IR spectroscopy, the Michelson interferometer is utilized instead of prisms and slits consisted indispersive infrared spectrometer. Beam splitter seperates an incident beam into two paths and then recombines them again. Thus, the intensity variations of the exit beam can be measured by a detector as a function of travel path differences. The signal produced as a function of changes between the two beams. Figure 2.13 shows the schematic diagram of a Michelson interferometer.

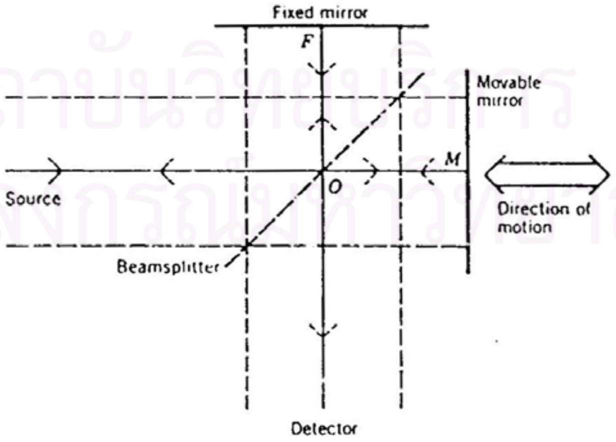


**Figure 2.13** Schematic diagram of Michelson interferometer [20]

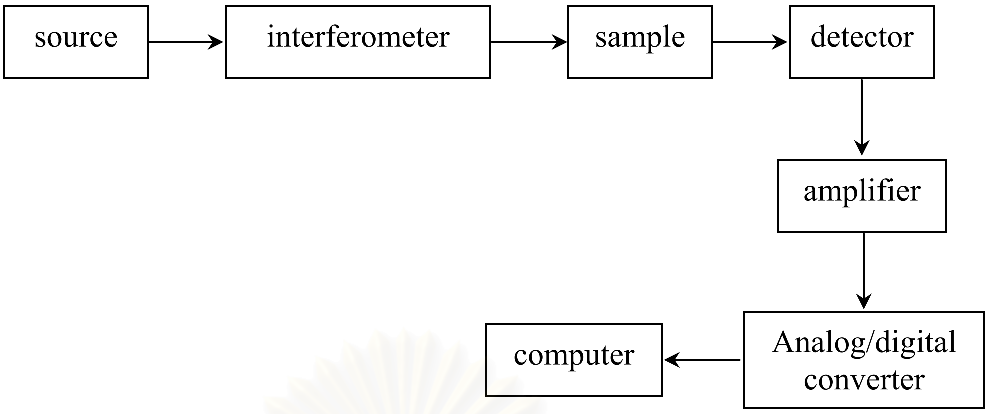


**Figure 2.14** Schematic of a typical FT-IR converter spectrometer [20]

FT-IR spectrometer is based on the interference of light between two beams, producing an interferogram. Time and frequency domains are interconvertible by the Fourier transform method. The basic components of FT-IR spcetometer are shown schematically in Figure 2.14. The radiation generated by the IR source passes through an interferometer, then being absorbed by a sample before reaching a detector. Upon the signal amplification, in which high-frequency contributions have been eliminated by a fiter, the data are converted into a digital from by an analog-to-digital converter. Then they are transferred to the computer for Fourier transformation. The finally FT-IR spectrum is obtained from the ratio of a single beam of the sample against that of the reference.

# CHAPTER 3

# LITERATURE REVIEW

Mitchell T. Huang and H. Ishida, 1999 [5] investigated the dynamic mechanical of reactive diluent modified benzoxazine-based phenolic resin. The viscosity of a difunctional benzoxazine resin is reduced by use of a monofunctional benzoxazine monomer or a difunctional epoxy monomer as reactive diluents to further improve processability. The influence of the monofunctional benzoxazine on the thermal and dynamic mechanical properties of the modified polybenzoxazine is examined as a function of composition. Glassy state properties, such as stiffness at room temperature, are unaffected by the incorporation of the monofunctional benzoxazine. Thermal stability of the monofunctional modified polybenzoxazine below 200 °C is not significantly affected. Properties sensitive to network structure, however, are affected by the presence of the monofunctional benzoxazine. The incorporation of the monofunctional benzoxazine reduces crosslink density and produces a looser network structure, while the difunctional epoxy increases crosslink density and produces a more connected network structure.

H. Ishida and D.J. Allen, 1996 [6] blended the benzoxazine with epoxy based on DGEBA. The benzoxazine are copolymerized with an epoxy resin in order to modify their performance. The addition of epoxy to the polybenzoxazine network greatly increases the crosslink density of the thermosetting matrix and strongly influences its mechanical properties. Copolymerization led to significant increases in the glass transition temperature, flexural stress, and flexural strain at break over those of the polybenzoxazine homopolymer, with only a minimal loss of stiffness. By understanding the structural changes induced by variations of epoxy content and their effect on material properties, the network can be tailored to specific performance requirements.

H. Kimura et al., 1999 [7] synthesized terpenediphenol based benzoxazine from terpenediphenol, formaline and aniline. Curing behavior of the benzoxazine with epoxy resin and the properties of the cured resin were investigated. Consequently, the curing reaction did not proceed at low temperatures, but it proceeded rapidly at higher temperatures without a curing accelerator. The properties of the cured resin both from neat resins and from reinforced resin with fused silica were evaluated, respectively. The cured resins showed good heat resistance, mechanical properties, electrical insulation, and especially water resistance, compared with the cured resin from bisphenol A type novolac and epoxy resin.

H. Kimura et al., 2001 [8] synthesized poly (p-vinylphenol) (VP) based benzoxazine from VP, formaline and aniline. The curing behavior of the benzoxazine with epoxy resin and the properties of the cured resin were investigated. Consequently, the curing reaction did not proceed at low temperatures, but it proceeded rapidly at higher temperatures without a curing accelerator. The reaction induction time or curing time of the molten mixture from VP based benzoxazine and epoxy resin was found to decrease, compared with those from conventional bisphenol A based benzoxazine and epoxy resin. The curing reaction rate of VP based benzoxazine and epoxy resin increased more than that of conventional bisphenol A based benzoxazine and epoxy resin. The cured resins from VP based benzoxazine and epoxy resin showed good heat resistance, mechanical properties, electrical insulation, and water resistance compared to the cured resin from VP and epoxy resin using imidazole as the catalyst.

H. Ishida and Y. Rodriguez, 1995 [24] studied the curing reactions of benzoxazine precursors based on bisphenol A and aniline to determine the feasibility of processing them into final phenolic parts. Benzoxazine precursors are able to overcome most of the shortcomings of traditional phenolic resins, and retain the excellent heat resistance and fire and smoke properties of these resins. This new type of phenolic material cures via a ring-opening mechanism that does not produce any condensation or other reaction by-products. Phenol is not used as raw material, which reduces considerably the environmental and health risks. According to differential scanning calorimetry (DSC), the curing of benzoxazine precursors is an autocatalysted reaction until vitrification is reached, and diffusion begins to control the curing process afterwards. Isothermal and non-isothermal (d.s.c.) tests are performed. Calculations of the activation energy and the overall reaction order are made by various procedures. The verification times and kinetic rate constants are also calaulated.

S. Rimdusit and H. Ishida, 2000 [25] found the synergism in the glass-transition temperature (Tg) of ternary systems based on benzoxazine, epoxy, and phenolic resins. The systems showed the maximum Tg up to about 180°C in benzoxazine / epoxy / phenolic-5 / 4 / 1 mass ratio. Adding a small fraction of phenolic resin enhanced the crosslink density and, therefore, the Tg in the copolymers of benzoxazine and epoxy resins. To obtain the ultimate Tg in ternary system, 6-10 wt% phenolic resin was needed. The molecular rigidity from benzoxazine and the improved crosslink density from epoxy contribute to the synergistic behavior. The mechanical relaxation spectra of the fully cured ternary systems in a temperature range of –140 to 350°C showed four types of relaxation transitions : gamma transition at –80 to -60°C, beta transition at 60-80°C, $alpha_1$ transition at 135-190°C, and $alpha_2$ at 290-300°C. The partially cured specimens showed an additional loss peak that was frequency-independent as a result of the further curing process of the materials.

S. Rimdusit and H. Ishida, 2000 [10] have developed new polymeric system based on the ternary mixture of benzoxazine, epoxy, and phenolic novolac resins. Low melt viscosity resins rendered void-free specimens with minimal processing steps. The material properties showed a wide range of desirable reliability and processability, which were highly dependent on the composition of monomers in the mixture. A glass transition temperature as high as $170^oC$ and considerable thermal stability at 5% weight lossup to $370^oC$ could be obtained from these systems. Phenolic novolac resin acted mainly as an initiator for these ternary systems while low melt viscosity, flexibility and improved crosslink density of the materials were attributed to the epoxy fraction. Polybenzoxazine imparts thermal curability, mechanical properties as well as low water uptake to the ternary systems.

T. Takeichi et al., 2000 [3] prepared poly(urethane-benzoxazine) films as novel polyurethane/phenolic resin composites from blending a benzoxazine monomer benzoxazine and urethane prepolymer that was synthesized from 2,4-tolylene diisicyanate (TDI) and polyethyleneadipate polyol (MW ca. 1000) in 2:1 molar ratio.

DSC of the polymer blend showed an exotherm with maximum at ca. 246$^{o}$C due to the ring-opening polymerization of benzoxazine, giving phenolic OH funtionalities that reast with isocyanate groups in urethane prepolymer. The poly (urethane-benzoxazine) films obtained by thermal curing were transparent, with color ranging from yellow to pale wine with increase benzoxazine content. All the films had one glass transition temperature (Tg) from viscoelastic measurements, indicating no phase separation in poly(urethane-benzoxazine) due to in situ polymerization. The $T_g$ increased with the increase of benzoxaxine content. The films containing 10 and 15% of benzoxaxine had characteristics of an elastomer, with elongation at break at 244 and 182%, respectively. The films containing more than 20% of benzoxaxine had characteristics of plastics. The poly(urethane-benzoxazine) films showed excellent resistance to the solvents such as tetrahydrofuran, N,N-dimethyl formamide, and N-methyl-2-pyrrolidinone that easily dissolve urethane prepolymer. Thermal stability of urethane prepolymer was greatly enhanced even with the incorperation of a small amount of benzoxaxine.

T.Takeichi and Y. Guo, 2001 [4] prepared poly(urethane-benzoxazine) films from blending a monofunctional benzoxazine monomer, 3-phenyl-3,4-dihydro-2H-1,3-benzoxazine, and urethane prepolymer that was synthesized from 2,4-tolylene diisocyanate and polyethylene adipate polyol (MW ca. 1000) in 2:1 molar ratio followed by casting as films and thermal curing of the films. The poly (urethane-benzoxazine) films obtained by thermal curing at 190$^{o}$C were yellow and transparent. All the films had only one glass transition temperature (Tg) from vicoelastic measurements, indicating good misibility between urethane prepolymer and poly benzoxazine due to the in-situ copolymerization of benzoxazine and urethane prepolymer. The Tg shifted increasingly with the increase benzoxazine content. The films containing less than 50% of benzoxazine had characteristics of elastomer, with elongation at break more than 200%. This elastic film exhibited good resilience with excellent reinstating behavior. The films containing more than 60% of benzoxazine had characteristics of plastics. The poly (urethane-benzoxazine) films showed excellent resistance to the solvents such as tetrahydrofuran, N,N-dimethyl formamide, N-methyl-2-pyrrolidinone and DMSO

Wen–Yen Chiange and Chung-Dien Tsai, 1999 [26] prepared polyurethane and phenolic resin to form maleimide-terminated PU/allyl nonyl novolac resin ABCPs. The polyurethane was prepared from 4,4’-diphenyl methane diisocyanate (MDI) and poly(tetramethyleneoxide) [PTMO] of various molecular weights. The composition, compatibility, mechanical and thermal properties of these in homogeneous network polymers were investigated through differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), the tensile strength tester and transmission electron microscopy (TEM) micrographs.The results revealed that the miscibility made only a little improvement but the tensile strength had clear improvement when the PU's soft segment, i.e. PTMO, was higher, because of the entanglement between components.

Hong Yee Low and Hatsuo Ishida, 1999 [27] investigated the structural effects of phenol on thermal and thermo-oxidative degradation of polybenzoxazines. The thermal behavior of a series of polybenzoxazines based on aniline and various phenols was examined under inert and oxidative environments. Under an inert environment, the various phenols substantially affected the char yield of polybenzoxazines without altering the mechanism of mannich base cleavage. Under an oxidative environment, the various phenols had a significant influence on the degradation behavior of polybenzoxazines below 600$^{o}$C. The mechanism of the mannich base cleavage under oxidative degradation has been proposed.

Y.-X. Wang and H. Ishida, 1999 [28] studied the cationic ring-opening polymerization of benzoxazines. With certain initiators, rings could be opened and polymerized at room temperature. Fourier transform infrared spectroscopy. $^{1}$H and $^{13}$C nuclear magnetic resonance spectroscopy, size exclusion chromatography, differential scanning calorimetry, and thermogravimetric analysis had been used to monitor the polymerization process and to characterize the obtained polymers. High performance bisphenol-A/aniline based polybenzoxazine with glass transition ($T_g$) at 220$^{o}$C and char yield of approximately 60% at 800$^{o}$C under nitrogen obtained.

# CHAPTER 4

# EXPERIMENT

## 4.1 Raw Materials

Benzoxazine monomer based on bisphenol, aniline and paraformaldehyde was synthesized. The monomer synthesis was based on the patented solventless synthesis [29]. The bisphenol A was supplied by Thaipolycarbonate Co. Aniline and paraformaldehyde were purchased from Asia Pacific Specialty Chemicals Co. and Merk Co., repectively. Urethane prepolymer was prepared from isophorone diisocyanate and polyether polyol. The isophorone diisocyanate was obtained from Degussa-Huls AG and the polyether polyol was taken from Mitsui Chemical, Inc. Dow chemical Co. contributed two types of flexible epoxy, i.e. D.E.R. 732.

## 4.2 Preparation of Resins

Benzoxazine monomer was synthesized using bisphenol A, aniline and paraformaldehyde at 1:2:4 molar ratio. The mixture was constantly stirred at 110$^{o}$C for approximately 30 minutes to yield a light yellow and low viscosity liquid monomer.[10] The benzoxazine monomer was crushed to the powder and was kept in a refrigerator.

The urethane prepolymer was prepared by using isophorone diisocyanate with diol (MW 1000, 2000 and 3000) at 1:2 molar ratio. Isophorone diisocyanate and diol were mixed in a distillation flask and the mixture was stirred under nitrogen stream at 90$^{o}$C for two hours. 0.4 g of dibutyltin dilaurate was used as a catalyst in the reaction. After that, the mixture (urethane prepolymer) was cooled to room temperature and was kept in a refrigerator.

## 4.3 Sample Preparation

The benzoxazine monomer was mixed with flexible epoxy or urethane prepolymer to provide Ba:PU or Ba:EPOXY at the desirable mass fraction. The mixture was heated to about 80°C in an aluminum pan and was thoroughly mixed by hand for about ten minutes until a homogeneous mixture was obtained. The mixture can be kept at room temperature for further use. The polymer alloys mixture were remelted at 80°C and the polymer alloys were cured at the temperature range of 100-200°C for 1-2 hr. Part of the mixture was taken for differential scanning analysis. The molten resin was poured into the aluminum foil mold and was cured in an oven. All the specimens were cured at 200°C for 1-3 hr. The specimens were left to cool down to room temperature and were taken to characterization.

## 4.4 Sample Characterization

### *Differential Scanning Calorimetry (DSC)*

A differential scanning calorimeter (DSC) model 2910 TA Instrument from Polymer Engineering Laboratory Research was used to study the curing behaviors in both benzoxazine resin/epoxy and benzoxazine resin/urethane prepolymer. All samples were put in aluminum pans with lids and were scanned using the heating rate of 10°C/min from room temperature to 300°C under $N_2$ purging. The mass of the sample was measured to be approximately 8-10 mg. The weights of reference and sample pans with lids were measured to be within 14±0.2 mg.

### *Dynamic Mechanical Analyzer (DMA)*

A dynamic mechanical analyzer (DMA) model DMTA Mk III Rheometric scientific from Polymer Engineering Laboratory Research was used to investigate the specimens dynamic mechanical properties. The test was performed under bending mode using 1 kg of load cell. The strain was applied sinusoidal with a frequency of 1 Hz. The specimen was heated at the rate of 2°C/min from room temperature to 350°C and the dimension was 5 mm × 35 mm × 1 mm.

### *Thermogravimetric Analysis (TGA)*

A thermogravimetric analysis model TGA/SDTA 851$^e$ from Mettler-Toledo model TGA/SDTA 851$^e$ was used to study thermal stability and the decomposition of the cured polymer alloys. 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. The experiment was done using the heating rate of 20$^o$C/min under nitrogen purging. The temperature was ramped from 30$^o$C to 900$^o$C using the sample mass of about 20 mg.

### *Universal Testing Machine*

A universal testing machine model 2000R LLOYD from Polymer Laboratory Engineering Research was used to determine flexural properties. The test followed from ASTM D 790. The specimen rested on two supports and was loaded by means of a loading nose midway between the supports. The dimension was 25 mm in width, 50 mm in length, and 1.6 mm in thickness. The specimen, arranged in a three-point bending configuration with L/D ratio = 16, were test at a constant cross head speed at 0.8 mm./min. and 25 mm. in support span. Load-deflection curves were plotted to determine the flexural yield strength, and the total work measured by the area under the load-deflection curve.

### *Fourier transform infrared spectroscopy*

FT-IR spectra of samples under varous curing conditions were acquired *via* Bruker Vector 33 FT-IR spectometer equipped with a KBr beamsplitter and a deuterated triglycine sulfate (DTGS) detector. All spectra were taken as a function of time with 32 scans at a resolution of 4 cm$^{-1}$ and spectra range of 4000-400 cm$^{-1}$. *In situ* monitoring of the structural change was deduced from the observed spectrum. The polymerization reactions of the samples were examined at room temperature. Premelted samples, 0.5-1.0 mg, were casted as thin films on potassium bromide (KBr) disks at 80 °C. All of the samples used in this study were sufficiently thin with optical thickness under the Beer-Lambert's law. The samples were then mounted on a sample holder.

Because the thickness of the sample in the IR beam could be altered during the reaction due to the low viscostiy of the monomers at the high temperature, an internal reference band was assigned for quantitative analysis. The band at 2967 $cm^{-1}$, which is assigned to the C-H stretching of methyl group, was chosen as the internal standard.

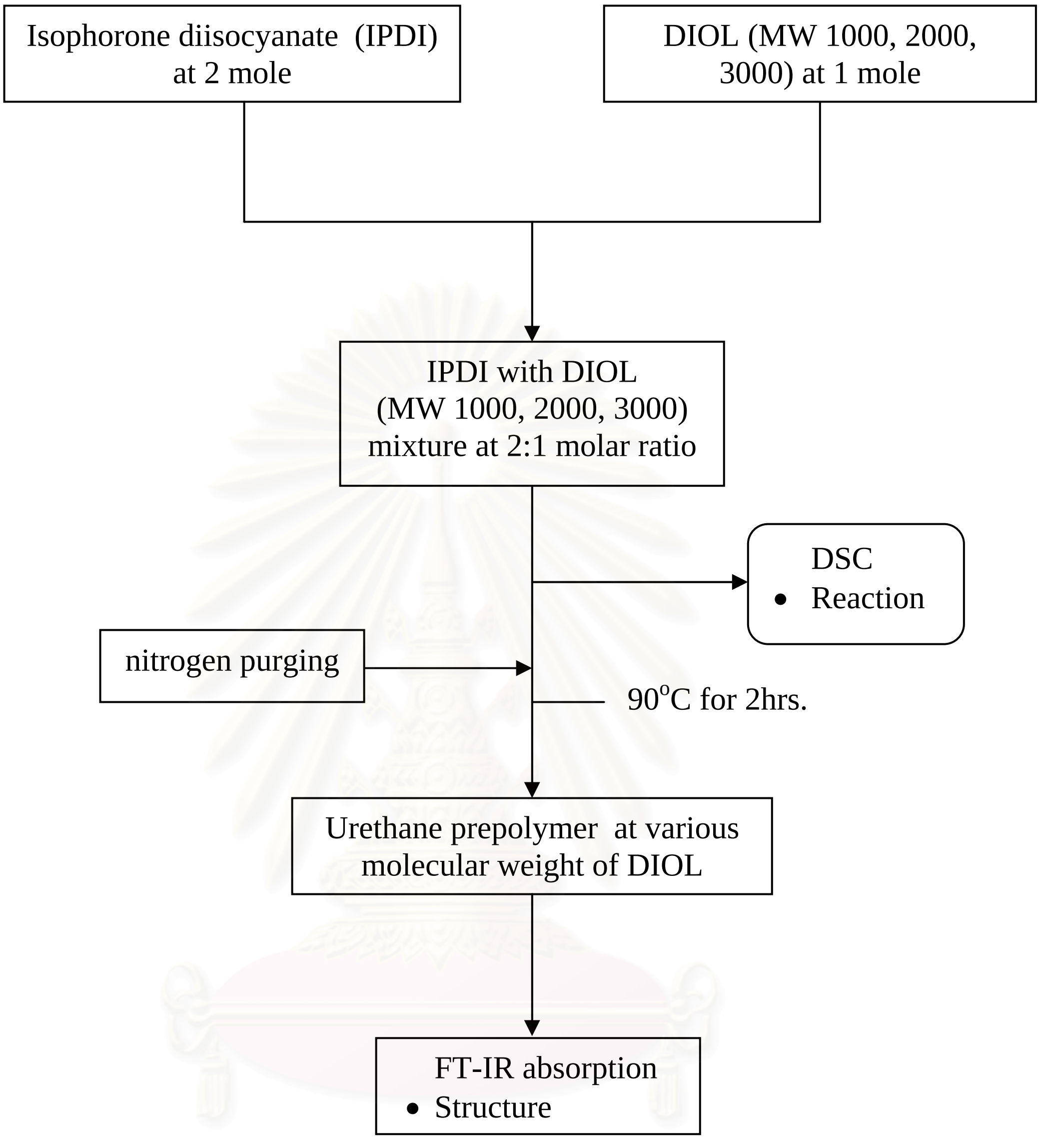


**Figure 4.1** The schematic diagram of preparation of urethane prepolymers.

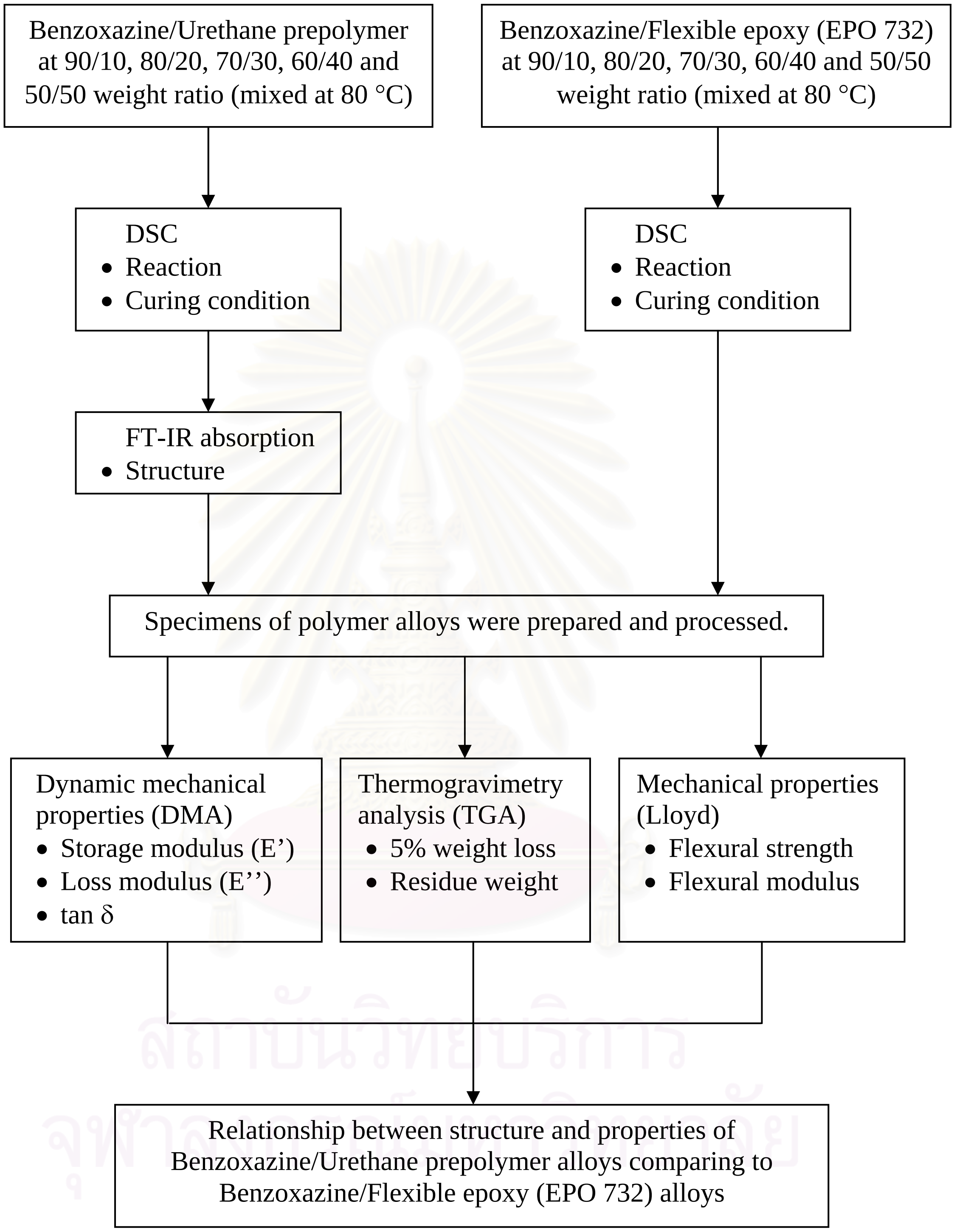


**Figure 4.2** The schematic diagram of experimental works on Benzoxazine/Urethane prepolymer and Benzoxazine/Flexible epoxy (EPO 732).

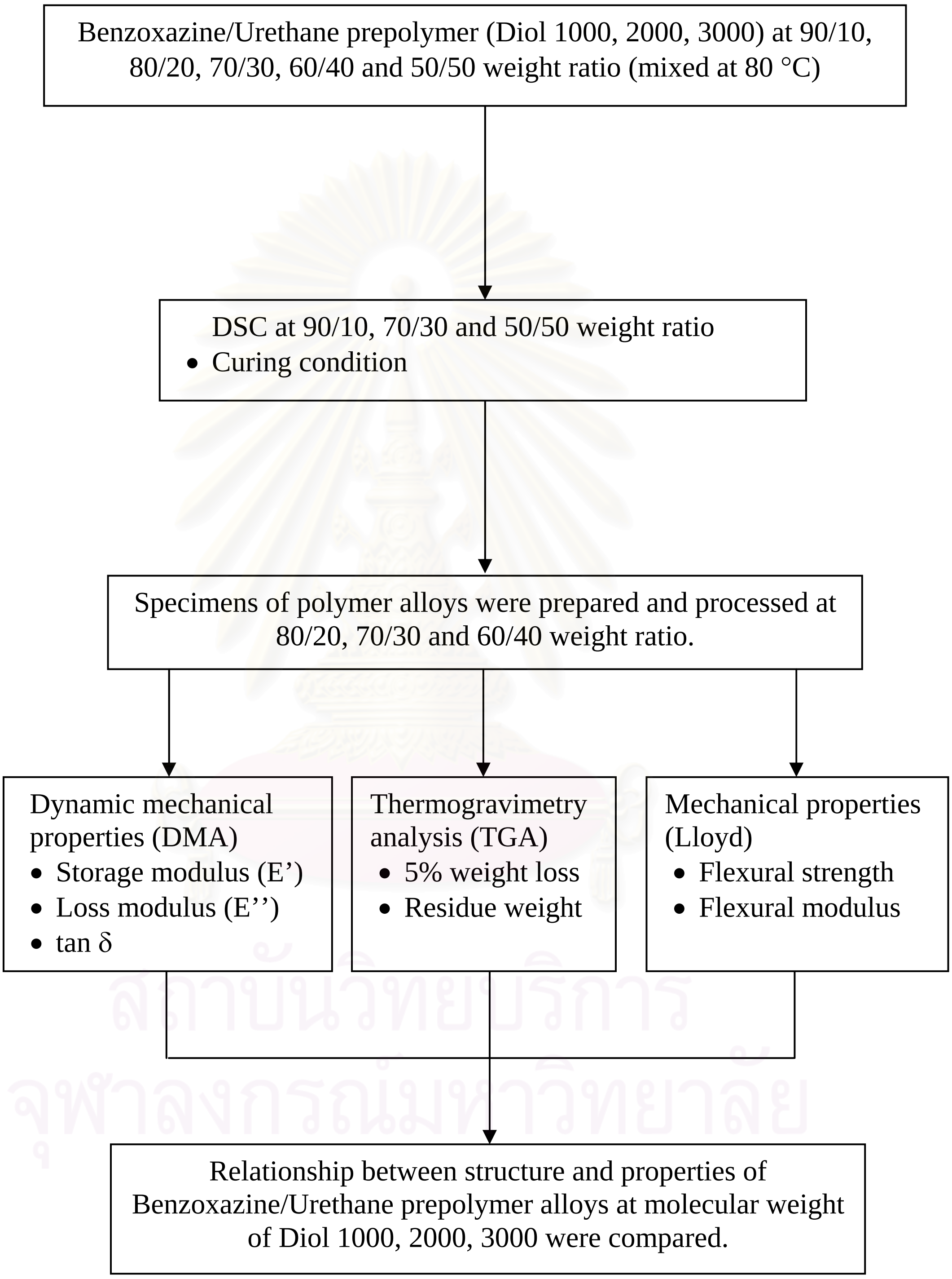


**Figure 4.3** The schematic diagram of experimental works on the effect of Diol on the properties of Benzoxazine/Urethane prepolymer alloys.

# CHAPTER 5

# RESULTS AND DISCUSSION

## 5.1 Benzoxazine/Urethane prepopymers and Benzoxazine/flexible epoxy

### 5.1.1 FT-IR Spectroscopy

In this work, urethane (PU) prepolymer was synthesized by the reaction of polyether polyol (Diol-1000, 2000 and 3000) with isophorone diisocyanate (IPDI). The basic structures of PU prepolymer were studied by FT-IR spectroscopic technique. The important functional groups of PU prepolymer are N=C=O, C=O, $CH_2$ and $CH_3$ which were, then, used to characterize the presence of the polymer in the alloy system.

Figure 5.1 shows the FT-IR spectra taken from the mixture of IPDI and Diol at the molar ratio of 2:1 before and after their reaction to form urethane prepolymers. The N=C=O stretching absorption peak is usually located between 2280-2240 $cm^{-1}$. The peak observed at 2270 $cm^{-1}$ in our spectrum was, then, assigned to this N=C=O stretching of the urethane prepolymer.The carbonyl absorption (C=O) is usually located between 1730-1700 $cm^{-1}$ consisting of hydrogen-bonded urethane groups. Therefore, the peak observed at 1730 $cm^{-1}$ consisting in Figure 5.1 was assigned to the urethane carbonyl group. The appearance of C=O absorption in the urethane prepolymer indicating the reaction of the isocyanate group (IPDI) with the hydroxyl group of polyether polyol thus rendering the urethane’s carbonyl signal. It can be observed that the C=O peak clearly appeared at 1730 $cm^{-1}$ and the N=C=O peak at 2270 cm-$^{1}$ decreased due to the reaction with the polyol. The remaining N=C=O peaks are from the unreacted terminal N=C=O groups of the starting IPDI.

Several C-H stretching bonds are located between 3000-2800 $cm^{-1}$. The four peaks observed at 2972, 2931, 2898 and 2872 $cm^{-1}$ were assigned to the asymmetric

C-H stretching of $CH_3$, asymmetric C-H stretching of $CH_2$, symmetric C-H stretching of $CH_3$ and symmetric C-H stretching of $CH_2$, respectively.

The reaction between benzoxazine monomer (BA) and NCO terminated PU prepolymer was also monitored by FT-IR spectroscopy. Figure 5.2 shows an example of FT-IR spectra in the case of BA/PU (Diol 1000) at a fixed mass ratio of 70/30. The characteristic IR absorptions of BA were found at 942 and 1232 $cm^{-1}$ which were assigned to the C-O-C stretching mode and the tri-substituted benzene of the oxazine ring (Figure 5.2 a), respectively. As the curing process proceeded, an infinitely three dimension network was formed. According to the polymerization mechanism reported by Dunkers and Ishida [30], the oxazine ring is opened by the breakage of a C-O bond of the oxazine ring. Then the benzoxazine molecule transformed from a ring structure to a network structure. During this process, the tri-substituted benzene ring, backbone of benzoxazine ring, became tetra-substituted benzene ring. It led to the formation of a phenolic Mannich base polybenzoxazine (PBA) structure. These absorptions disappeared after the thermal treatment at 150 °C for 5 hours followed by 180 °C for 4 hours (Figure 5.2 b). In addition, a broad intensive IR absorption band appeared at 3498 $cm^{-1}$ was assigned to the phenolic hydroxyl group. These indicate that benzoxazine monomer thermally polymerized through its ring opening reaction to give PBA. It was evidently confirmed by FT-IR that the blend of BA and PU prepolymer (Figure 5.2 c) contained both benzoxazine resin and urethane prepolymer characteristic absorptions, such as those at 942 and 1232 $cm^{-1}$ from benzoxazine species and that of 2281 $cm^{-1}$ from NCO group of PU prepolymer. After being fully cured, the absorption at 942 $cm^{-1}$ (C-O-C bond) shifted to 957 $cm^{-1}$ and the absorption at 2281 $cm^{-1}$ (NCO group) disappeared (Figure 5.2 d). These results are in good agreement with the previous report by T. Takeichi, et. al.[3,4]

### 5.1.2 Differential Scanning Calorimetry (DSC)

The DSC thermograms of the mixtures between IPDI and Diol 1000, 2000 and 3000 are shown in Figure 5.3. The experiment was conducted from room temperature up to 160 °C using the heating rate of 10 °C/min. The area of the exothermic peak of IPDI/Diol 1000> IPDI/Diol 2000> IPDI/Diol 3000 because the number of reacting functional groups in IPDI/Diol 1000 was the highest and that of IPDI/Diol 3000 was the lowest comparing at the same mass ratio. In addition, we can observe that the reaction between IPDI and Diol can occur at relatively low temperature. The maximum temperature of the exothermic peak of IPDI/Diol 1000, IPDI/Diol 2000 and IPDI/Diol 3000 were 91, 93, 93°C, respectively. Therefore, the IPDI/Diol prepolymers were all synthesized at $90^{o}$C according to the obtained results from the DSC thermograms.

Figure. 5.4 shows the DSC thermograms in the temperature range of 30-300 °C using the heating rate of 10 °C/min of the benzoxazine monomer, the flexible epoxy (EPO 732), and the urethane prepolymer. The thermograms show the curing exotherm of the benzoxazine monomer with a peak maximum at about 225 °C, which is the characteristics of the thermal curability of this resin [10]. On the contrary, the flexible epoxy and urethane prepolymer show no sign of a curing reaction in this temperature range because no initiators or catalysts were added. In the last two systems, we, however, observed the endotherm curves at about 250 and 265 °C as a result of evaporation of the flexible epoxy and urethane prepolymer, respectively.

The DSC results of the benzoxazine monomer, benzoxazine monomer with urethane prepolymer (Diol 2000) and benzoxazine monomer with flexible epoxy (EPO 732) are shown in Figure 5.5. The thermograms were obtained by conducting the experiment in the temperature range of 30-300 °C using the heating rate of 2 °C/min. The low heating rate was selected in order to separate as much as possible the thermal events in the systems. The composition of benzoxazine in the mixture was fixed at 70 wt%. In the BA/PU (Diol 2000) system, we can observe the single exothermic peak of the curing reaction suggesting that the reaction of BA with BA itself and BA with PU to form the network structure took place simultaneously at the same temperature range. On the other hand, the system of BA and EPO 732 showed the slight splitting of the curing peak at the temperature of 190 °C. The curing behavior of benzoxazine and epoxy binary mixture was reported previously by Rimdusit and Ishida as two separate reactions. The reaction of BA with BA was observed to occur at lower temperature than the reaction of BA with epoxy resin due to the diluent effect from the presence of epoxy resin [25].

Figure 5.6 illustrates the DSC thermograms of benzoxazine/urethane prepolymer (Diol 2000)-70/30 at various curing conditions. The heat of reaction determined from the area under the peak is 178.3 J/g for the uncured mixture, and decreased gradually to 140.3 J/g after heat treatment at 150 $^{o}$C for 1h., the reaction enthalpy is reduced to 124.9 J/g, 55.45 J/g, 24.82 J/g after being further cured at 170 $^{o}$C for 1h., 190 $^{o}$C for 1h., 200 $^{o}$C for 1h, respectively. After the final heat treatment at 200$^{o}$C for 2h., the exothermic heat of reaction was as low as 13.38 J/g corresponding to approximately 92.5% conversion. The slight shift of the curing peak with increasing reaction conversion was also observed. The phenomenon is similar to the curing reaction of benzoxazine and epoxy reported previously [25]. The behavior might be due to the diffusion controlled mechanism after gelation of the resin mixtures.

Figure 5.7 shows the DSC thermogram of benzoxazine-urethane prepolymer (Diol 2000) alloys using the heating rate of 10 $^{o}$C/min at the temperature range of 30-300 $^{o}$C. The resin mixture compositions of BA/PU were 50/50, 70/30 and 90/10 mass ratios, respectively. The revelations of their corresponding curing exotherms are clearly presented, i.e. 230$^{o}$C, 243$^{o}$C and 250$^{o}$C in 90/10, 70/30 and 50/50 mass ratio of BA/PU polymer alloys, respectively. From Figure 5.7, we can evidently see that the curing reaction of these binary systems can proceed without the need of a catalyst or a curing agent for the polymerization process. The reaction between the isocyanate group on urethane prepolymer with phenolic hydroxyl group on polybenzoxazine is expected to proceed after the phenolic hydroxyl group from the ring opening of the benzoxzine monomer was produced. The position of the peak maxima ranges from about 230$^{o}$C in BA/PU(Diol 2000)-90/10 to about 250 $^{o}$C in BA/PU(Diol 2000)-50/50. Hence, the retardation of the curing reaction of the benzoxazine resin is observed as a result of the presence of the urethane prepolymer. This can be explained as the effect of dilution of the benzoxazine monomers with the urethane prepolymer. After the generation of hydroxyl group by the ring opening of the benzoxazine monomers occurred, the isocyanate of urethane prepolymer can, then, react with the hydroxyl group of the polybenzoxazine. The curing retardation effect was more pronounced with increasing the amount of urethane prepolymer (Diol 2000). The thermogram also showed the decrease of the area under the curves when the amount of benzoxazine monomer decreased. These can be attributed to the changes in the number of mole and the functional groups of each component in polymer alloys At the same mass, the number of molecules of urethane prepolymers were lower than the number of molecules of benzoxazine monomers. In addition, a benzoxazine monomer is tetrafunctional while difunctional urethane prepolymer can only react with two hydroxyl groups of the polybenzoxazine. Thus, we can observe the decreasing of the heat of reaction with decreasing benzoxazine monomers in the binary mixture. This result is in good agreement with those reported in Refs. 3 and 4.

Table 5.1 summarizes the curing characteristics from DSC experiments of benzoxazine/urethane prepolymer alloys at different mass ratios and curing temperatures. After curing at 170 °C for 1h., the peak area decreased by ca. 20-30% and almost more than 90% of the peak area after further curing at 200 °C for 2 h. The final curing condition for the formation of benzoxazine/urethane prepolymer alloys was, therefore, 200 °C for 2h. The maximum peak shifted to the higher temperature when the mass fraction of urethane prepolymer increased as mentioned earlier. The degree of conversion of all samples was determined according to the following relationship:

$$\%\text{conversion} = \left[1 - \frac{H_{rxn}}{H_0}\right] \times 100 \tag{5.1}$$

where $H_{rxn}$ is the heat of reaction of the partially cured specimens, as determined from DSC results, and $H_o$ is the heat of reaction of the uncured resin. The conversion indicated that the curing reaction of polymer alloys could rapidly occur at high temperature.

Figure 5.8 illustrate the curing characteristics of benzoxazine/flexible epoxy (EPO 732) at a 70/30 mass ratio. Two major characteristics were observed from the figure. Firstly, the exothermic peak position was found to be approximately the same as that of the BA/PU alloys comparing at the same mass ratio. Secondly, the sign of degradation peak at the temperature above 260°C was also observed. Due to the overlap of the exothermic curing peak with the degradation event from the presence of epoxy (EPO 732) fraction, the heat fraction and the corresponding degree of conversion of these binary mixtures cannot be determined directly from the thermograms. The optimal curing conditions of the benzoxazine/epoxy alloys were determined under varied curing temperatures. The exothermic peak of the alloys almost disappeared after prolonged curing at 200°C for 1h.

Figure 5.9 is the DSC thermogram at various compositions of benzoxazine-flexible epoxy (EPO 732) alloys using the heating rate of 10 °C/min in the temperature range of 30-300 °C. The polymer alloys still maintain their self-polymerizability upon heating of the benzoxazine fraction and need no catalyst or curing agent for the polymerization to proceed [5, 7, 8]. The thermogram showed the decreasing of the area under the curing peaks when the amount of benzoxazine monomer decreased. The retardation of the curing reaction of polybenzoxazine was, however, observed which could be seen from the shift of the exothermic peaks to higher temperature, i.e. 230°C in the 90/10, 240°C in the 70/30, and 248°C in the 50/50 BA/EPO 732 alloys. The retardation effect of the epoxy diluent clearly increases with increasing the amount of the flexible epoxy (EPO 732). The exothermic peak at about 260 °C is assigned to the degradation of flexible epoxy, EPO 732.

### 5.1.3 Dynamic mechanical analyzer (DMA)

The dynamic mechanical properties of BA/PU (Diol 2000) alloys are shown in Figures 5.10-5.12. The specimen’s compositions are ranging from 0-50% by weight of PU fraction. All samples had been fully cured to yield the crosslinked structures. The dynamic mechanical properties of the polymer alloys were obtained as a function of temperature from room temperature up to 300 °C based on a heating rate of 2 °C/min.

The thermal events in polymers can be described in terms of free volume. The changes of free volume can be monitored as molecular changes or physical changes, such as a volumetric change, internal movement of polymer molecules by the heat adsorption or heat emission during that change, the decrease of stiffness and the increase of mobility by a change in relaxation time.[31] The storage modulus of a solid polymer at its glassy state tends to decrease with increasing the PU fraction in the alloys as a result of the more flexible characteristics of the elastomeric PU used (Figure 5.10). The urethane prepolymer molecule contains a large number ether linkage in which the internal movement of molecule is very high comparing with the rigid phenolic structure of the polybenzoxazine [5]. The storage modulus of the polymer alloys also decreased with increasing temperature. The glass transition temperature was ranging from –70$^{o}$C to -20 $^{o}$C for urethane elastomer and 170 $^{o}$C for bisphenol A/aniline based polybenzoxazine [3-5, 30]. Moreover, the decreasing rate of the alloy’s modulus slightly increased when the PU fraction in the alloys increased because of the greater mobility at the coreresponding temperature compared to the polybenzoxazine used. In the other words, the thermal stability of polybenzoxazine is greater than that of the PU elastomer. In addition, the modulus in the rubbery plateau tended to increase with the mass fraction of PU up to 30 wt% and decreased after that. This suggests that the increase in the PU content of the polymer alloys results in a higher crosslinked density. In the other words, the presence of PU systems in the alloys facilitates the softening and make the materials more flexible as seen from the decrease of the room temperature modulus while the crosslinked density was enhanced as seen from the greater rubbery plateau modulus.

The loss moduli as a function of PU contents are shown in Figure 5.11. In this case, the Tg of each polymer alloy composition was defined using the maximum of the loss modulus. The glass transition temperatures of polyurethane elastomer and bisphenol A/aniline based polybenzoxazine were reported to be about –70$^{o}$C to -20 $^{o}$C and 165 $^{o}$C, respectively. This showed the synergy of the system mentioned as Tg increased with the mass fraction of PU up to 30 wt%. We also observed a broader glass transition temperature when the amount of PU increased as clearly depicted in Figure 5.11. These results show the various network homogeneity in polymer alloys. We can see the decreasing peak of loss modulus when PU mass fraction increased. In

50% mass fraction of PU in alloy, no peak maxima in loss modulus or a sign of Tg was detected within the examined temperature range, i.e. Tg might be greater than the degradation of the alloys.

In various cases, the properties of multicomponent systems can be related linearly with the composition of each component, i.e. following the rule of mixture. The property value of polymer alloys located between the properties values of each homopolymer. However, the properties of polymer alloys are better than those of homopolymer in some cases depending on the morphology after the polymerization reaction [5, 6, 25]. Morphological features have been the central issue in the study of the multicomponent system because their domain sizes, shapes, and interfacial bonding characteristics determine the mechanical or thermal properties. A proper understanding of these features often allows one to develop synergistic behavior [26].

All transition temperatures were determined with DMA under the same test conditions. Because synergistic behavior was observed in the BA/PU alloys system. Two main factors, crosslink density and molecular rigidity are believed to contribute to the synergistic behavior of our BA/PU systems, and the source of the behavior should come from the contribution of both benzoxazine and urethane prepolymer. The degree of crosslinking of these binary system is directly proportional to the rubbery plateau moduli in the dynamic mechanical spectra. In our case, the maximum detectable glass transition temperature i.e. 30 wt% urethane prepolymer in polymer alloy reached 220°C. This can be explained by the reduction of free volume, the effect of permanent chain entanglement [26] and the increase of crosslink density.

However, it has also been reported that polybenzoxazine possesses a lower crosslinking density and has greater Tg value than that of urethane prepolymer used [25]. This may be due to the more rigid molecular structure and possible much higher intramolecular and intermolecular forces on polybenzoxazine compared with the epoxy and can be seen from the moduli of the binary systems at room temperature that increase with an increasing amount of the benzoxazine fraction in the systems. As mentioned previously, room temperature moduli increase with an increasing urethane prepolymer fraction of binary systems. The greater molecular rigidity of benzoxazine resin and the higher crosslinking density of urethane prepolymer, therefore, render synergistic behavior in the Tg in this material with the Tg maxima, as shown in Figure 5.11.

When the benzoxazine monomer and urethane prepolymer were well mixed and the thermally cured process proceeded to form the network of BA/PU alloys. After the isocyanate groups of urethane prepolymer molecules reacted with the hydroxyl groups of benzoxazine molecules [3, 4]. There was also the connection between polybenzoxazine and urethane prepolymer. The increasing in crosslink density of polymer alloys as observed from DMA thermograms. This result shows the urethane prepolymer increased the crosslink density in polymer alloys. On the contrary, the usage of urethane prepolymer based toluene diisocyanate and polyethyleneadipate polyol (MW 1000) as the precursor with benzoxazine monomer resulted in the decreasing of Tg as reported by T. Takeichi, et. al [3, 4]. This was because the molecules of this precursor, which are small, could not reduce the free volume and bring the permanent chain entanglement. The effect of a crosslink density on a Tg of the polymer network can be accounted for using Fox and Loshaek equation [10]:

$$Tg = Tg(\infty) - \frac{k}{M_n} + k_x\rho \qquad (5.2)$$

where $Tg(\infty)$ is the Tg of infinite molecular weight linear polymer, $k$ and $k_x$ are the numerical constants, $M_n$ is the averaged molecular weight and ρ is the crosslink density. From the equation, the higher the crosslink density is, the greater the Tg of the polymer is, which is in good agreement with the experimental results. In addition, the increase of PU composition showed the broadening of Tg, which can be attributed to the more heterogeneity in the alloy’s network due to the presence of the PU fraction.

Tan δ curves, obtained from the ratio of energy loss (G”) to storage energy (G’) in sinusoidal deformation, are shown in Figure 5.12. The magnitude of the tan δ peak maximum reflects the large scale mobility associated with alpha relaxation while the width of the tan δ relates to the network homogeneity, i.e. more elastic with increasing the amount of PU fraction in the binary mixture [5, 6]. Figure 5.12 shows the tan δ of the BA/PU at various compositions. The peak height of the tan δ was found to decrease with increasing the mass fraction of the PU while the peak maximum shifted to higher temperature. This confirmed the reduction in segmental mobility chain with increasing crosslinked density as PU fraction in the alloy increases [5, 6]. The width at half height of tan δ curves were broader in the PU rich systems, which implies the network heterogeneity in polymer alloys [5,6]. However, the transparency and the single peak of tan δ of each alloy confirmed the single microscopic domain of these alloys, i.e. no sign of phase separation. As a consequence, our binary mixtures between BA/PU show a synergistic behavior in their glass transition temperature. The behavior was also observed previously by Rimdusit and Ishida in BA/EPOXY systems [25].

Figures 5.13 to 5.15 show the reproduced results of the DMA thermogram in the temperature range of 60 to 350$^{o}$C at the heating rate of 2 $^{o}$C/min. The dynamic mechanical analyzer model GABO EPLEXER from Mahidol University was used to recheck the BA/PU (Diol 2000) alloys in the composition range of 20-40 wt% of urethane prepolymer. When urethane prepolymer (Diol 2000) increased, the storage modulus (G’) of polymer alloys decreased. The increment of the crosslink density and glass transition temperature was also observed in storage modulus (G’) and loss modulus (G”), respectively. At the temperature about 330$^{o}$C, we had observed the second peak, which may be due to thermal degradation of the polymer alloys as noticeable smell of the degradation products as well as the large drop in the specimens modulus were evident at this point.

Figures 5.16 to 5.18 illustrate the DMA thermograms of the polymer alloys between BA and EPO 732 in the composition range of 10-50 wt%. The specimens were also optically transparent and void-free due to the low viscosity epoxy used. Samples containing various amount of epoxy were investigated for their dynamic mechanical properties in the temperature range of 30-300 $^{O}$C at heating rate of 2$^{O}$C/min. From Figure 5.16, the effect of incorporating epoxy resin into polybenzoxazine was seen as to systematically enhance the room temperature modulus of the resulting alloys up to 20 wt% and then the modulus was decreased with the amount of epoxy.

The glass transition temperature of polymer alloys composition was detected in the mechanical spectrum as the maximum of loss modulus (G”). The DMA spectra show the decreasing of Tg with the amount of the epoxy. The highest Tg of polymer alloy, 162$^{o}$C, was observed in the specimen containing 10 wt.% epoxy. Figure 5.17 shows that the maximums of loss modulus shift to the lower temperature with benzoxazine mass fraction decreased. From Fox and Loshaek equation [10], the lower the crosslink density is, the lower the Tg of the polymer, which is in good agreement with the experiment results.

Loss tangent, tan$\delta$, of the BA/EPO 732 is shown in Figure 5.18. The peak height of the tan $\delta$ decreases with increase mass fraction of the epoxy resin which means the elastic of alloys increase with the amount of epoxy and the maximum shifts to lower temperature indicating the increasing of glass transition temperature with benzoxazine. We also observed a broader of the width at half height of tan $\delta$ when the amount of EPO 732 increased. Comparing with the BA/PU alloys, the BA/EPO 732 alloys show the lower broaden than BA/PU alloys indicating the network homogeneity of BA/PU is lower. On the contrary, the width at half height of tan $\delta$ of benzoxazine/epoxy (DGEBA-based) shows nearly constant at all alloy compositions and implies that the distribution of the network homogeneity does not change [5]. Epoxy (DGEBA-based) contains benzene ring while flexible epoxy (EPO 732) contains ether linkage. This showed that the epoxy (DGEBA-based) have higher similarity structure to benzoxazine structure than flexible epoxy (EPO 732).

Ishida, et al. [5, 6, 10] investigated the thermomechanical properties of benzoxazine/epoxy (DGEBA-based) alloys and observed the enhancement in the Tg of the alloys. They found that the glass transition temperature increased with the amount of epoxy up to 30 wt%. This contrasted to our benzoxazine-flexible epoxy systems and may be due to the enhancement of free volume in the obtained alloy network from the poorer packing flexible epoxy used. Epoxy (DGEBA-based) contains benzene ring, which can reduce free volume more than the linear, multiple ether linkage of the flexible epoxy.

### 5.1.4 Mechanical properties (Lloyd)

The effects of urethane prepolymer (PU Diol 2000) and flexible epoxy (EPO 732) on mechanical properties of their polymer alloys are illustrated in Figure 5.19 and 5.20, respectively. The specimens for flexural analysis were loaded until failure. Both flexural stress and strain at break could be measured for the BA/EPO and BA/PU alloys series. Flexural strength and strain represents the ability of material to absorb maximum force at rupture. This ability concerns with storing and dissipating forces in polymers in the form of movement, rotation and vibration of molecule, which is transformed to heat, deformation or sound, etc.

As seen in Figure 5.19, the flexural strength of BA/PU (Diol 2000) at 90/10 and 80/20 weight ratio increased when compared with polybenzoxazine homopolymer. The flexural strength decreased when the amount of PU was higher than 20 wt%. The flexural modulus of BA/PU (Diol 2000) decreased with the increasing mass fraction of PU. Figure 5.20 shows the flexural stress and strain of BA/EPO 732. The flexural strength and modulus gradually increased until the composition of EPO 732 was 30%. The flexible molecules (urethane prepolymer and EPO 732) enhanced the flexural strength and flexural strain by inhibition of crack growth, absorbing and dissipating force in polymer alloys. The results reveal that, within the 10 wt% of PU and 30 wt% of EPO 732 content studied was sufficient to improve flexural strength.

Figures 5.21 and 5.22 show the flexural strength and flexural modulus of polymer alloys of BA/PU and BA/EPO 732, respectively. The flexural strength values of BA/PU are 120 MPa in 100/0, 140 MPa in 90/10, 120 MPa in 80/20, 85 MPa in 70/30, 60 MPa in 60/40, and 30 MPa in 50/50 and flexural strength values of EPO732 alloys are 170 MPa in 90/10, 180 MPa in 80/20, 212 MPa in 70/30, 165 MPa in 60/40, and not break in 50/50 under this condition. We also observed the strength of the alloys did not relate in the linear relationship with the composition of the alloys. This shows the optimum composition to improve the strength of the alloys indicating the rigid and brittle materials became the tough and ductile materials. There were a number of important factors that may be responsible for this phenomenon. The addition of PU and EPO 732 caused a greater percentage of the phenolic hydroxyl groups, which reacted with epoxide and isocyanate functional group of flexible epoxy and urethane prepolymer, respectively. This effect shows in the increasing of flexural strength and flexural strain in polymer alloys. Additionally, the increased percentage of urethane prepolymer and flexible epoxy compositions acted as a plasticizer in the polymer alloys. Thus, the additional of the more flexibility segments to the polybenzoxazine matrix in higher percentage must also contribute to the decrease in strength, modulus and the increase in strain. The phenomenon is as expected and was reported also by various authors [3,4]

### 5.1.5 Thermogravimetric analysis (TGA)

Figure 5.23 shows the TGA scans of benzoxazine resin, urethane prepolymer (Diol 2000), and flexible epoxy (EPO 732) at the heating rate of 20$^{o}$C/min under nitrogen purging. The TGA spectra show decomposition temperatures of each composition at 5 wt% loss of resin to be 320 $^{o}$C, 325 $^{o}$C and 255 $^{o}$C, respectively. Char yield of the benzoxazine polymer was 25 wt% which was in good agreement with the value reported by other [3, 27, 28]; however, there was no char residue of urethane prepolymer and flexible epoxy.

The degradation behavior of our polymer alloys are shown in Figures 5.24 and 5.25. The samples consisted of BA in the composition range of 10-50 wt%. All samples were fully cured to form the crosslinked structures. The thermal properties of the polymer alloys were obtained as a function of temperature, starting from room temperature to around 850 °C using heating rate of 20 °C/min. Normally, it is possible to predict sites of chemical attack in reactions such as hydrolysis in suitable polymers, from the examination of available functional groups, but it was much more difficult to predict general patterns of degradation due to the heat. It might be considered that a good starting point would be an examination of bond energies as a guide to which bonds would be first to break. However, the general features of particular importance in relation to degradation processes are amorphous or crystalline state, glass transition temperature, functional groups presence, and presence of tertiary hydrocarbon atoms [33]. The TGA thermograms of polybenzoxazines have been reported in many researches [27, 28]. Low and Ishida [27] studied the structural effect of phenols on the thermal and thermo-oxidative degradation of polybenzoxazines. They found that the degradation of phenolic linkage occurs simultaneously with the degradation of mannich base in bisphenol A/aniline based polybenzoxazine at around 330$^{o}$C.

Figure 5.24 shows the TGA thermograms of BA/PU at various compositions under nitrogen atmosphere. The materials have improved thermal stability when comparing with polybenzoxazine homopolymer. The decomposition temperatures at 5 wt% loss were approximately 340 $^{o}$C for all alloy compositions. This was due to the thermally weak chemical bond between BA and PU (Diol 2000) component [4]. These confirm the reaction of isocyanate of urethane prepolymer and hydroxyl of polybenzoxazine to increase the potentially weak moieties of phenolic linkage in polyenzoxazine structure. On the contrary, the char yield of the binary systems decreased significantly compared to the polybenzoxazine, i.e. the presence of polybenzoxazine improves the char yield of the alloys.

Figure 5.25 shows the TGA thermograms of BA/EPO732 at various compositions at a heating rate of 20 $^{o}$C under nitrogen flow. The decomposition temperatures at 5 wt% loss decreased with mass fraction of EPO 732. Furthermore, the char yield of the binary systems decreased significantly compared with the polybenzoxazine. These results indicated that polybenzoxazine can help improve the decomposition temperature and char yield of both polymer alloy system.

## 5.2 The effect of Diol molecular weight on properties of Benzoxazine/Urethane alloys

### 5.2.1 Differential Scanning Calorimetry (DSC)

Figure 5.26 to Figure 5.28 illustrates three different benzoxazine/urethane alloy at-70/30 mass ratio. From Figures 5.26-5.28, an exothermic peak due to the curing reaction of BA/PU binary system is clearly seen. The conversion of all BA/PU at various molecular weight of Diol are around 75% after heat treatment at 165 $^{o}$C for 5h., the conversion is increased to 95%, after cured at 165$^{o}$C for 5h + 180 $^{o}$C for 4h. The reason for choosing a rather low curing temperature, thus a prolonged curing time, was to allow enough time bubbles or voids to escape from the specimens.

Tables 5.2-5.4 summarize the results of DSC experiments at various molecular weight of urethane prepolymers. Similar DSC behaviors were observed for benzoxazine/urethane prepolymer alloys at other mass ratios using different molecular weight. The final curing condition for the full formation of benzoxazine/urethane polymer alloys in this case was, therefore, set at 165 $^{o}$C for 5h. + 180$^{o}$C for 4h.

### 5.2.2 Dynamic mechanical analyzer (DMA)

The dynamic mechanical properties of BA/PU alloys at three different molecular weights of Diol are shown in Figures 5.29-5.37. The specimens consisted of BA in the composition range of 60-80 wt%. The samples were fully cured to form highly crosslinked structures. From the DMA thermograms, the storage modulus of a solid sample in the glassy state tends to decrease when the mass fraction of PU increases (Figures 5.29, 5.30 and 5.31). The behavior was clearly explained as a result of toughening enhancement from the flexible PU used. We also observed the broadening of the glass transition temperature when the amount of PU increased. The various Diol molecular weights showed the effect on the rubbery plateau modulus and glass transition temperature enhancement. In the case of PU based on Diol 2000 and 3000, we also observed the increasing of modulus in the rubbery plateau of the BA/PU alloys with the mass fraction of PU signifying the increase in their corresponding crosslinked density. It was previously reported that increasing the PU content of the polymer alloys resulted in a higher crosslink density but lower glassy or room temperature modulus. Moreover, the glass transition temperatures tend to increas with the mass fraction of PU (Diol 2000 and 3000). However, the modulus in the rubbery plateau and the glass transition temperature of BA/PU (Diol 1000) showed an opposite trend, i.e. decreasing as the mass fraction of PU increases as shown in Figure 5.29.

From the DMA results, the enhancing behavior in the Tg of the alloys depended on the size or the molecular weight of urethane prepolymer. The resulting network morphology also may be different in BA/PU (Diol 1000) from the other two diol molecular weights in the alloys.The spectra of the loss modulus of BA/PU at diol molecular weight of 1000, 2000, and 3000 are shown in the respective order Figures 5.32, 5.33, and 5.34. The Tg of each polymer alloy composition was detected using the maximum of the loss modulus peak. The effect of diol fraction on the loss modulus alloy' Tg of BA/PU (Diol 1000) was found to be rather different from those of BA/PU (Diol 2000 and 3000), i.e. the glass transition temperature decreased with mass fraction of PU (Diol 1000) while these of PU (Diol 2000, and Diol 3000) tend to increase with the PU mass fraction. The effect of molecular weight is similar to that on the crosslinked density. In the other word, the glass transition temperatures of the three alloys are closely related to their crosslinked density.

In addition, Takeichi, et al. [3, 4] prepared urethane prepolymer /benzoxazine (based on monofunctional and bifunctional benzoxazine monomers). They used the urethane prepolymer based toluene diisocyanate (TDI) and polyethyleneadipate polyol (MW 1000) as the precursor with the benzoxazine monomers, resulting in the decrease of Tg with the mass fraction of urethane prepolymer. They results showed the similar trend comparing with our BA/PU (Diol 1000) alloys system.

From the Fox and Loshaek equation, the higher crosslink density of the alloy network is, the greater is the Tg of the polymer, which is in good agreement with our experimental results. Figures 5.36 and 5.37 show tan δ of BA/PU (Diol 2000 and 3000) at various compositions. The maximum of the tan δ decreases with increasing mass fraction of the PU and the maximum shifts to higher temperature. Since, the materials have higher crosslinked density, they are more elastic when the amount of PU is greater in the binary mixture. The observed of tan δ curves were broader with increasing the PU fraction. This may be ascribed by the broder distribution of the network structure. On contrary, Figure 5.35 shows tan δ of BA/PU (Diol 1000) at various compositions. Though maximum of tan δ decreases with increasing mass fraction of the PU, the peak maximum shifts to lower temperature, which is the trend already described in the previous section.

Figures 5.38-5.40 show the reproductive of DMA thermograms in the temperature range of 60 to 350 $^{o}$C using the heating rate of 2 $^{o}$C/min. The dynamic mechanical analyzer model GABO EPLEXER from Mahidol University was used to investigate the effect of the molecular weight of urethane prepolymer in BA/PU-70/30 alloys. The thermogram confirmed our previous tests i.e.when the molecular weight of urethane prepolymer increased, the storage modulus (G') of polymer alloys decreased. The increment of crosslinked density and glass transition temperature was observed in BA/PU (PU based Diol 2000, 3000). On the contrary, we observed the decrease of the rubbery plateau modulus and glass transition temperature of BA/PU (PU based Diol 1000) when compared at the same mass ratio. Further investigation on the effect of lower range of Diol molecular weight, i.e < 1000, would be significant in order to confirm this type of reversing in behaviors in Tg enhancement.

### 5.2.3 Mechanical properties (Lloyd)

Figures 5.41-5.43 show the flexural stress-strain curve of BA/PU series at various molecular weight of diol used. When the soft and elastic PU segments are added into a harder and more brittle polybenzoxazine the resulting stress-strain curve from the one which possesses the yield point, moved to a straight line. As the PU soft molecular segment is longer, the obtained strength and modulus decrease. In addition, the strength and strain decrease as the content of BA increases. The chain length of the PU's soft segment plays an important role in the flexural strength of the specimen. The shorter chain length possesses higher flexural strength and lower flexural strain compared at the same mass fraction. This is due to the fact that the lower molecular weight diol yielded BA/PU alloys with greater crosslinked density i.e. improved strength but less chain extension (lower elongation).

### 5.2.4 Thermogravimetric analysis (TGA)

Figures 5.44-5.46 show the TGA thermograms of BA/PU at various molecular weights of Diol (MW 1000, 2000 and 3000) under the scanning rate of 20 $^{o}$C under nitrogen flow. We can see that all alloys materials showed similar decomposition temperature at 5 wt% loss to be around 340 $^{o}$C. While the degradation temperature at 5 wt% loss of neat polybenzoxazine was reportd to be 325-330$^{o}$C [3,27]. This emphasizes the benefit of using this type of PU to enhance the degradation temperature of the polybenzoxazine though at a marginal level (15$^{o}$C). The char yield of BA/PU systems; however, increased significantly with the mass fraction of BA due to the prevalent benzene structure in the polymer alloys.

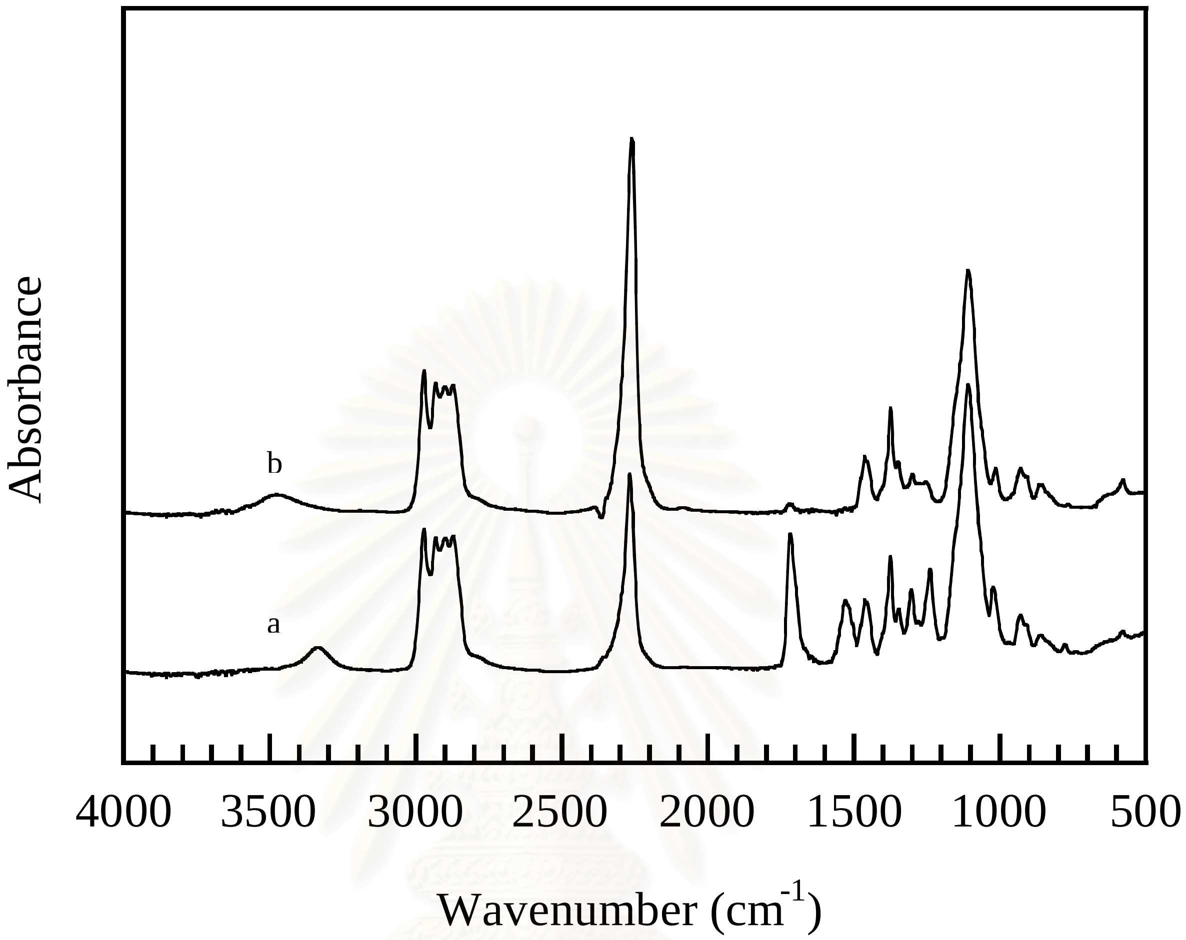


**Figure 5.1** FT-IR Spectra of Polyurethane Prepolymer a) IPDI+Diol (1000) before synthesis, b) IPDI+Diol (1000) after synthesis.

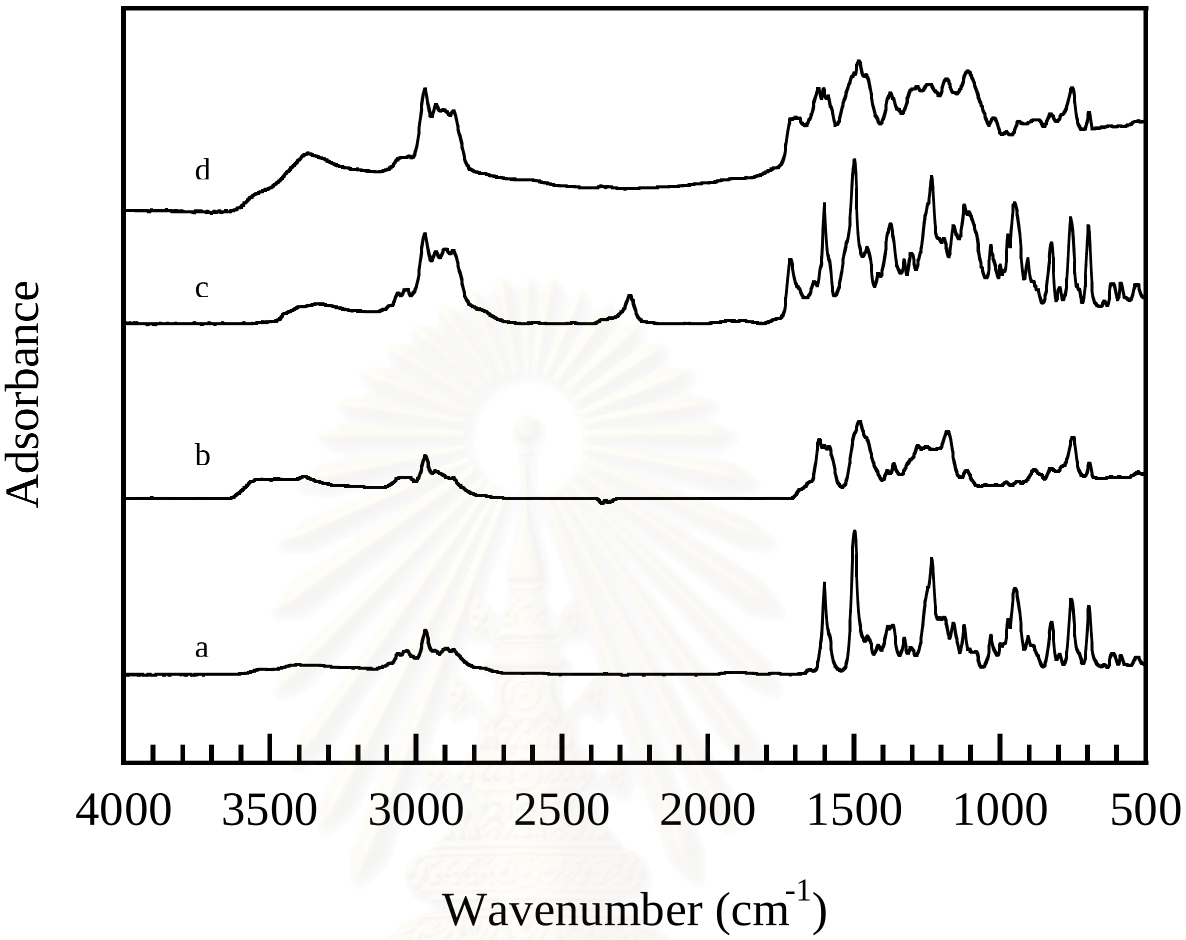


**Figure 5.2** FT-IR Spectra of compounds : (a) Benzoxazine monomer (BA), (b) Polybenzoxazine (PBA), (c) BA/PU (Diol 1000)-70/30 uncured, (d) BA/PU (Diol 1000)-70/30 fully cured.

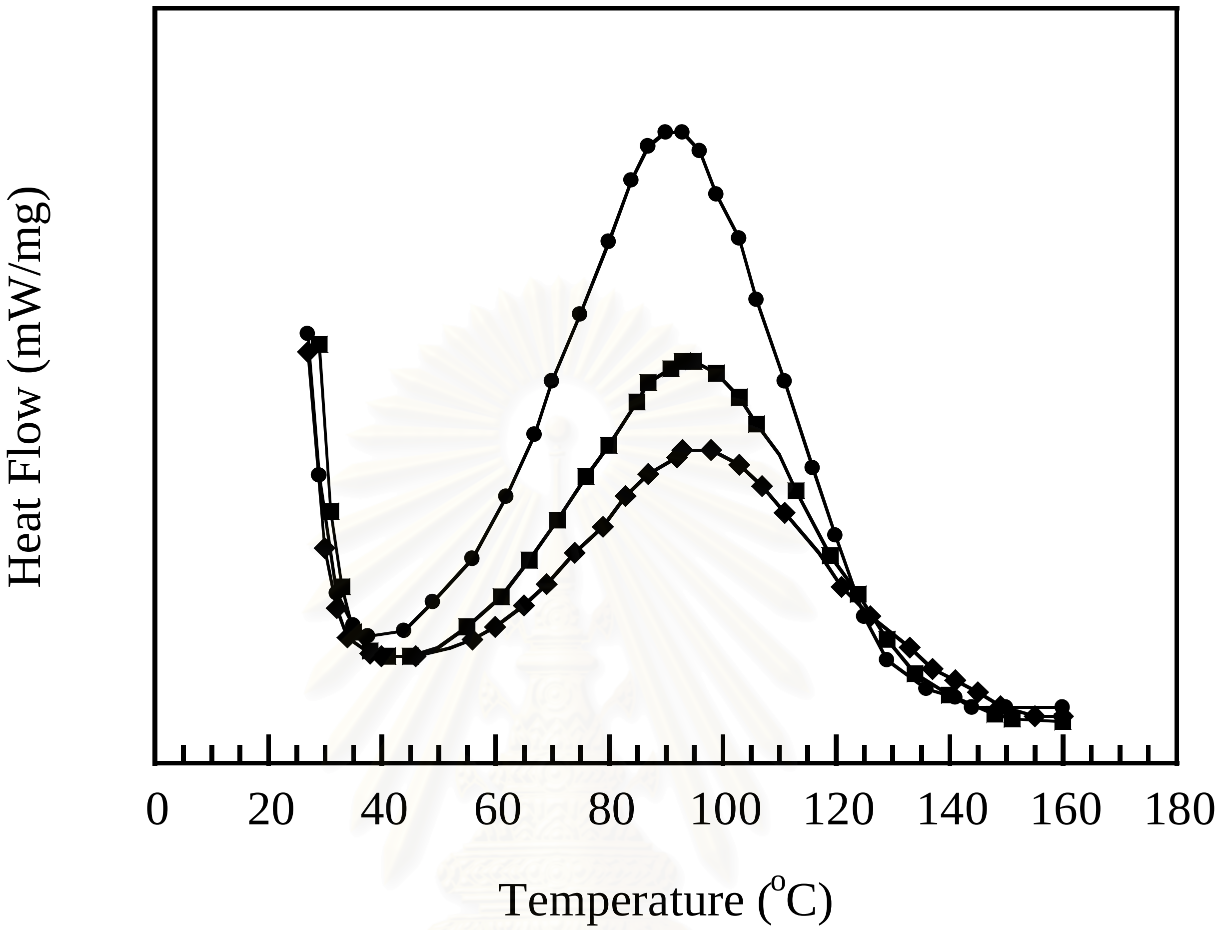


**Figure 5.3** DSC thermogram of Isophorone diisocyanate (IPDI)/Diol at 2:1 molar ratio: (●) IPDI/Diol (MW 1000), (■) IPDI/Diol (MW 2000), (◆) IPDI/Diol (MW 3000)

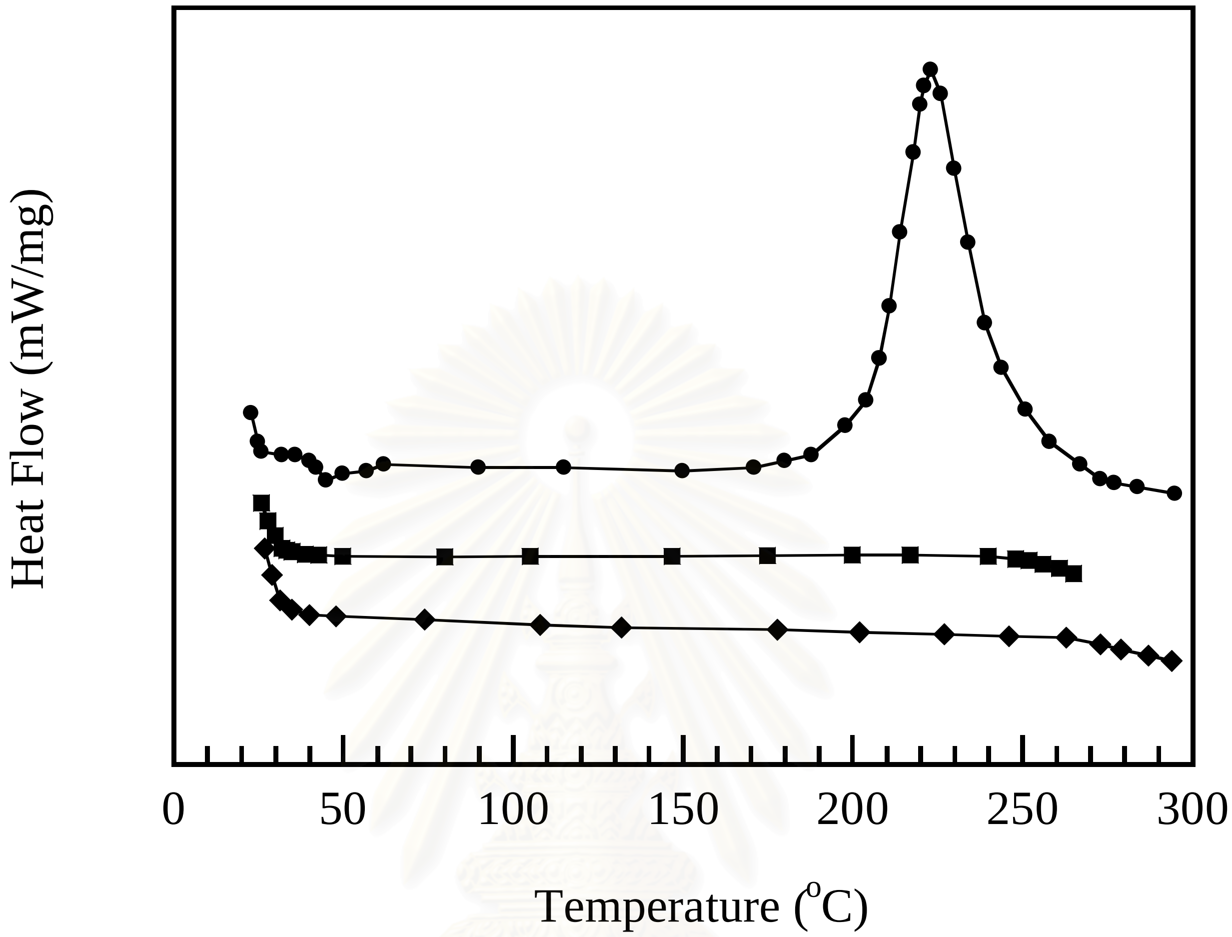


**Figure 5.4** DSC thermograms of three monomers: (●) benzoxazine monomer, (■) flexible epoxy (EPO 732), (◆) urethane prepolymer (PU)

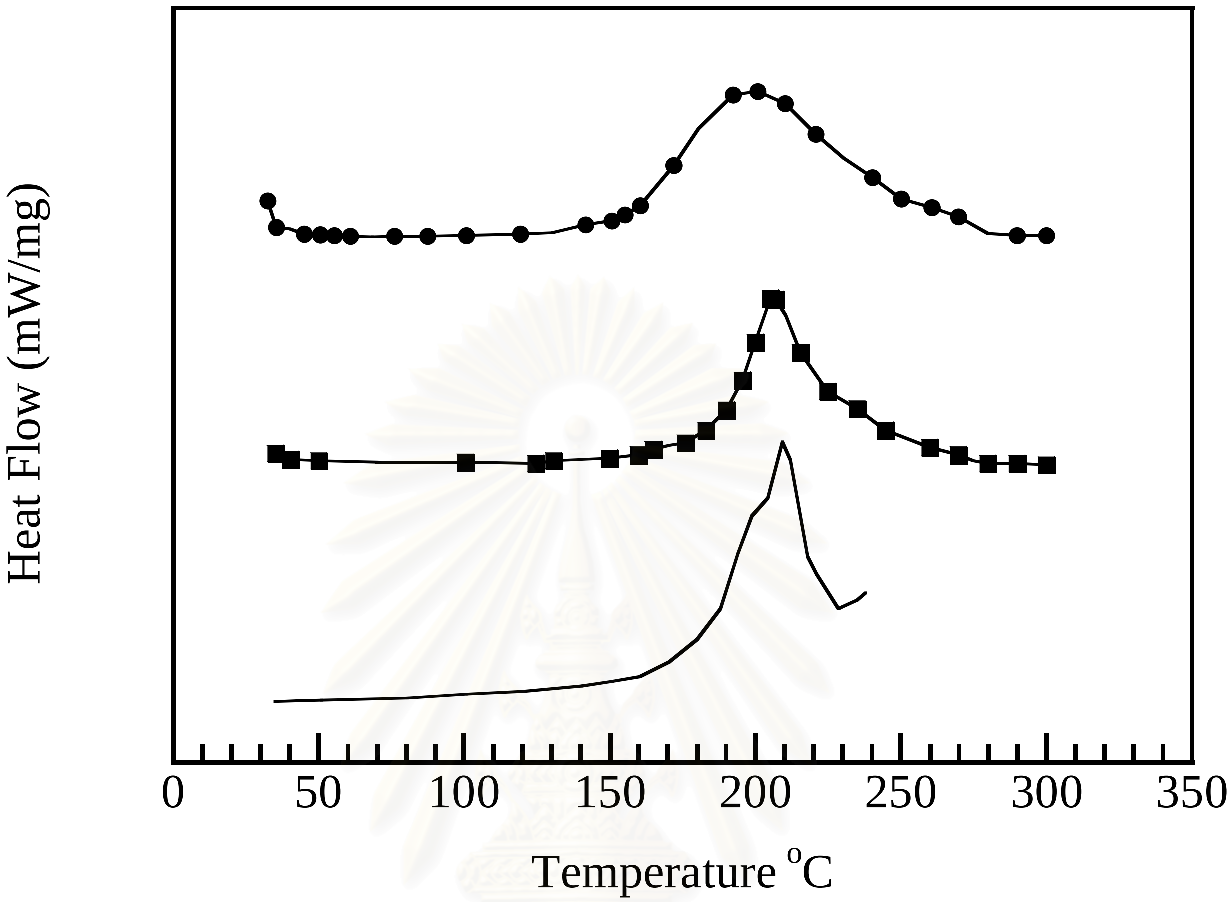


**Figure 5.5** DSC thermograms of binary systems at heating rate 2$^{o}$C/min:
(●) Benzoxazine monomer, (■) BA/PU (Diol 2000)-70/30, ( - ) BA/EPO (732)-70/30.

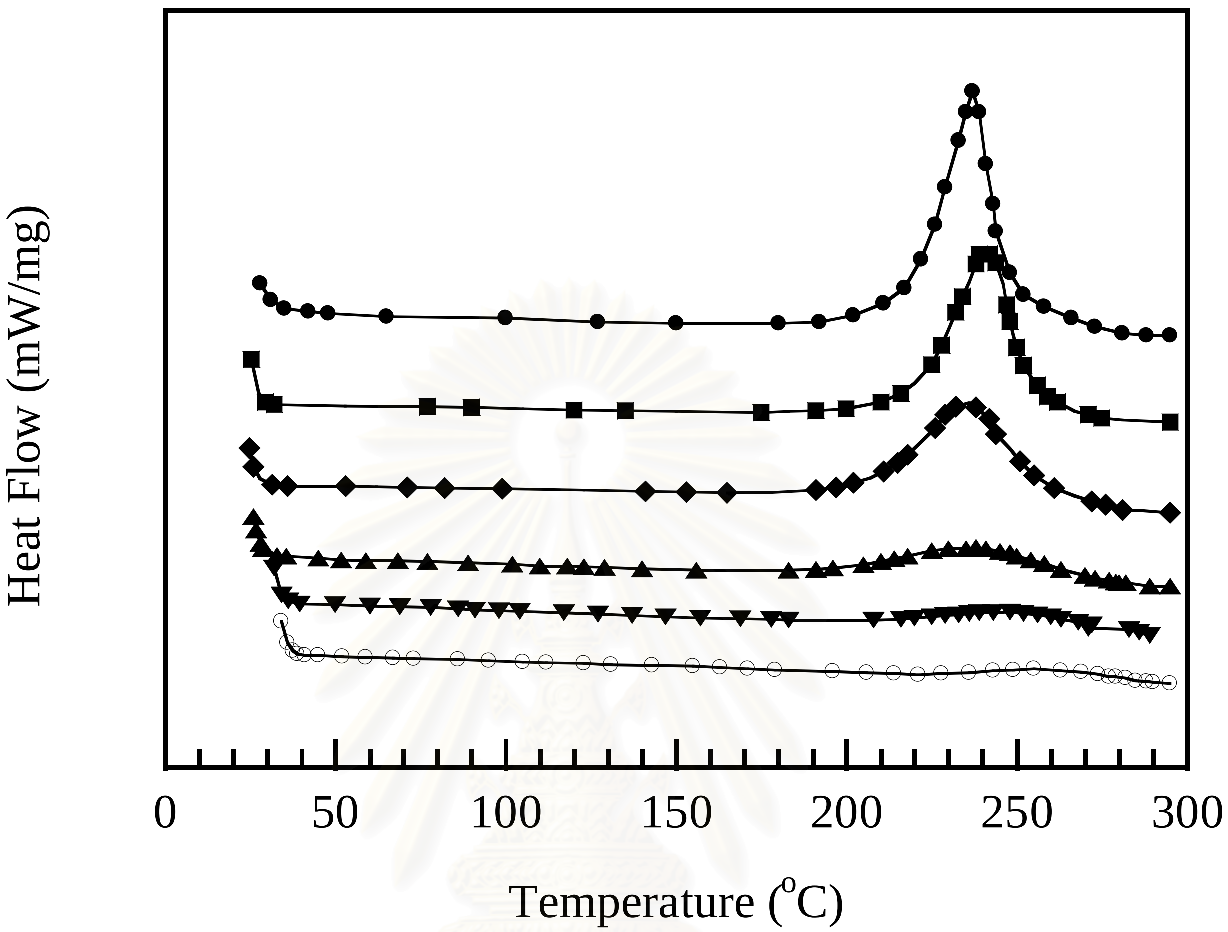


**Figure 5.6** DSC thermograms of BA/PU (Diol 2000)-70/30 at various curing conditions: (●) uncured, (■) 150°C/1h, (◆ ) 170°C/1h, (▲) 190°C/1h, (▼) 200°C/1h, (○) 200°C/2h.

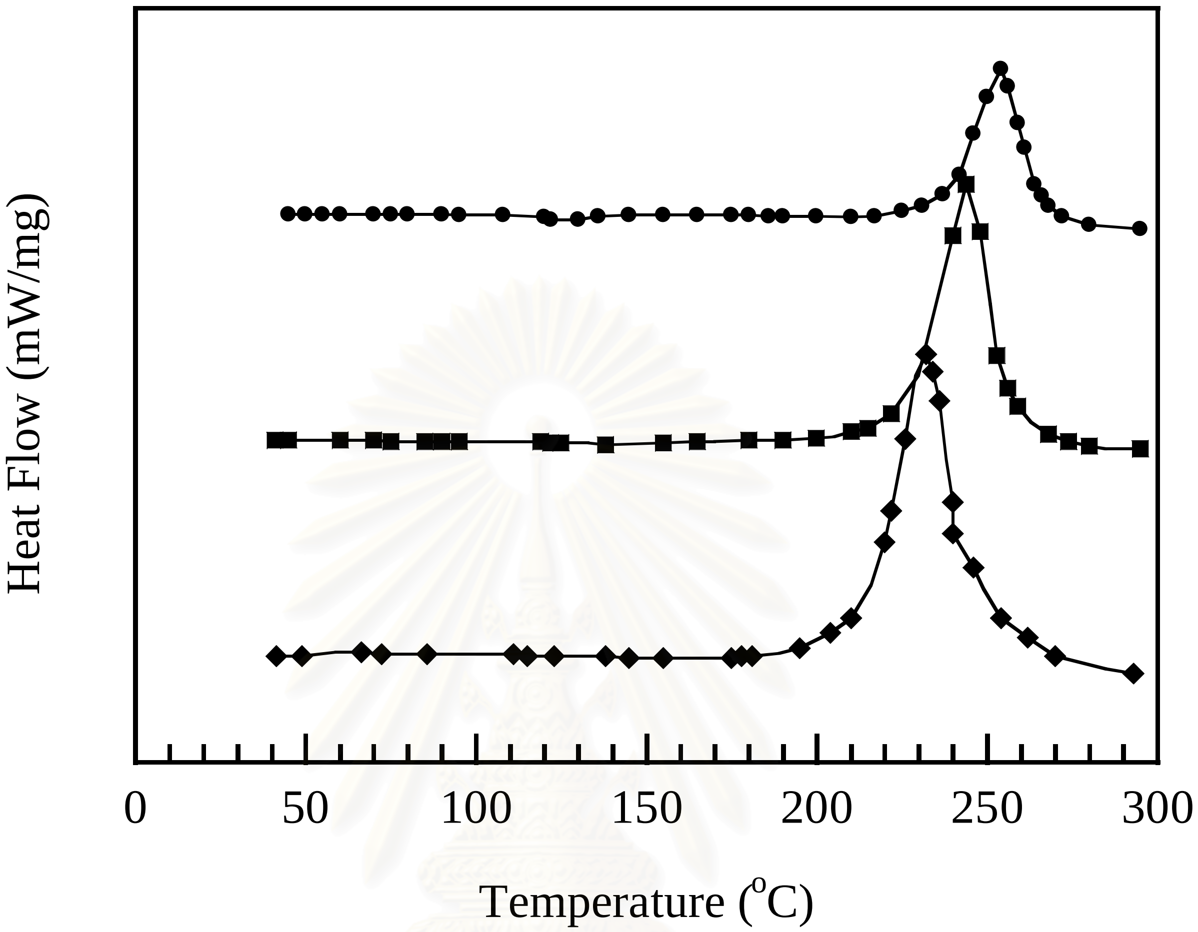


**Figure 5.7** DSC thermograms of BA/PU (Diol 2000) at various compositions: (●) 50/50, (■) 70/30, (◆) 90/10

**Table 5.1** DSC of BA/PU (Diol 2000)

| Sample Code | Curing Condition | Exothermic Peak | | |
|---|---|---|---|---|
| | | On Set Temperature (°C) | Peak Temperature (°C) | Conversion (%) |
| BA/PU (90/10) | Uncured | 150 | 229.05 | 0.00 |
| | 150 °C/1 hr | 160 | 228.23 | 8.56 |
| | 170 °C/1 hr | 160 | 229.77 | 24.34 |
| | 190 °C/1 hr | 180 | 239.69 | 67.88 |
| | 200 °C/1 hr | 195 | 247.82 | 85.84 |
| | 200 °C/2 hr | 195 | 254.52 | 91.75 |
| BA/PU (80/20) | Uncured | 160 | 232.90 | 0.00 |
| | 150 °C/1 hr | 160 | 235.98 | 15.66 |
| | 170 °C/1 hr | 160 | 230.90 | 33.16 |
| | 190 °C/1 hr | 175 | 240.14 | 69.76 |
| | 200 °C/1 hr | 200 | 249.95 | 86.54 |
| | 200 °C/2 hr | 210 | 254.61 | 91.7 |
| BA/PU (70/30) | Uncured | 175 | 237.84 | 0.00 |
| | 150 °C/1 hr | 175 | 241.58 | 21.31 |
| | 170 °C/1 hr | 175 | 236.00 | 29.95 |
| | 190 °C/1 hr | 175 | 238.45 | 68.9 |
| | 200 °C/1 hr | 200 | 248.00 | 86.08 |
| | 200 °C/2 hr | 220 | 258.53 | 92.5 |
| BA/PU (60/40) | Uncured | 175 | 244.60 | 0.00 |
| | 150 °C/1 hr | 190 | 247.26 | 11.52 |
| | 170 °C/1 hr | 175 | 243.89 | 19.87 |
| | 190 °C/1 hr | 175 | 237.69 | 53.57 |
| | 200 °C/1 hr | 200 | 246.43 | 82.66 |
| | 200 °C/2 hr | 225 | 261.82 | 92.25 |
| BA/PU (50/50) | Uncured | 200 | 251.31 | 0.00 |
| | 150 °C/1 hr | 195 | 250.81 | 18.59 |
| | 170 °C/1 hr | 195 | 250.51 | 23.71 |
| | 190 °C/1 hr | 170 | 239.60 | 34.24 |
| | 200 °C/1 hr | 175 | 247.31 | 77.49 |
| | 200 °C/2 hr | 225 | 257.86 | 92.26 |

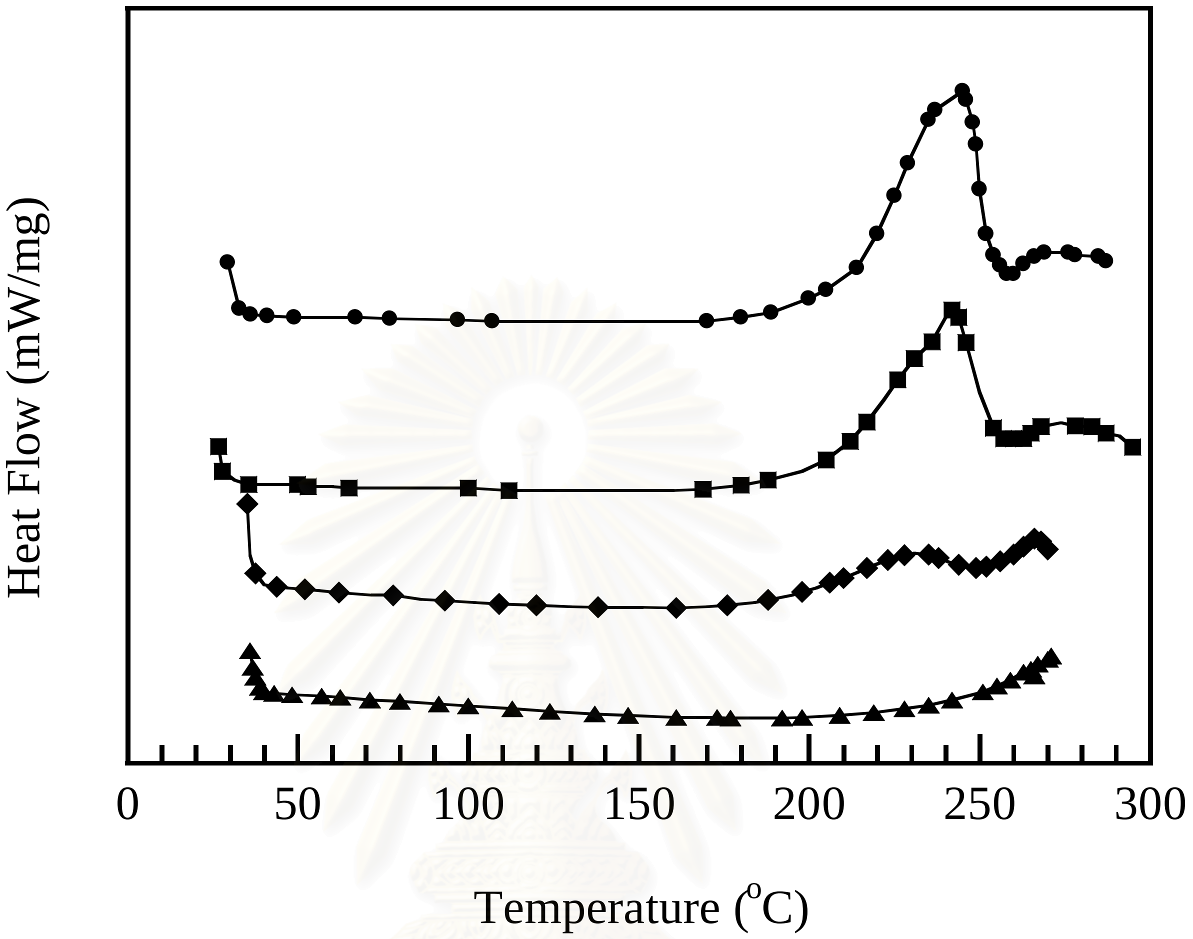


**Figure 5.8** DSC thermograms of BA/EPO (732)-70/30 at various curing conditions: (●) 150°C/1h, (■) 170°C/1h, (◆) 190°C/1h, (▲) 200°C/1h.

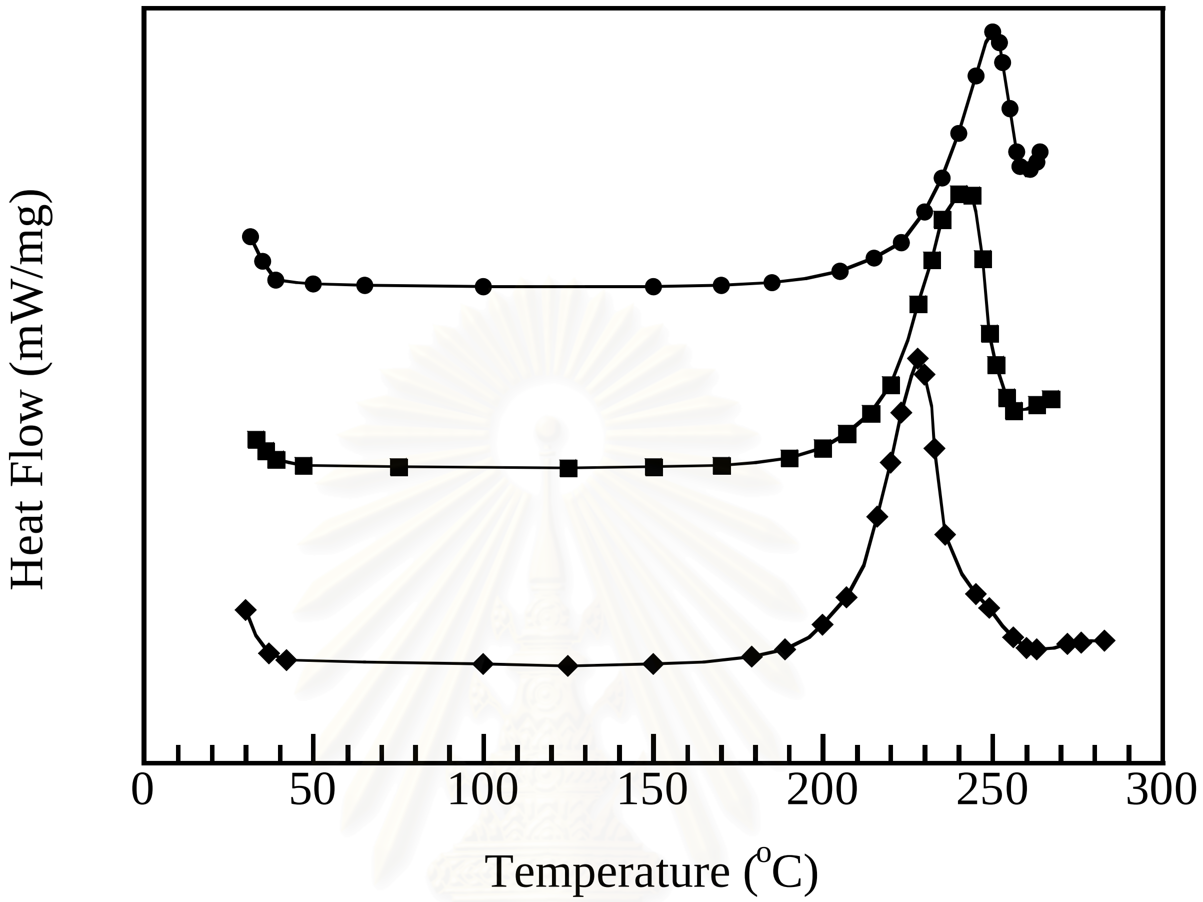


**Figure 5.9** DSC thermograms of BA/EPO 732 at various compositions: (●) 50/50, (■) 70/30, (◆) 90/10

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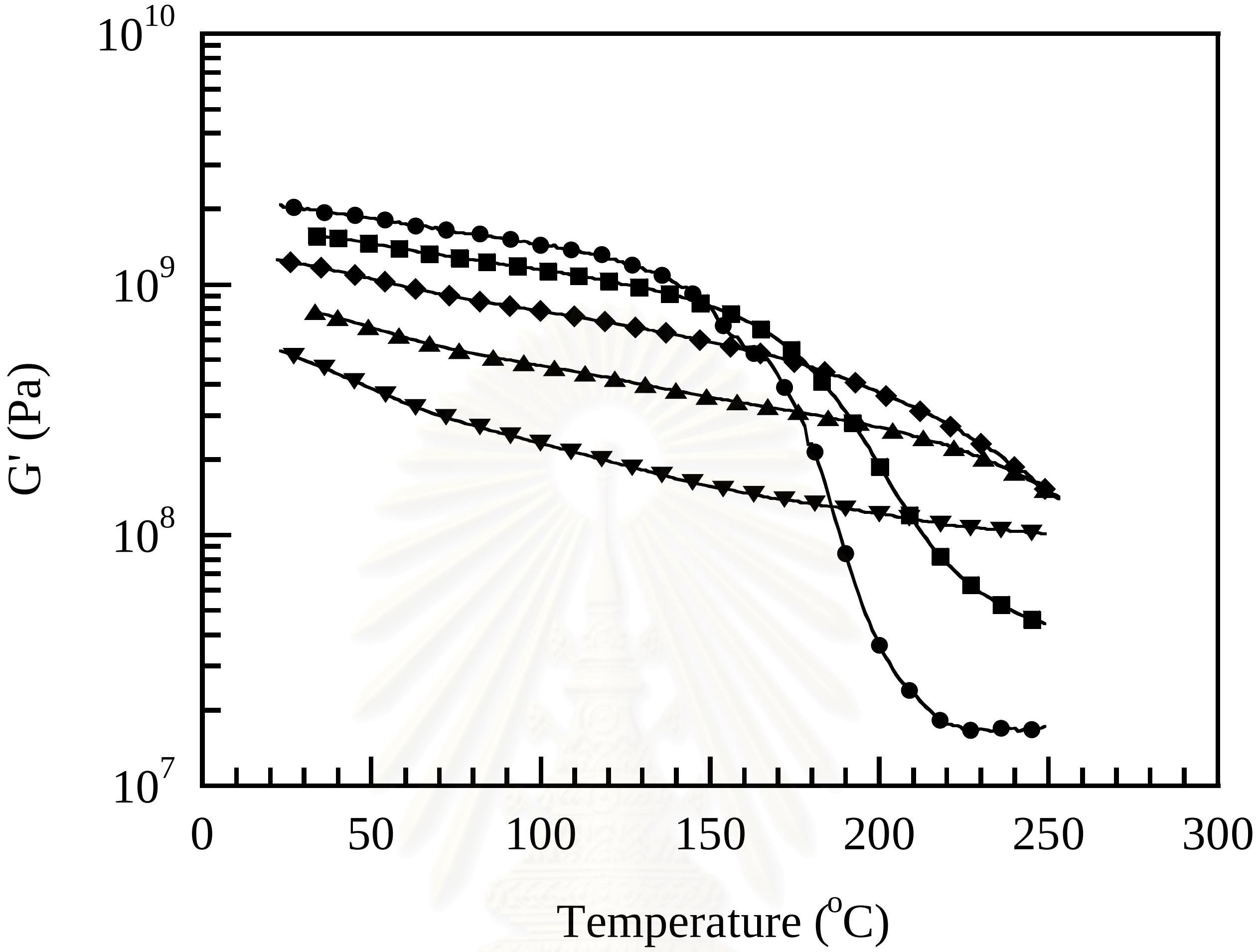

**Figure 5.10** Storage modulus of BA/PU (Diol 2000) at various compositions: (●) 90/10, (■) 80/20, (◆) 70/30, (▲) 60/40, (▼) 50/50.

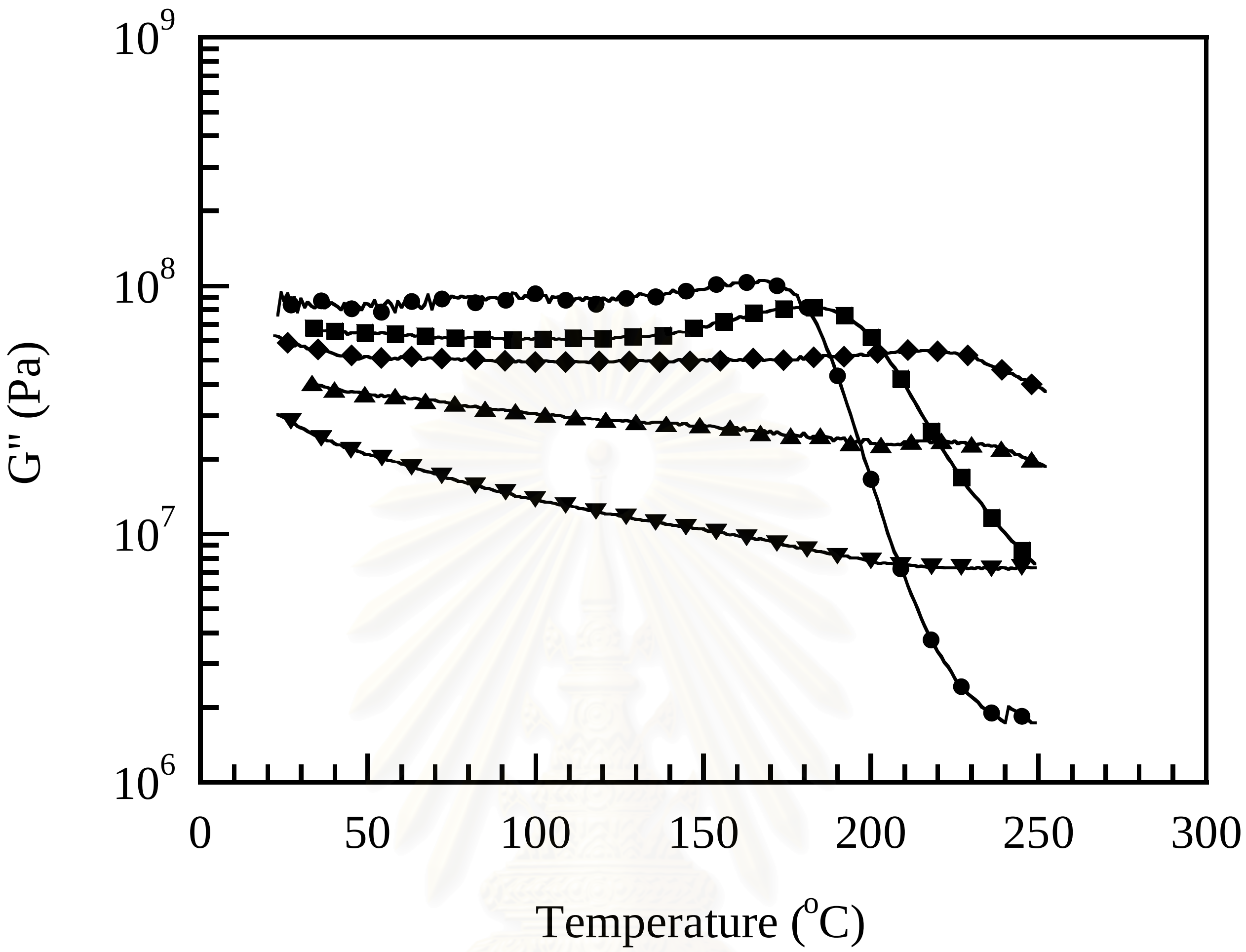

**Figure 5.11** Loss modulus of BA/PU (Diol 2000) at various compositions: (●) 90/10, (■) 80/20, (◆) 70/30, (▲) 60/40, (▼) 50/50.

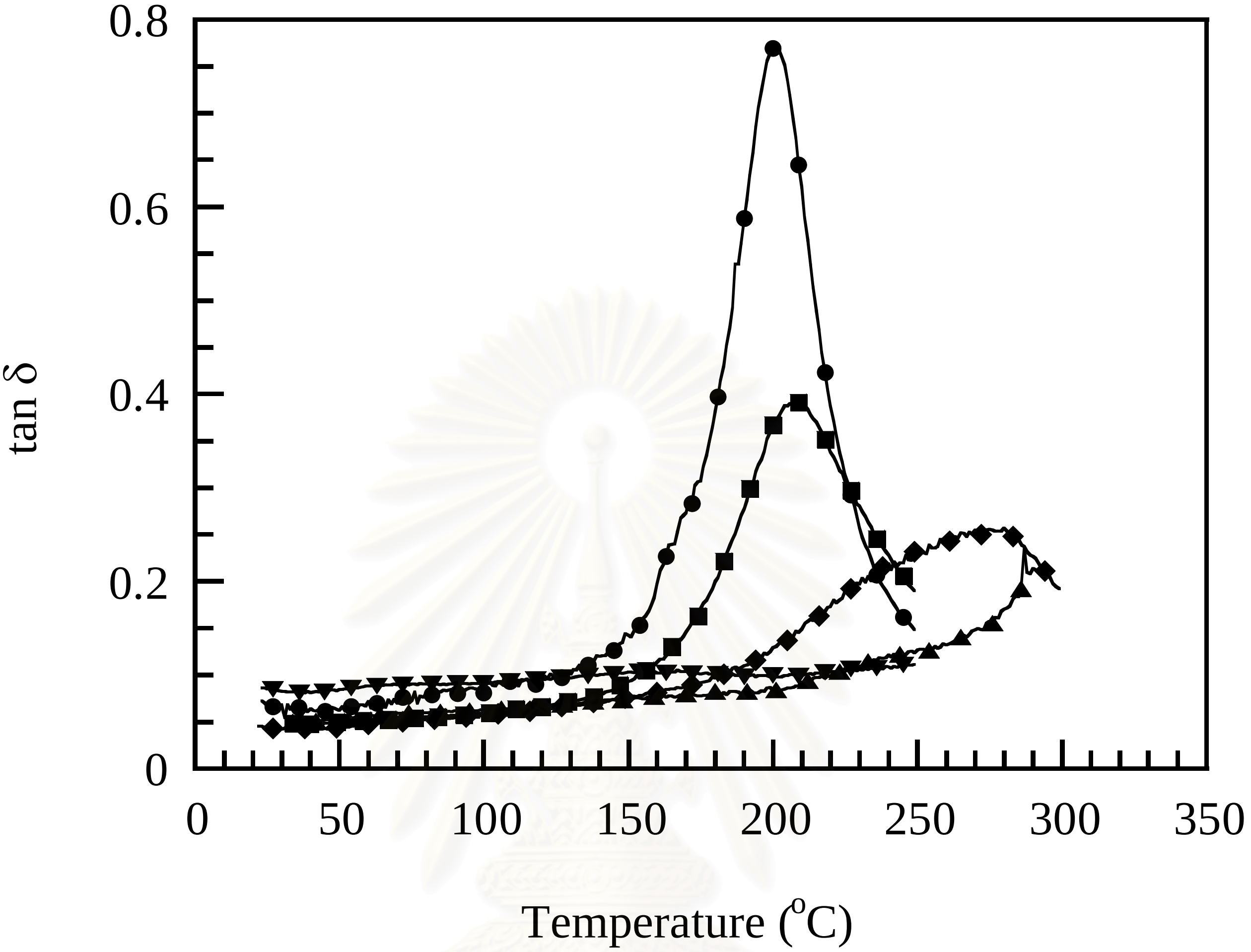

**Figure 5.12** Tan δ of BA/PU (Diol 2000) at various compositions: (●) 90/10, (■) 80/20, (◆) 70/30, (▲) 60/40, (▼) 50/50.

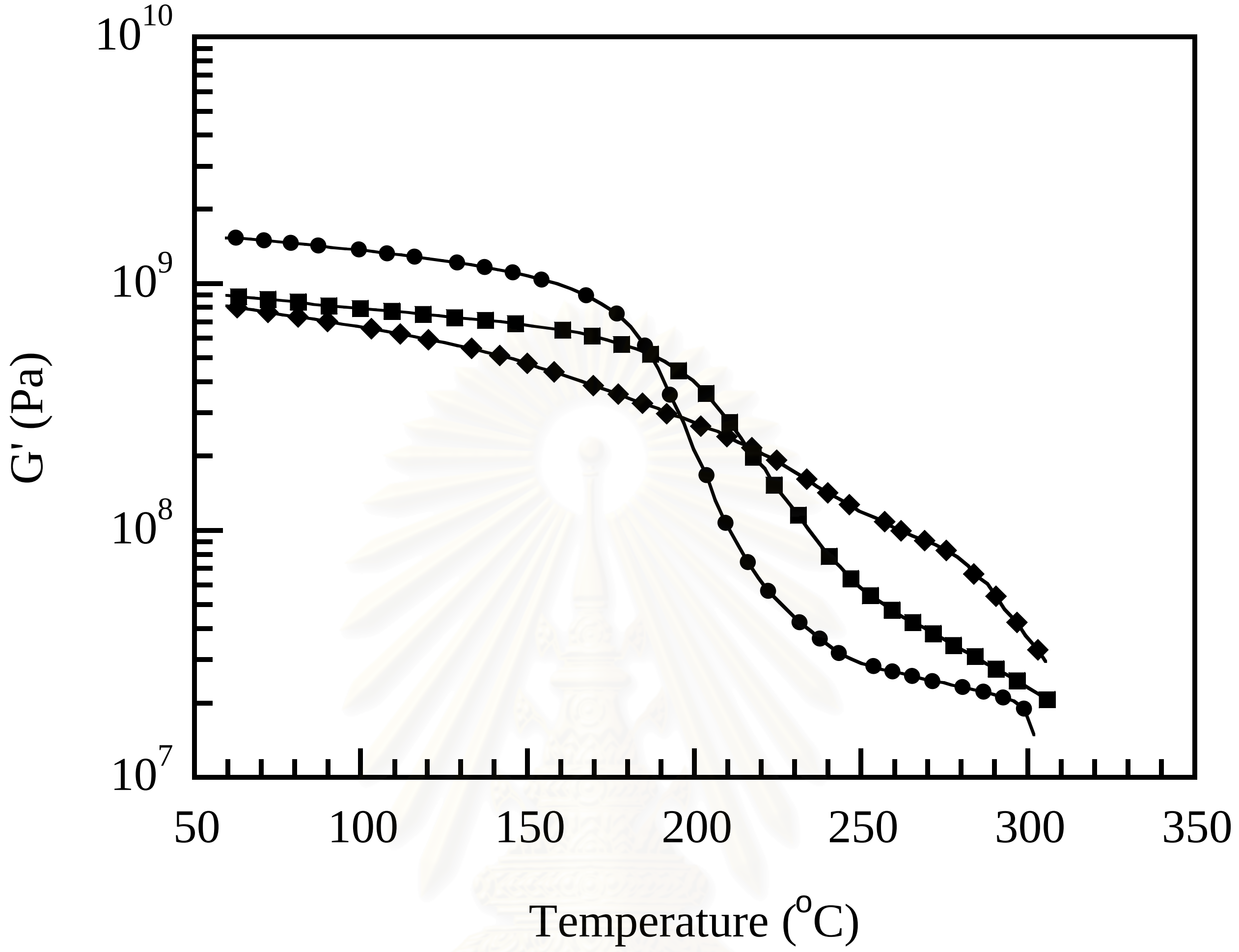

**Figure 5.13** Reproductive of storage modulus of BA/PU (Diol 2000) at various compositions: (●) 80/20, (■) 70/30, (◆) 60/40.

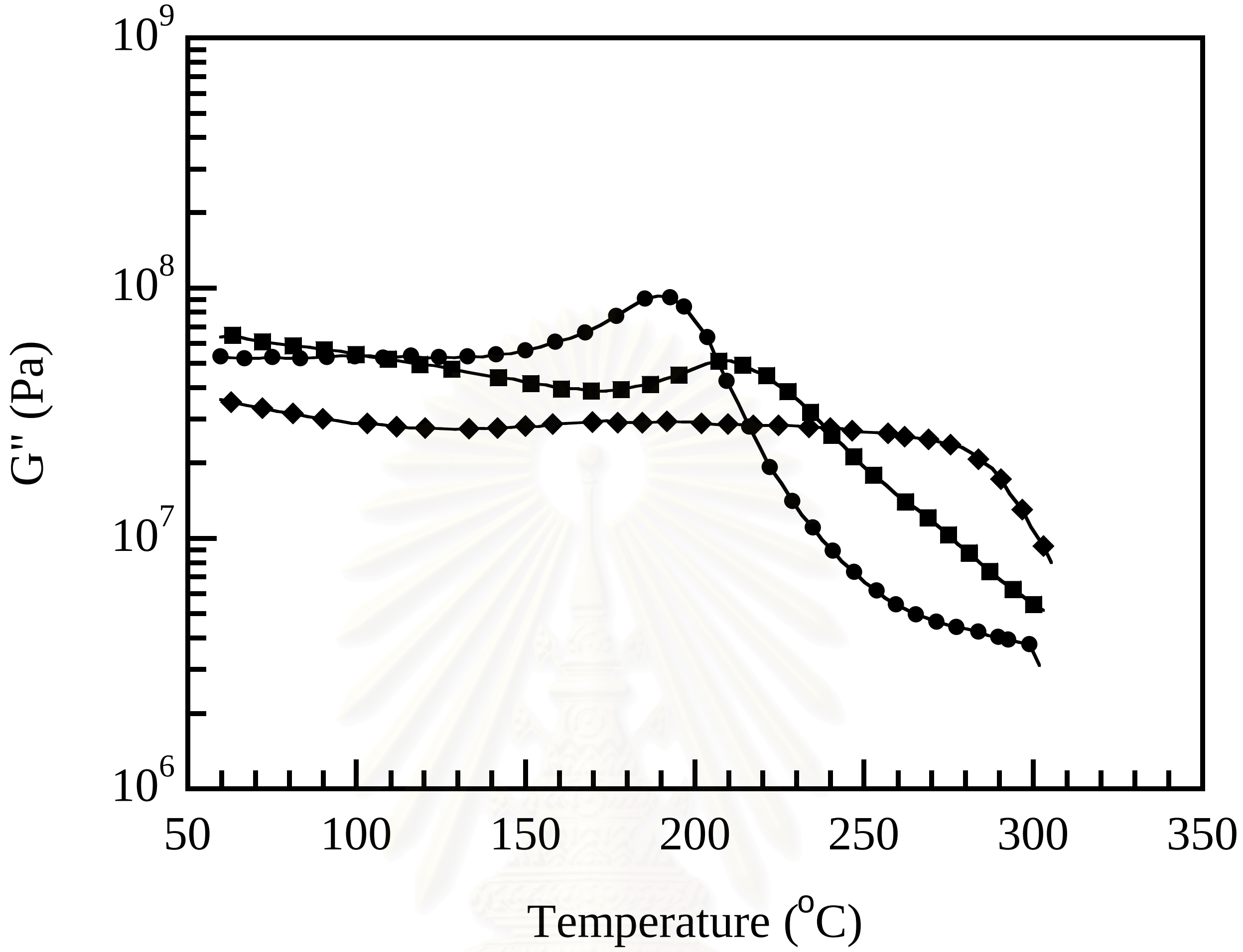

**Figure 5.14** Reproductive of loss modulus of BA/PU (Diol 2000) at various compositions: (●) 80/20, (■) 70/30, (◆) 60/40.

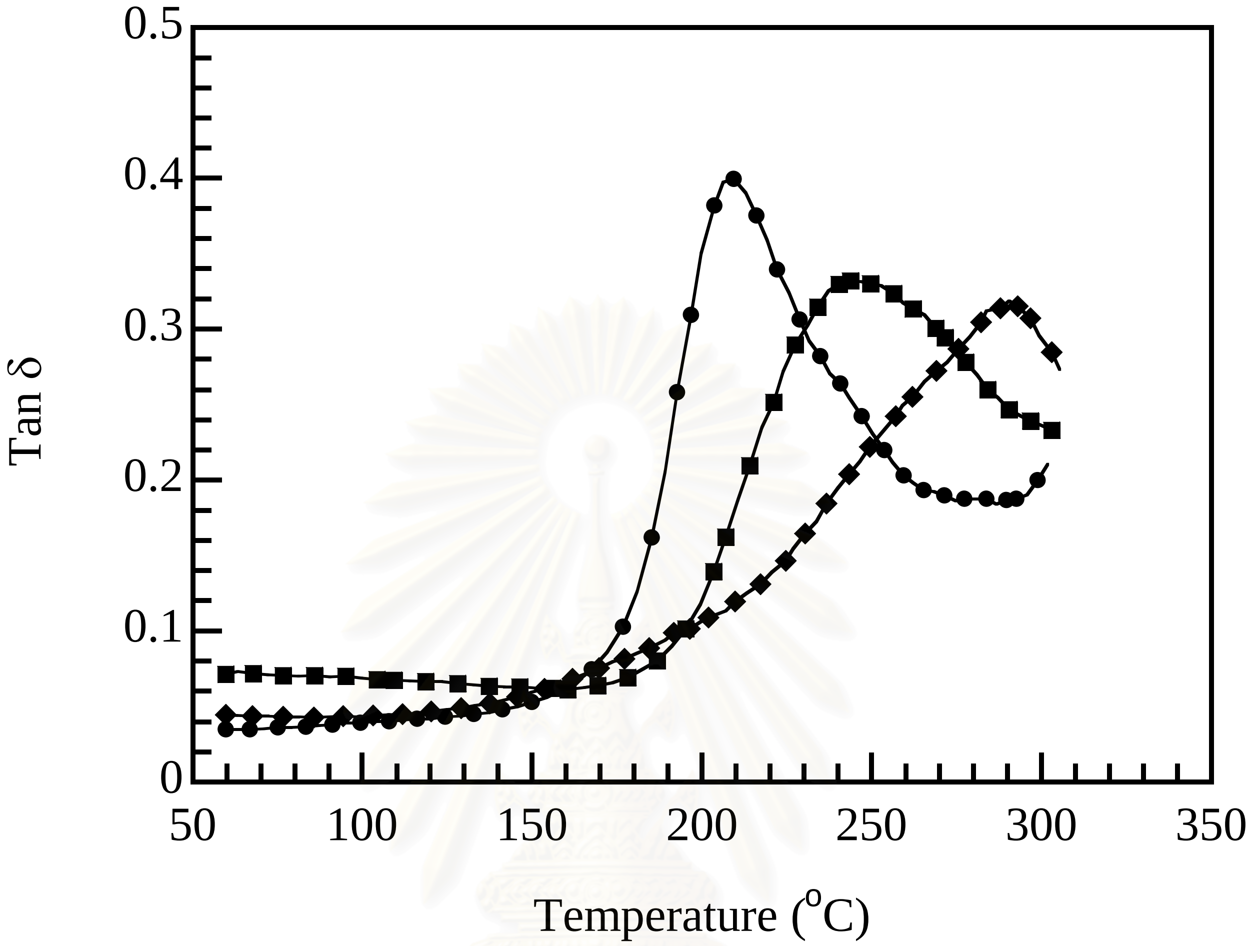

**Figure 5.15** Reproductive of tan δ of BA/PU (Diol 2000) at various compositions: (●) 80/20, (■) 70/30, (◆) 60/40.

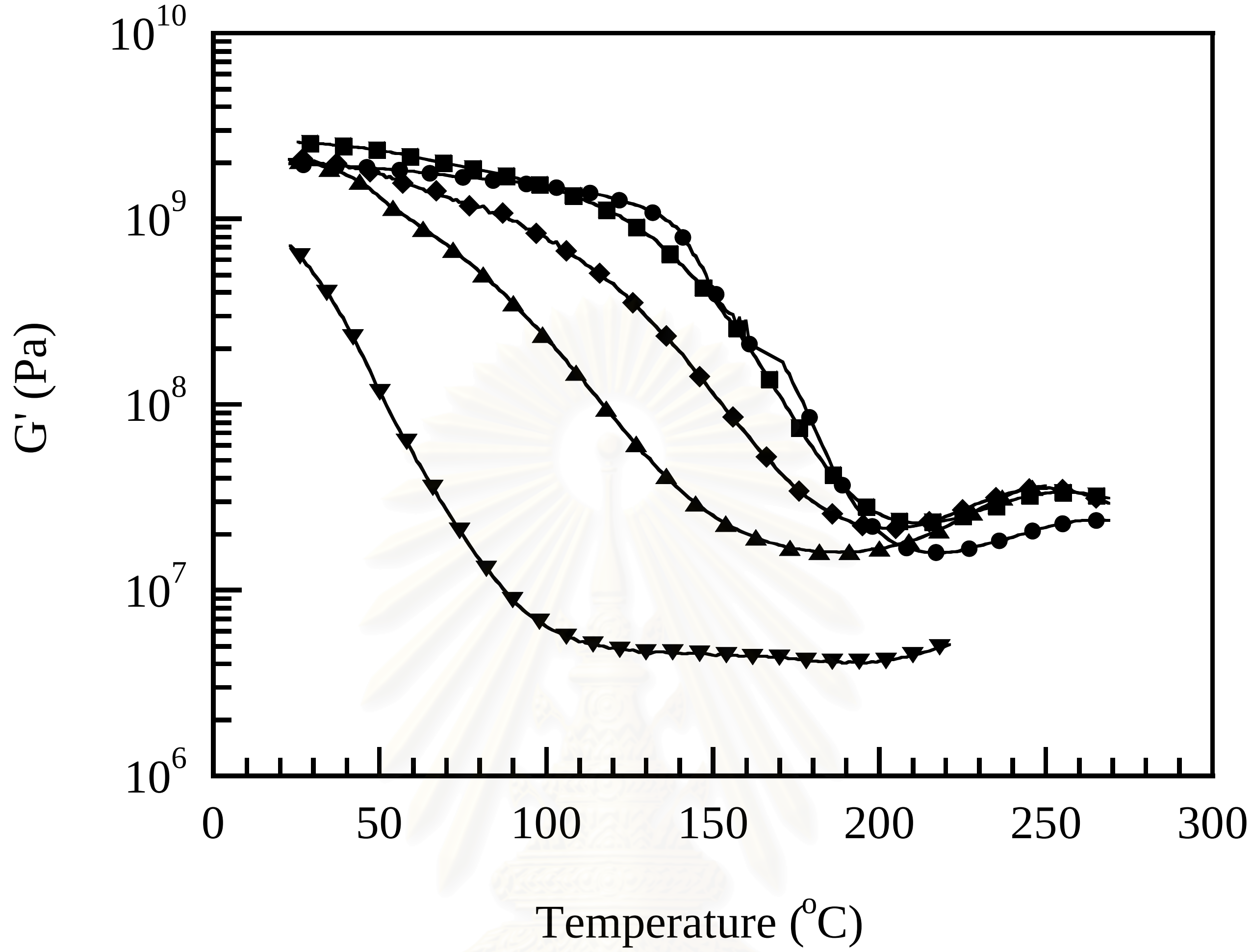

**Figure 5.16** Storage modulus of BA/EPO 732 at various compositions: (●) 90/10, (■) 80/20, (◆) 70/30, (▲) 60/40, (▼) 50/50.

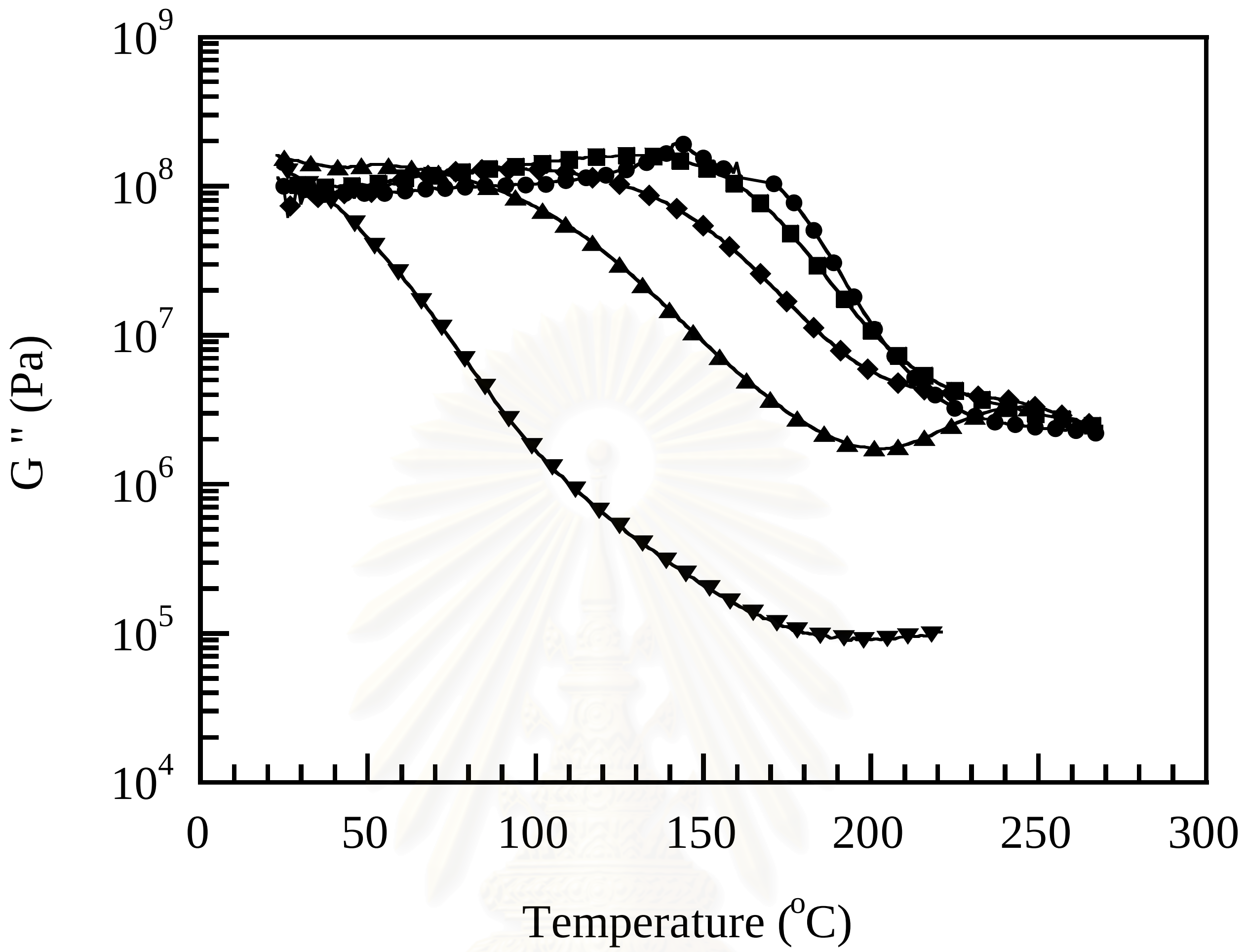

**Figure 5.17** Loss modulus of BA/EPO 732 at various compositions: (●) 90/10, (■) 80/20, (◆ ) 70/30, (▲ ) 60/40, (▼ ) 50/50.

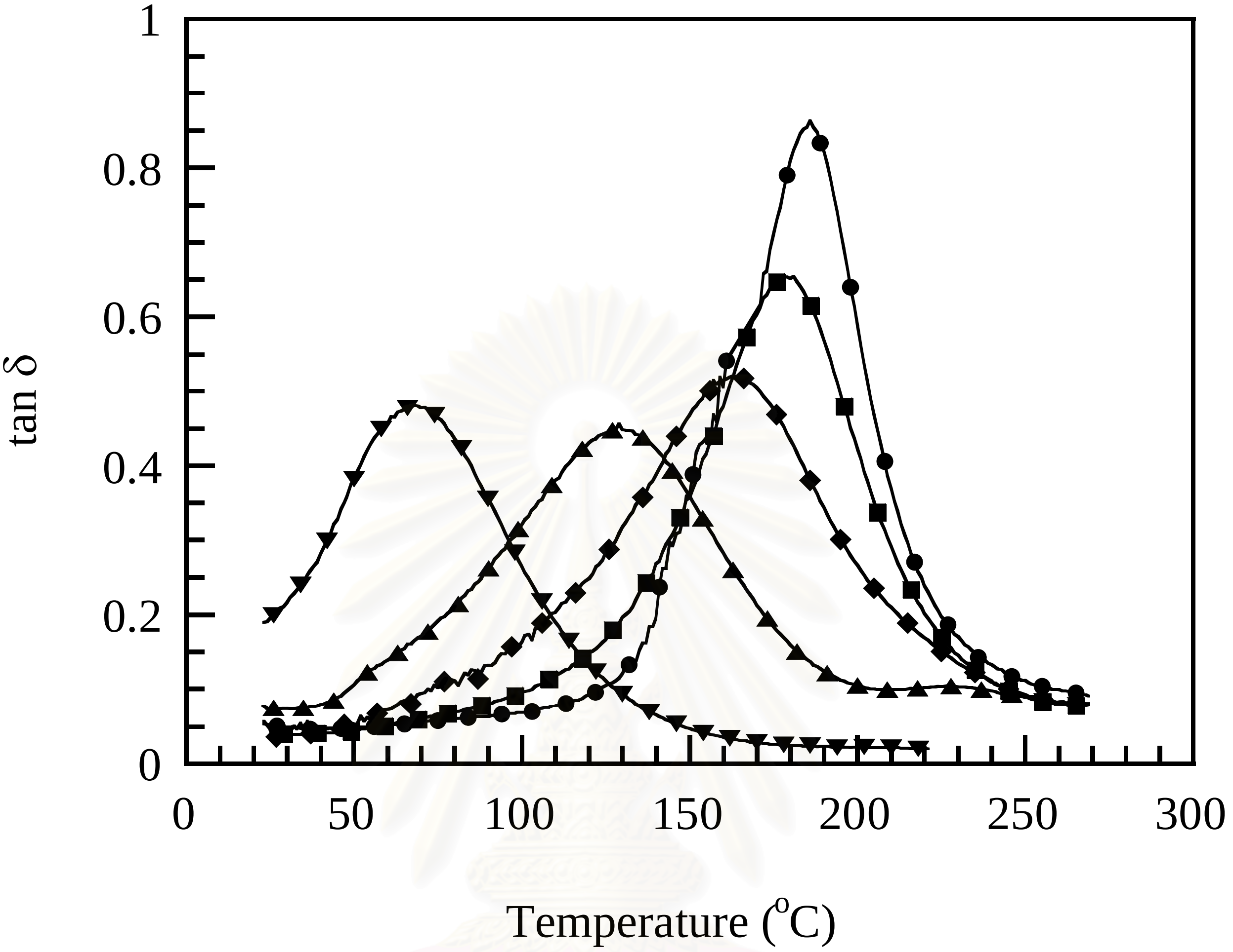

**Figure 5.18** Tan δ of BA/EPO 732 at various compositions: (●) 90/10, (■) 80/20, (◆) 70/30, (▲) 60/40, (▼) 50/50.

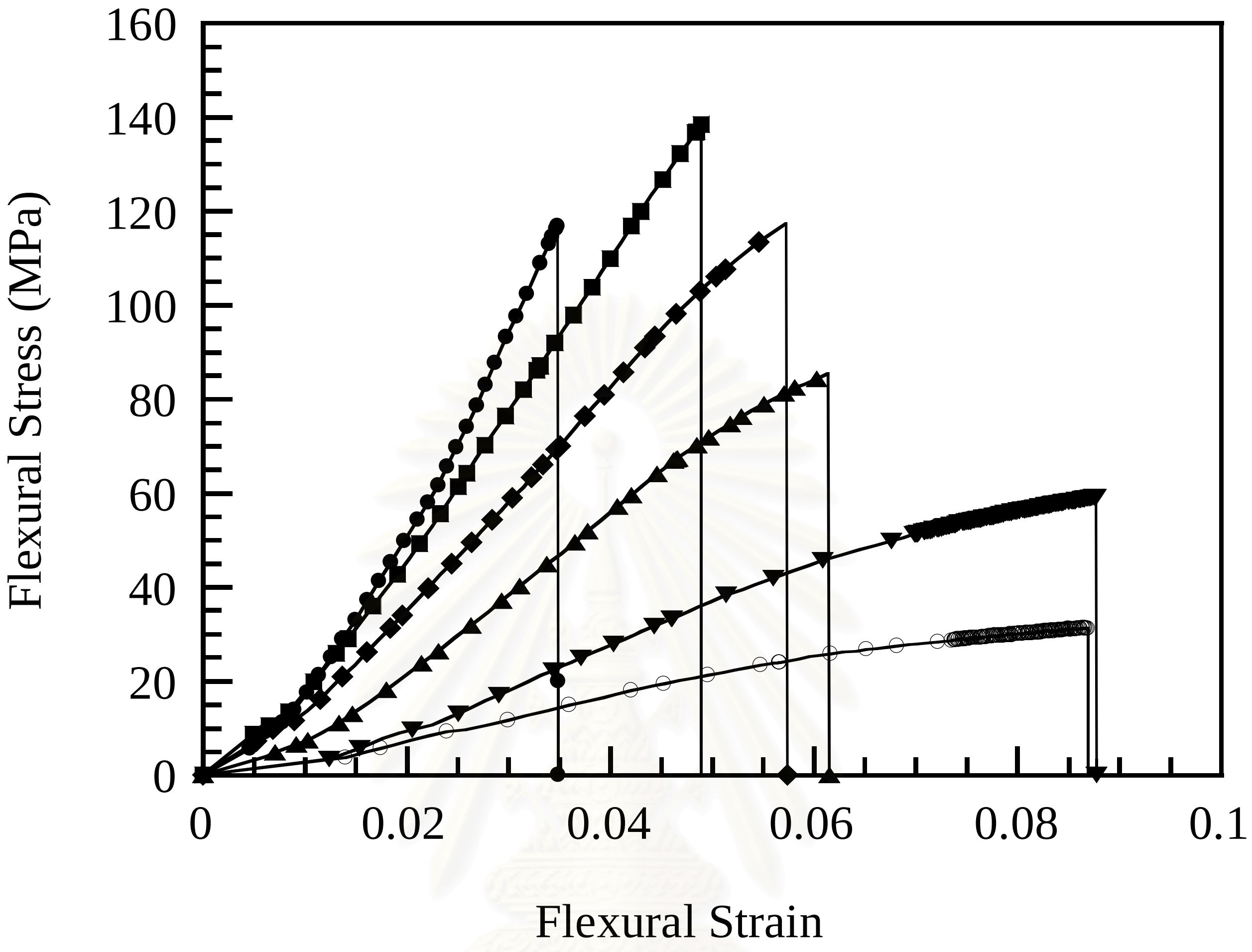

**Figure 5.19** Flexural stress & strain of BA/PU (Diol 2000) at various compositions: (●) 100/0, (■) 90/10, (◆) 80/20, (▲) 70/30, (▼) 60/40, (○) 50/50.

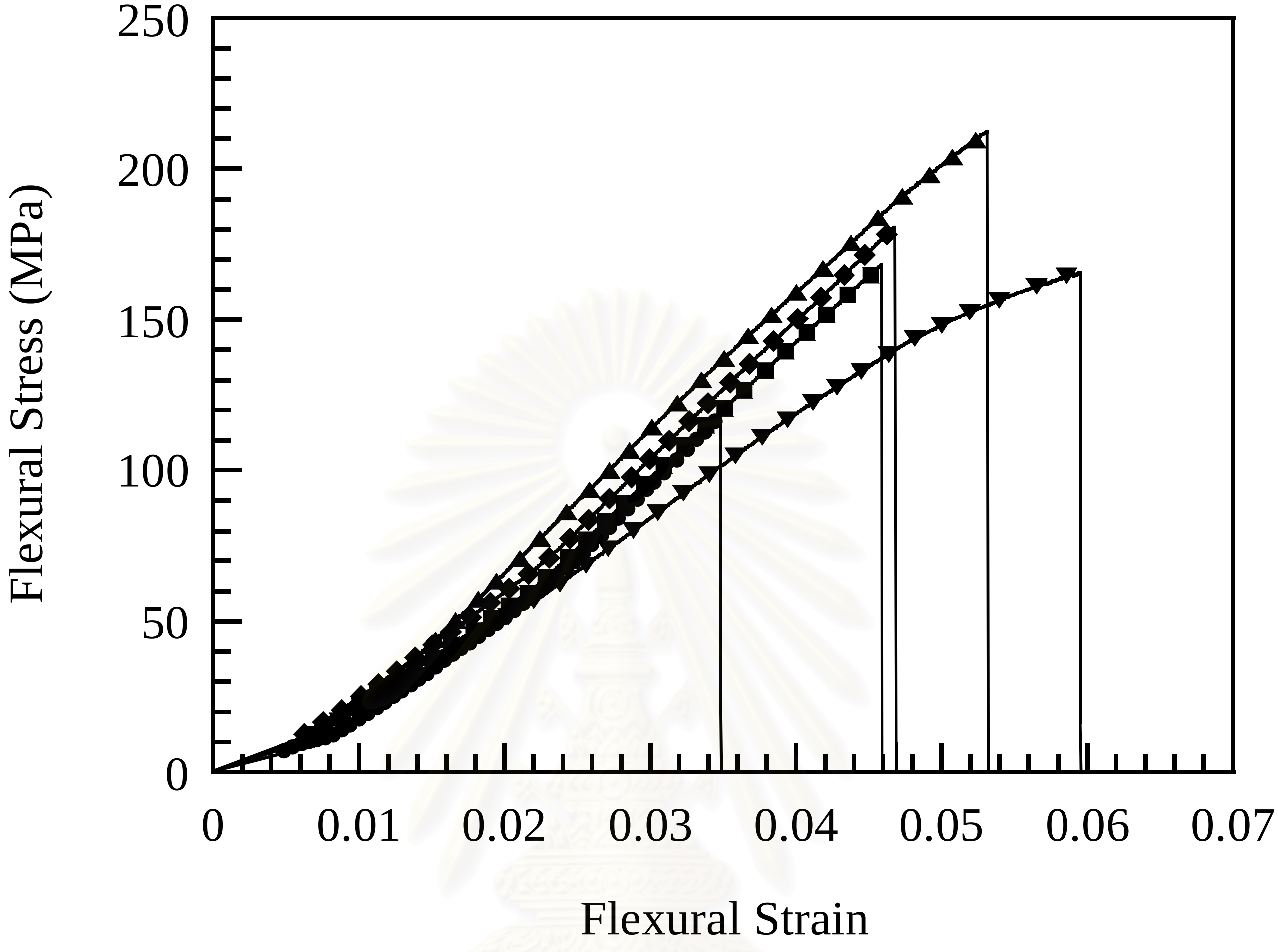

**Figure 5.20** Flexural stress & strain of BA/EPO 732 at various compositions: (●) 100/0, (■) 90/10, (◆) 80/20, (▲) 70/30, (▼) 60/40.

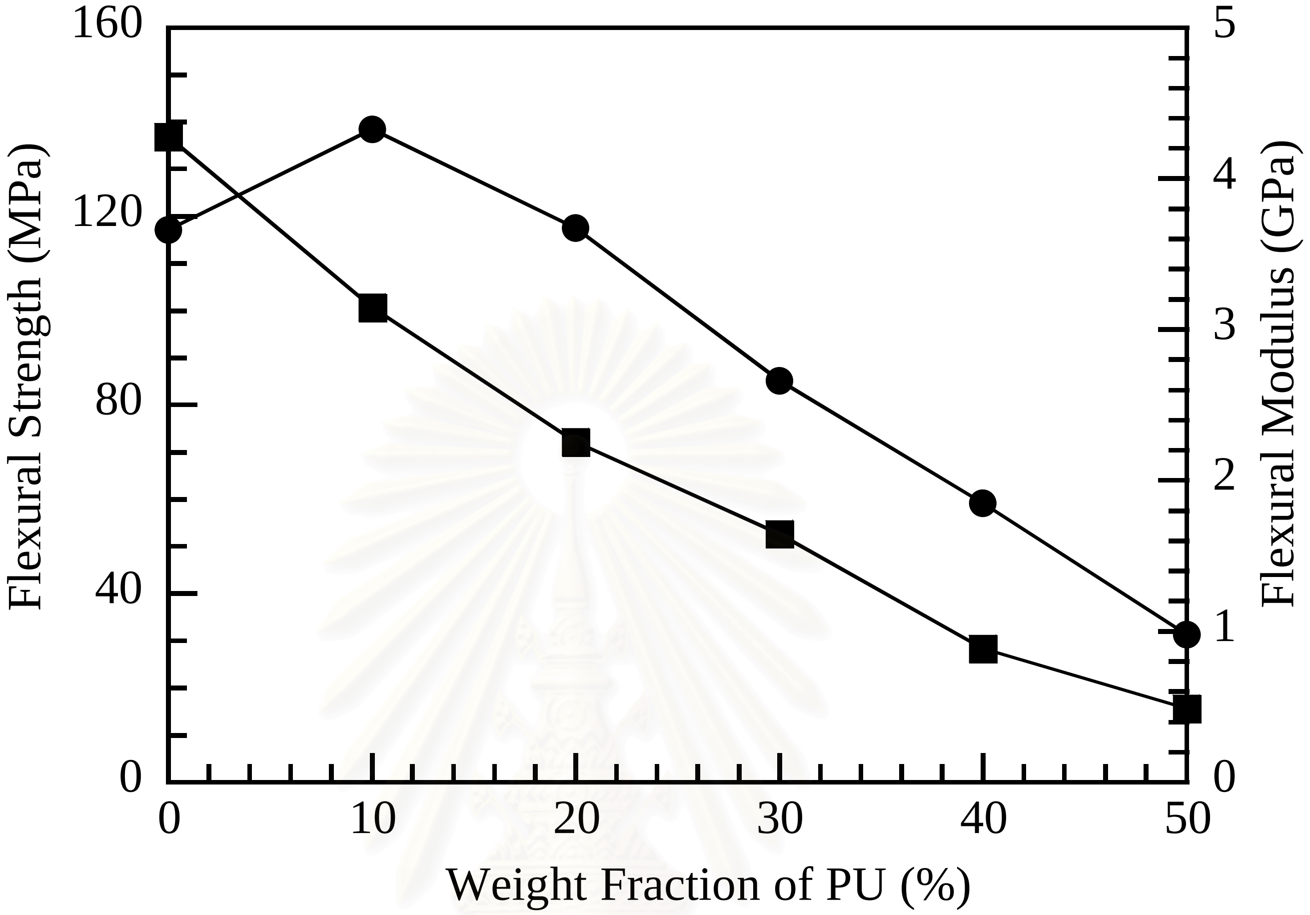

**Figure 5.21** Flexural Strength & Modulus of BA/PU (Diol 2000) at various compositions: (■) flexural strength , (●) flexural modulus.

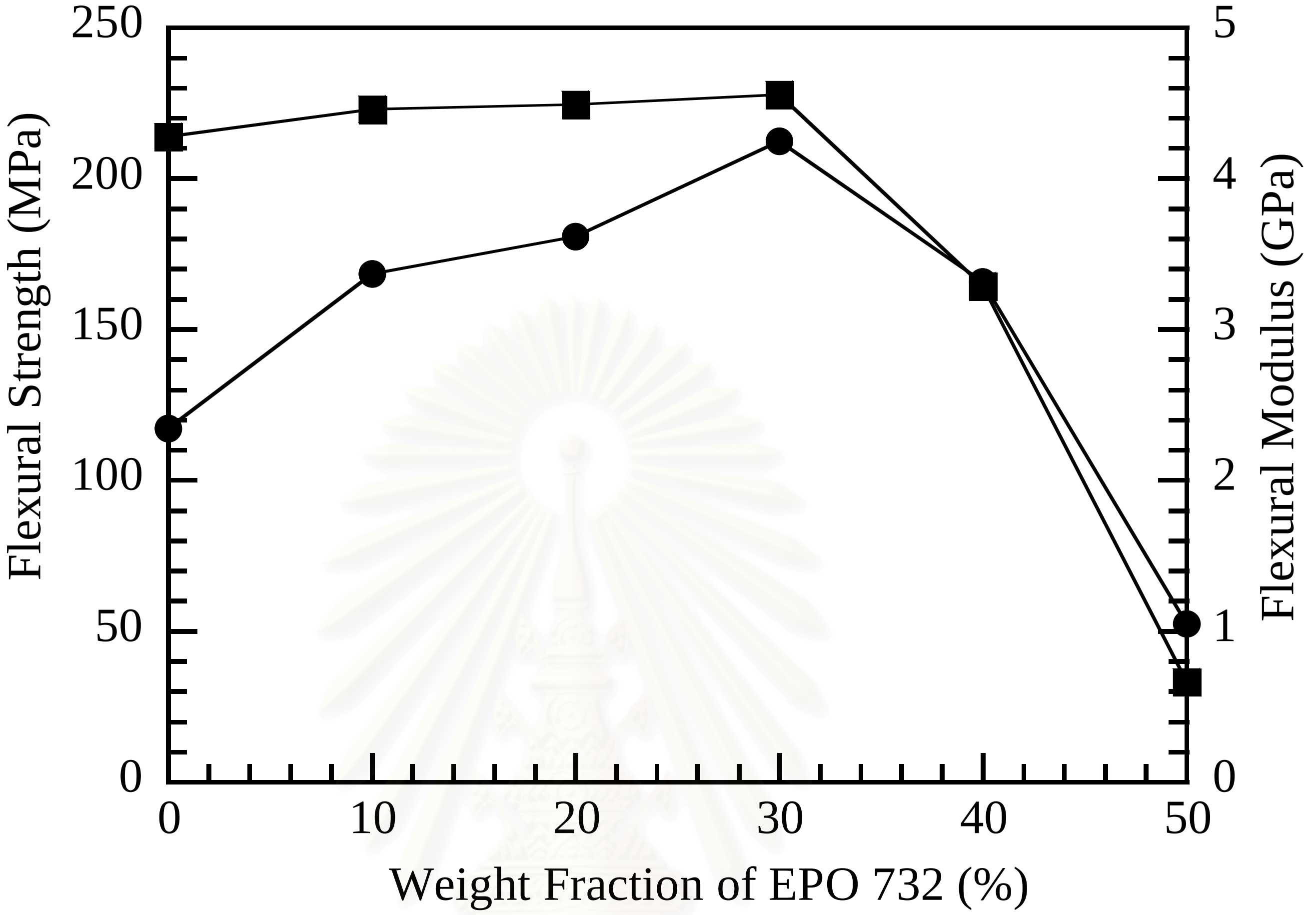

**Figure 5.22** Flexural Strength & Modulus of BA/EPO 732 at various compositions: (■) flexural strength , (●) flexural modulus.

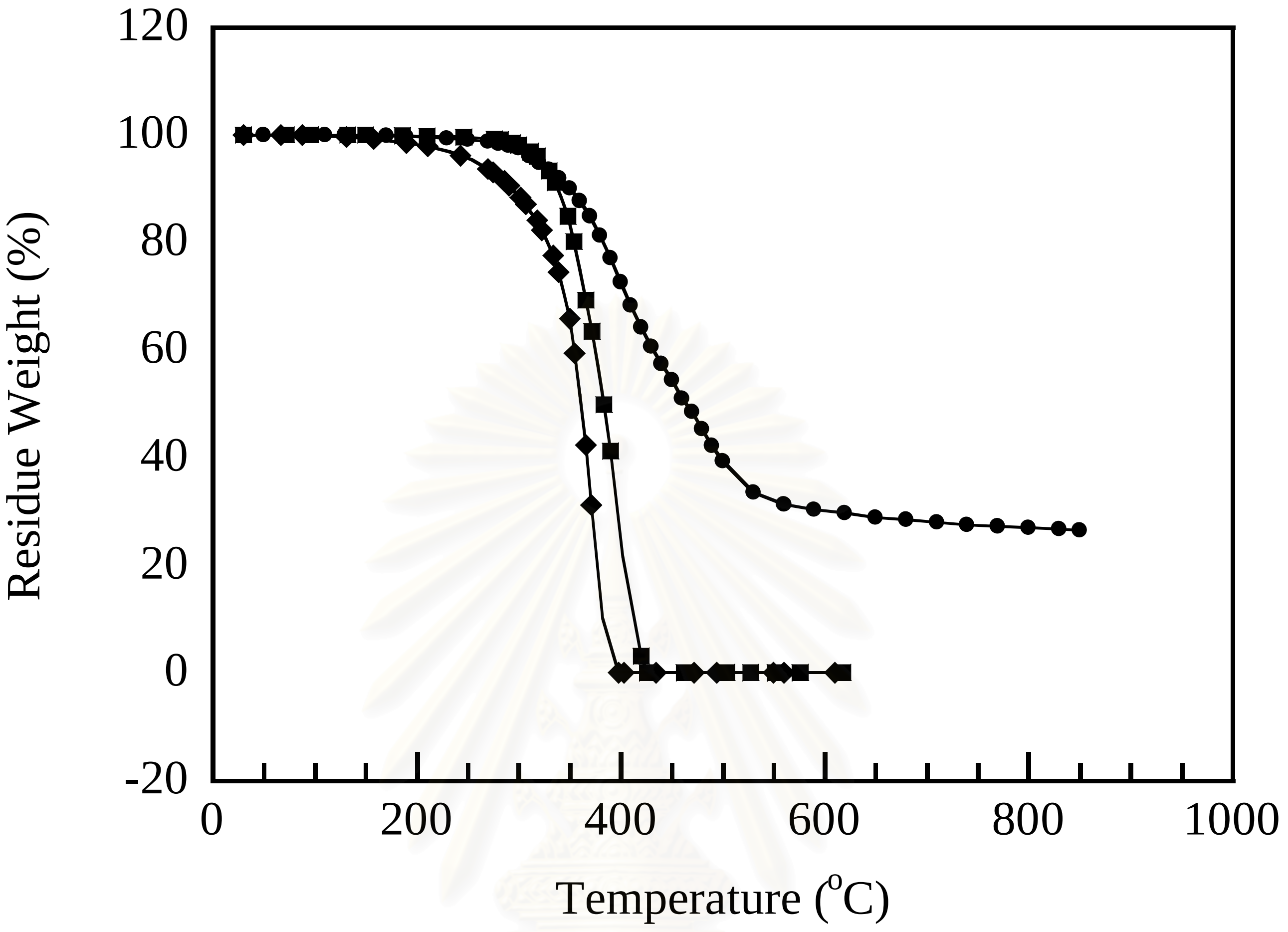

**Figure 5.23** TGA thermograms of three resins: (●) Polybenzoxazine, (■) urethane prepolymer (Diol 2000), (◆) flexible epoxy (EPO 732).

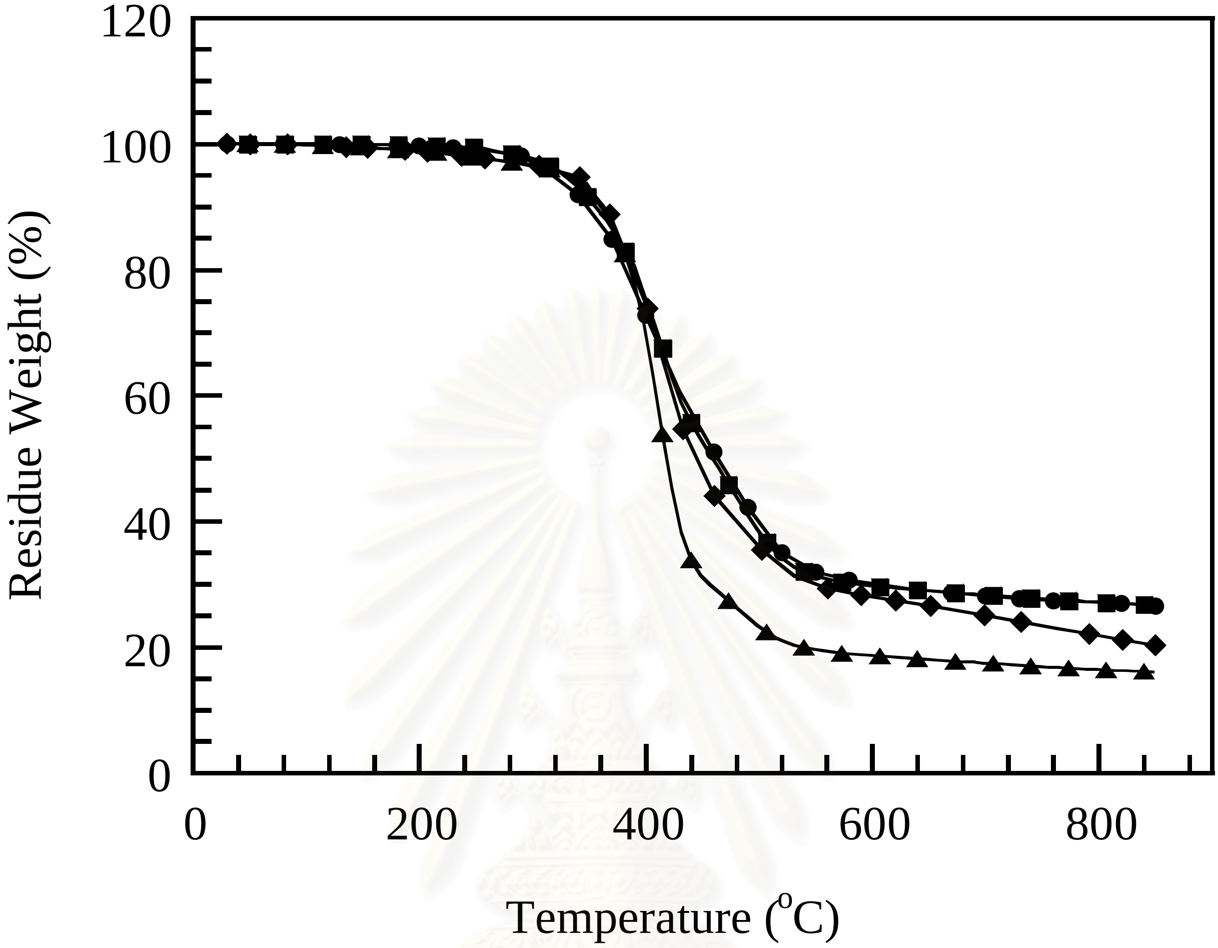

**Figure 5.24** TGA thermograms of BA/PU (Diol 2000) at various compositions: (●) 100/0, (■) 90/10, (◆ ) 70/30, (▲) 50/50.

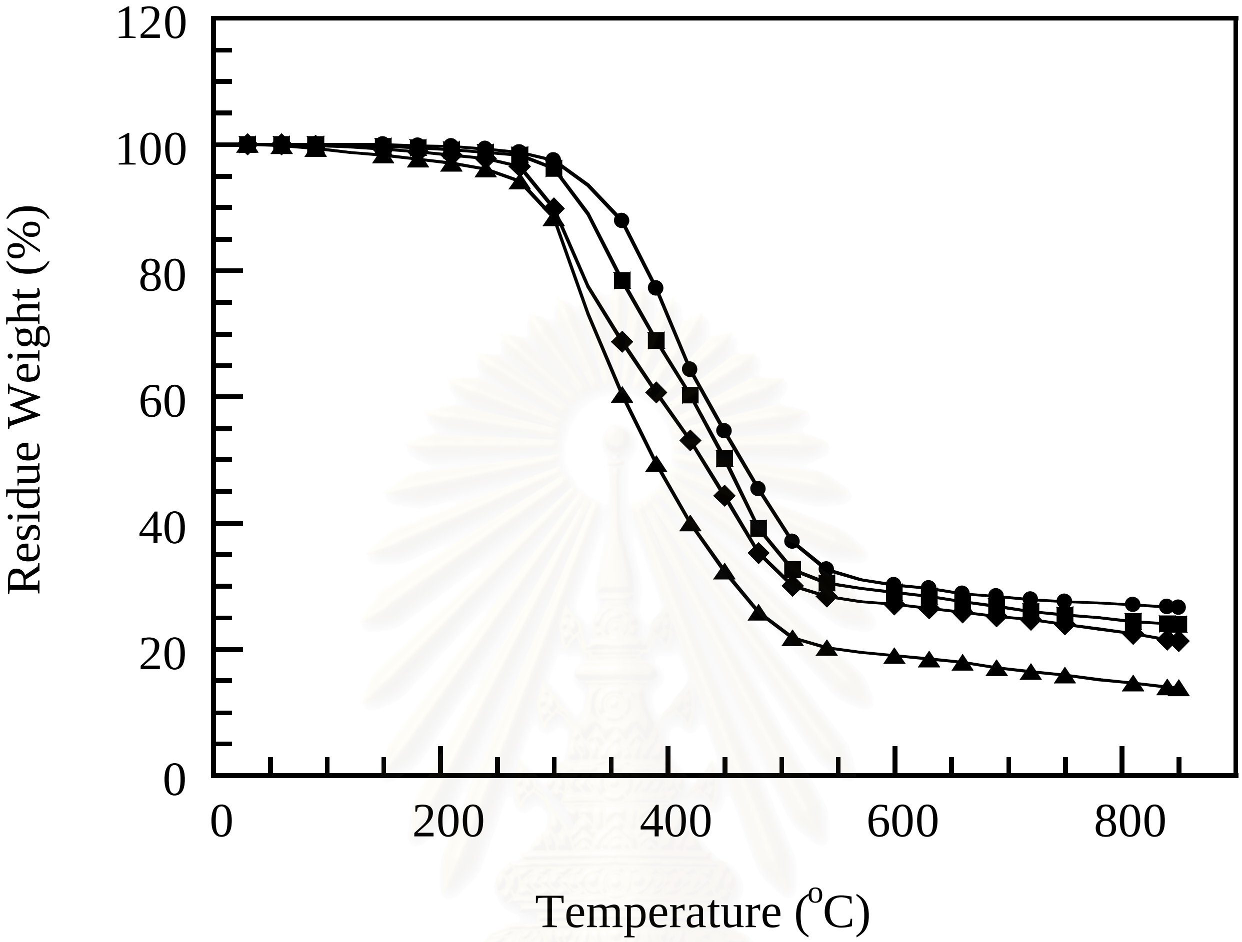

**Figure 5.25** TGA thermograms of BA/EPO 732 at various compositions: (●) 100/0, (■) 90/10, (◆) 70/30, (▲) 50/50.

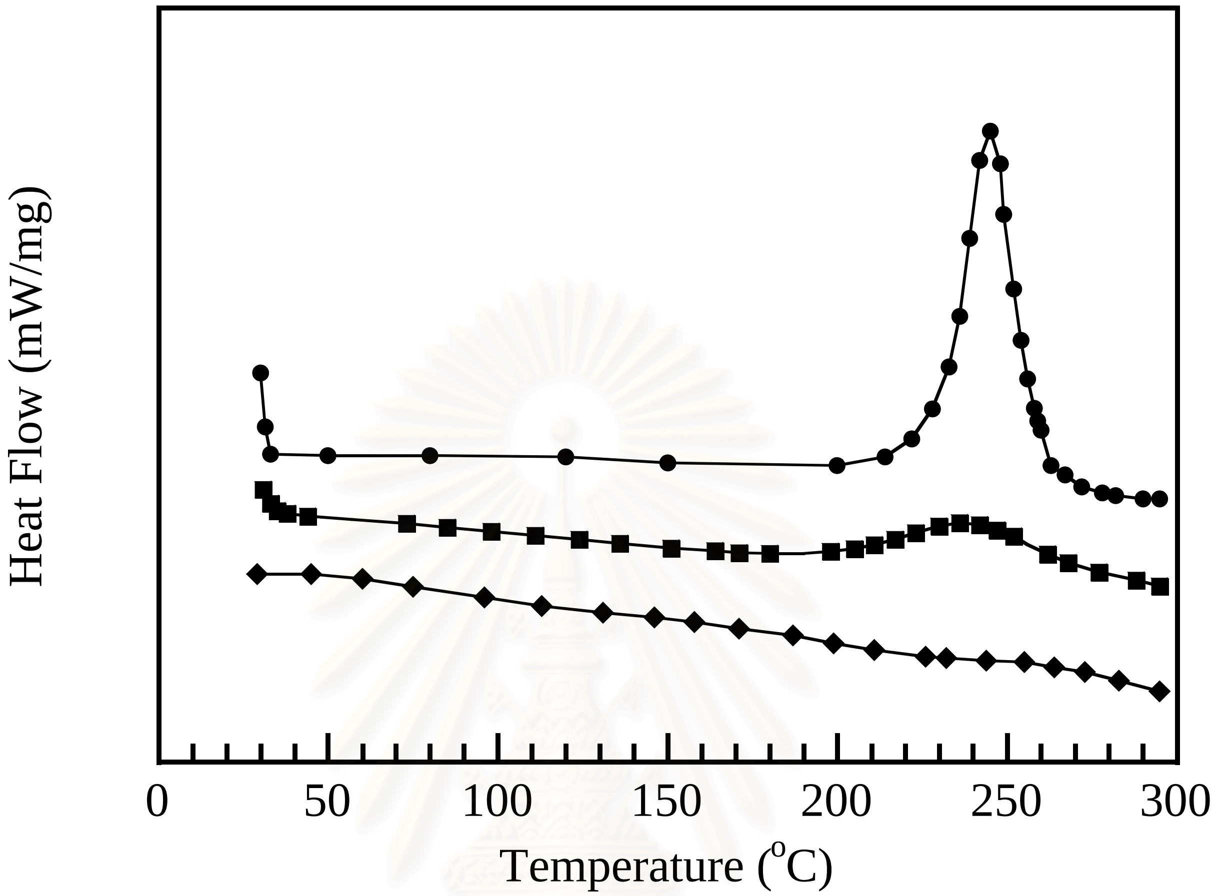

**Figure 5.26** DSC thermograms of BA/PU (Diol 1000)-70/30 at various curing conditions: (●) uncured, (■) 165°C/5h, (◆) 165°C/5h+180°C/4h

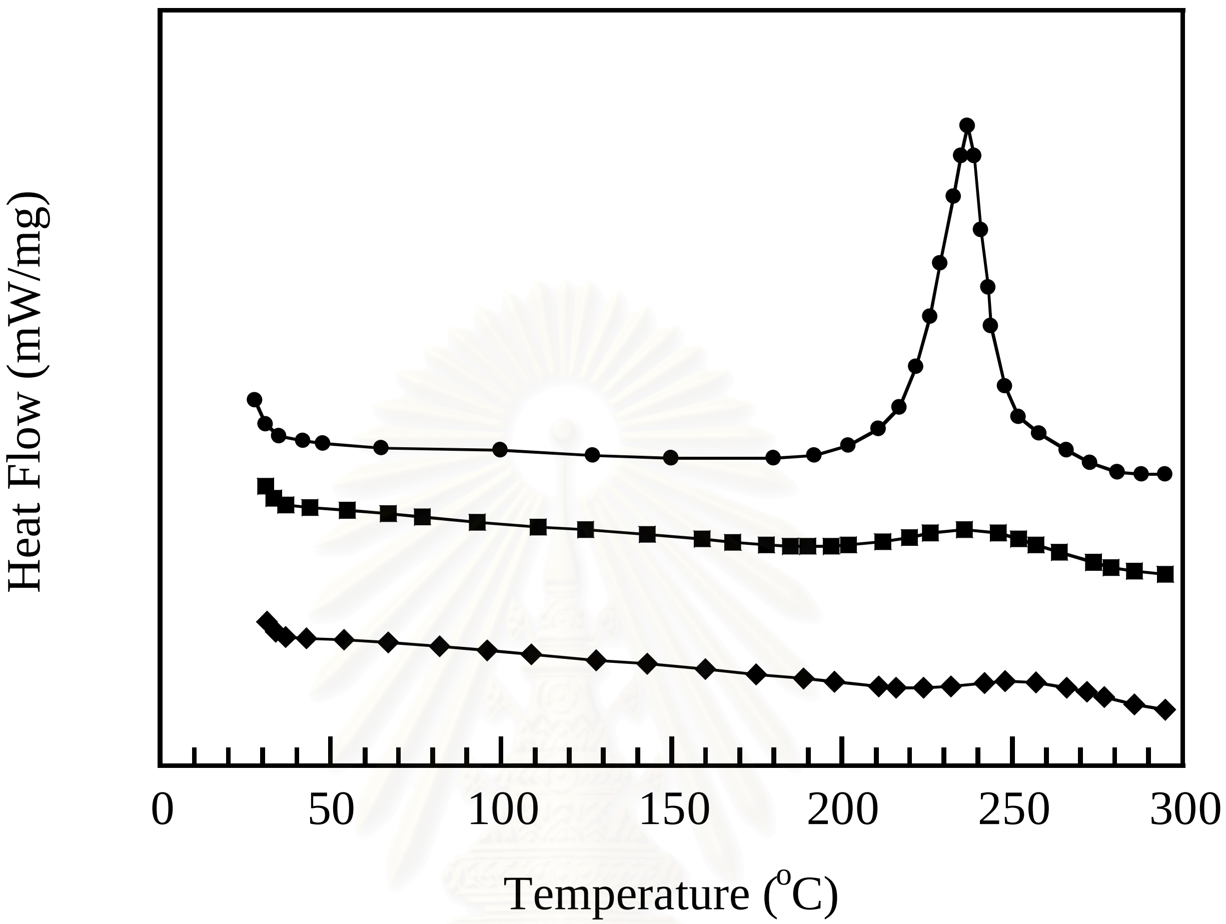

**Figure 5.27** DSC thermograms of BA/PU (Diol 2000)-70/30 at various curing conditions: (●) uncured, (■) 165°C/5h, (◆) 165°C/5h+180°C/4h.

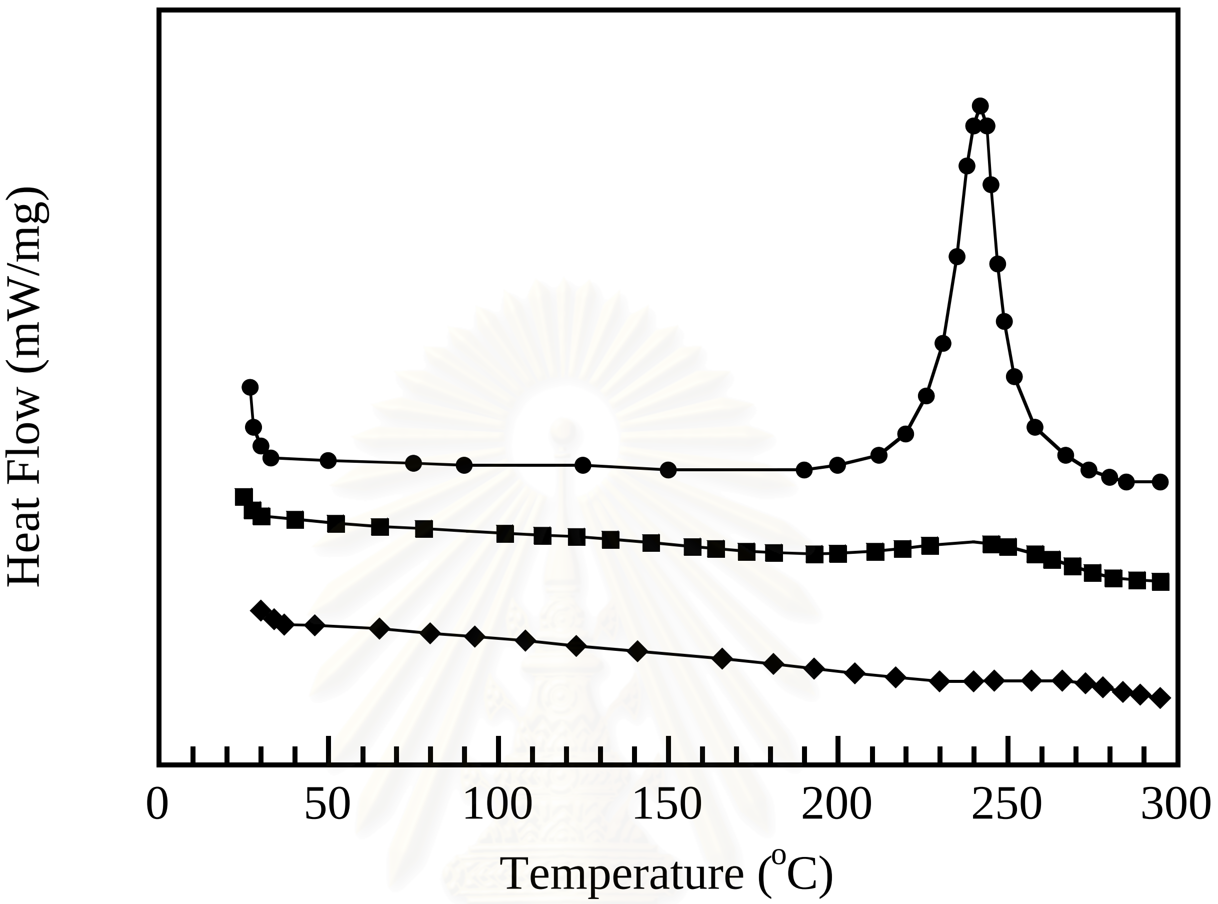

**Figure 5.28** DSC thermograms of BA/PU (Diol 3000)-70/30 at various curing conditions: (●) uncured, (■) 165$^{o}$C/5h, (◆) 165$^{o}$C/5h+180$^{o}$C/4h.

**Table 5.2** DSC of BA/PU (Diol 1000)

| Sample Code | Curing Condition | Exothermic Peak | | |
|---|---|---|---|---|
| | | On Set Temperature (°C) | Peak Temperature (°C) | Conversion (%) |
| BA/PU (90/10) | Uncured | 175 | 233.97 | 0.00 |
| | 165 °C/5 hr | 190 | 240.99 | 73.09 |
| | 180 °C/4 hr | 215 | 260.45 | 94.37 |
| BA/PU (70/30) | Uncured | 200 | 245.92 | 0.00 |
| | 165 °C/5 hr | 190 | 239.69 | 69.44 |
| | 180 °C/4 hr | 230 | 260.30 | 95.21 |
| BA/PU (50/50) | Uncured | 205 | 251.85 | 0.00 |
| | 165 °C/5 hr | 200 | 235.87 | 89.90 |
| | 180 °C/4 hr | 225 | 245.63 | 96.80 |

**Table 5.3** DSC of BA/PU (Diol 2000)

| Sample Code | Curing Condition | Exothermic Peak | | |
|---|---|---|---|---|
| | | On Set Temperature (°C) | Peak Temperature (°C) | Conversion (%) |
| BA/PU (90/10) | Uncured | 150 | 229.05 | 0.00 |
| | 165 °C/5 hr | 185 | 241.03 | 66.13 |
| | 180 °C/4 hr | 225 | 258.54 | 95.43 |
| BA/PU (70/30) | Uncured | 175 | 237.8 | 0.00 |
| | 165 °C/5 hr | 195 | 242.25 | 82.19 |
| | 180 °C/4 hr | 230 | 265.66 | 96.34 |
| BA/PU (50/50) | Uncured | 200 | 251.31 | 0.00 |
| | 165 °C/5 hr | 195 | 239.31 | 91.65 |
| | 180 °C/4 hr | 225 | 246.99 | 96.80 |

**Table 5.4** DSC of BA/PU (Diol 3000)

| Sample Code | Curing Condition | Exothermic Peak | | |
|---|---|---|---|---|
| | | On Set Temperature (°C) | Peak Temperature (°C) | Conversion (%) |
| BA/PU (90/10) | Uncured | 170 | 230.34 | 0.00 |
| | 165 °C/5 hr | 185 | 241.18 | 71.63 |
| | 180 °C/4 hr | 225 | 255.95 | 96.23 |
| BA/PU (70/30) | Uncured | 190 | 242.62 | 0.00 |
| | 165 °C/5 hr | 195 | 245.59 | 84.74 |
| | 180 °C/4 hr | 240 | 268.44 | 96.94 |
| BA/PU (50/50) | Uncured | 200 | 251.26 | 0.00 |
| | 165 °C/5 hr | 205 | 240.39 | 92.07 |
| | 180 °C/4 hr | 230 | 263.39 | 98.09 |

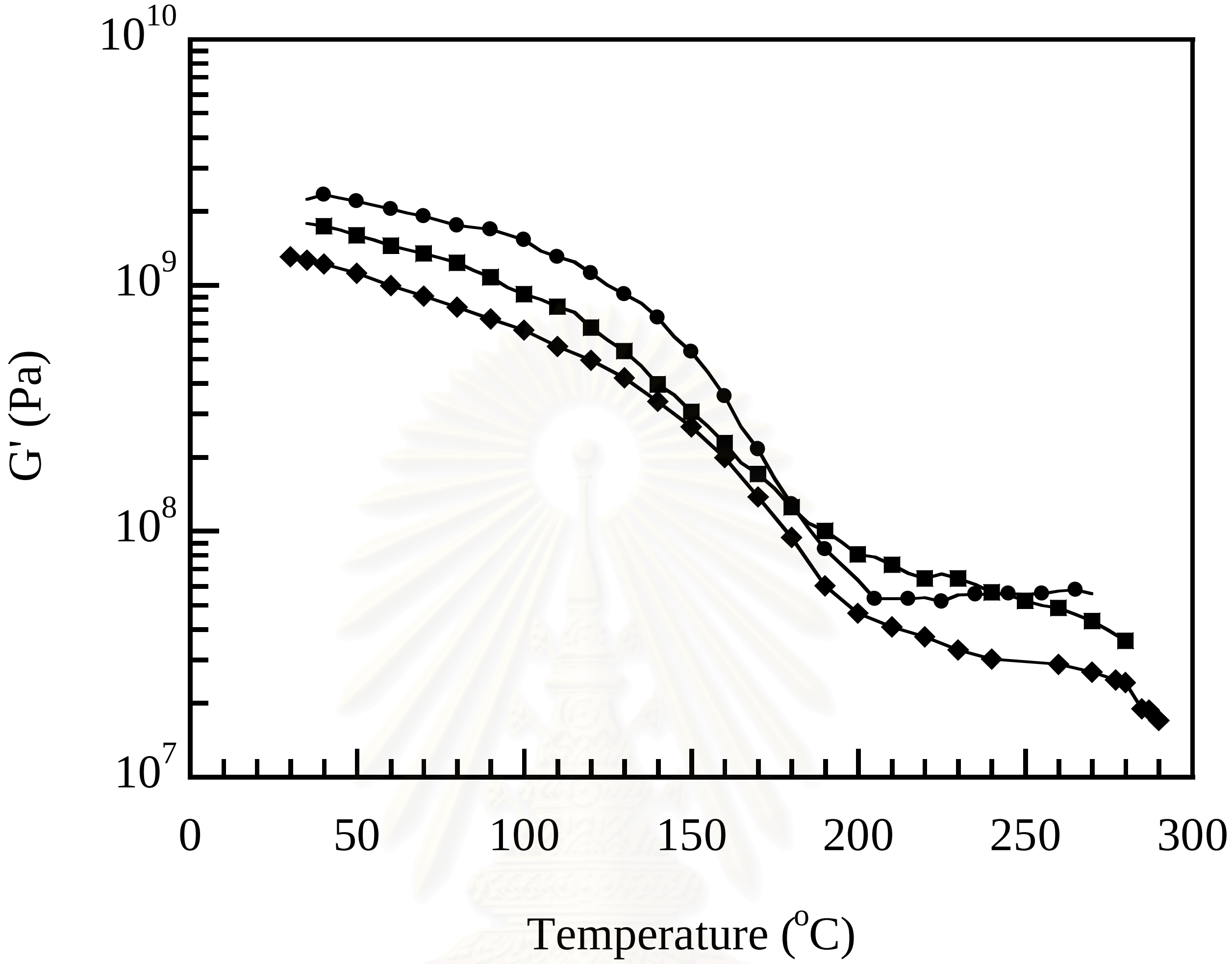

**Figure 5.29** Storage modulus of BA/PU (Diol 1000) at various compositions: (●) 80/20, (■) 70/30, (◆) 60/40.

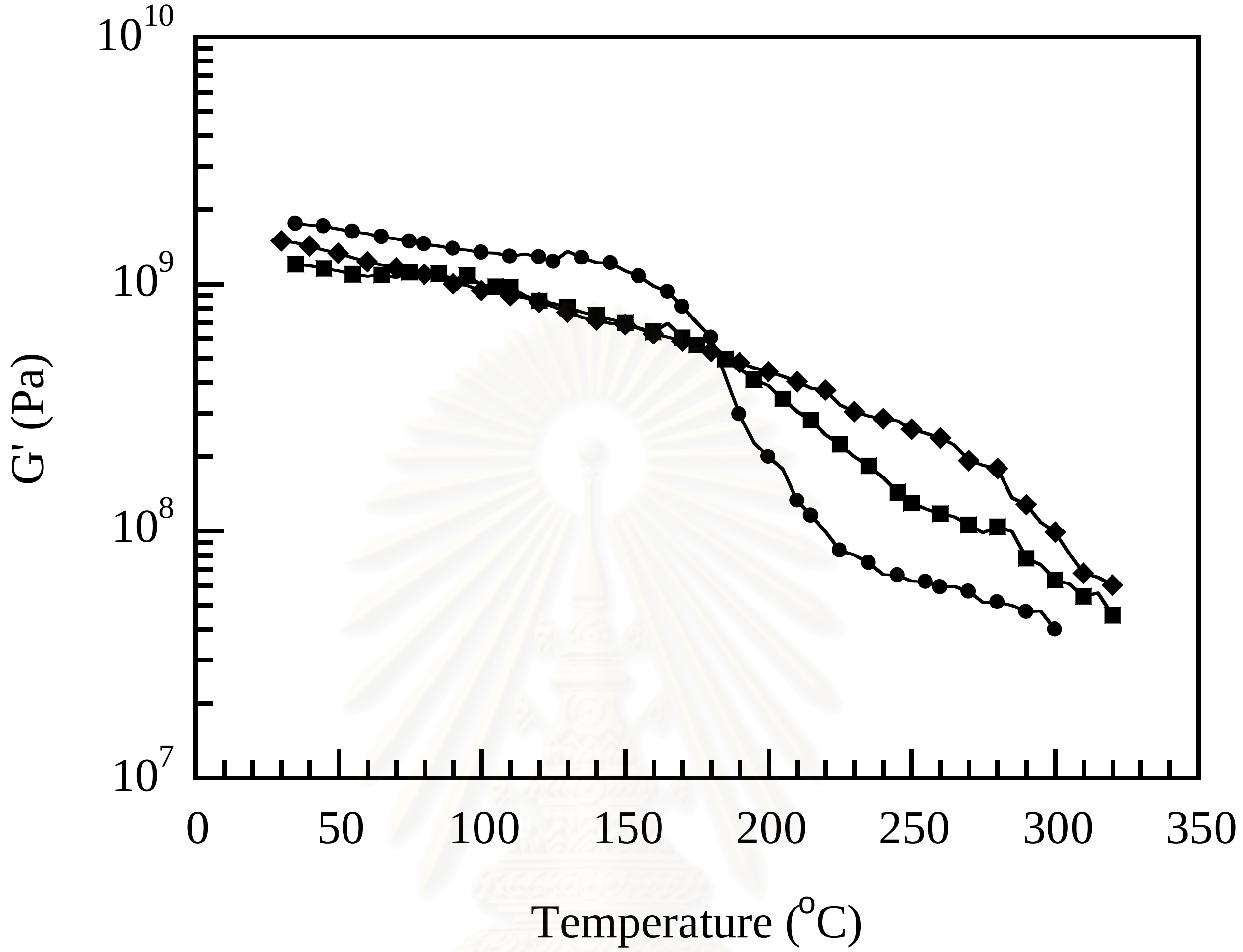

**Figure 5.30** Storage modulus of BA/PU (Diol 2000) at various compositions: (●) 80/20, (■) 70/30, (◆) 60/40.

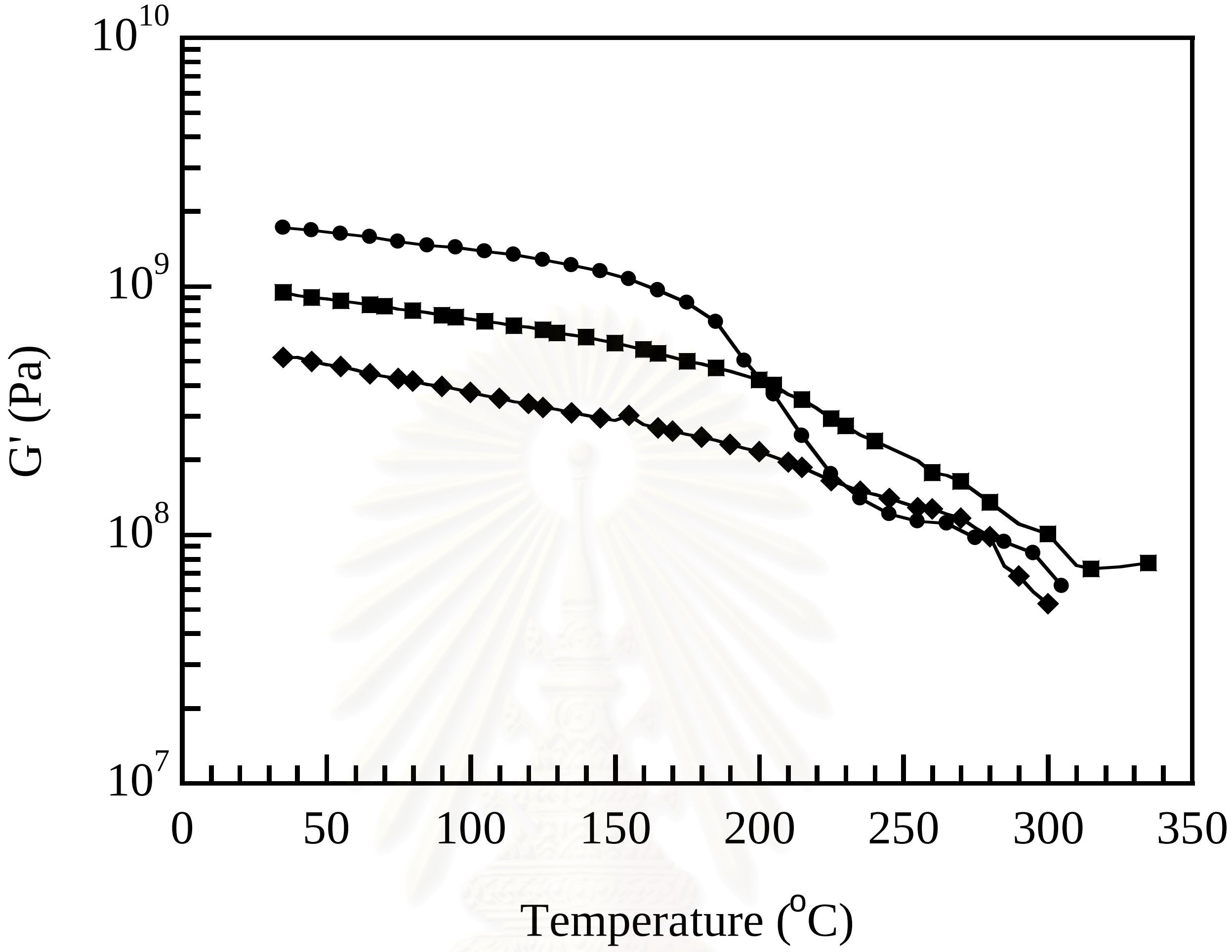

**Figure 5.31** Storage modulus of BA/PU (Diol 3000) at various compositions: (●) 80/20, (■) 70/30, (◆) 60/40.

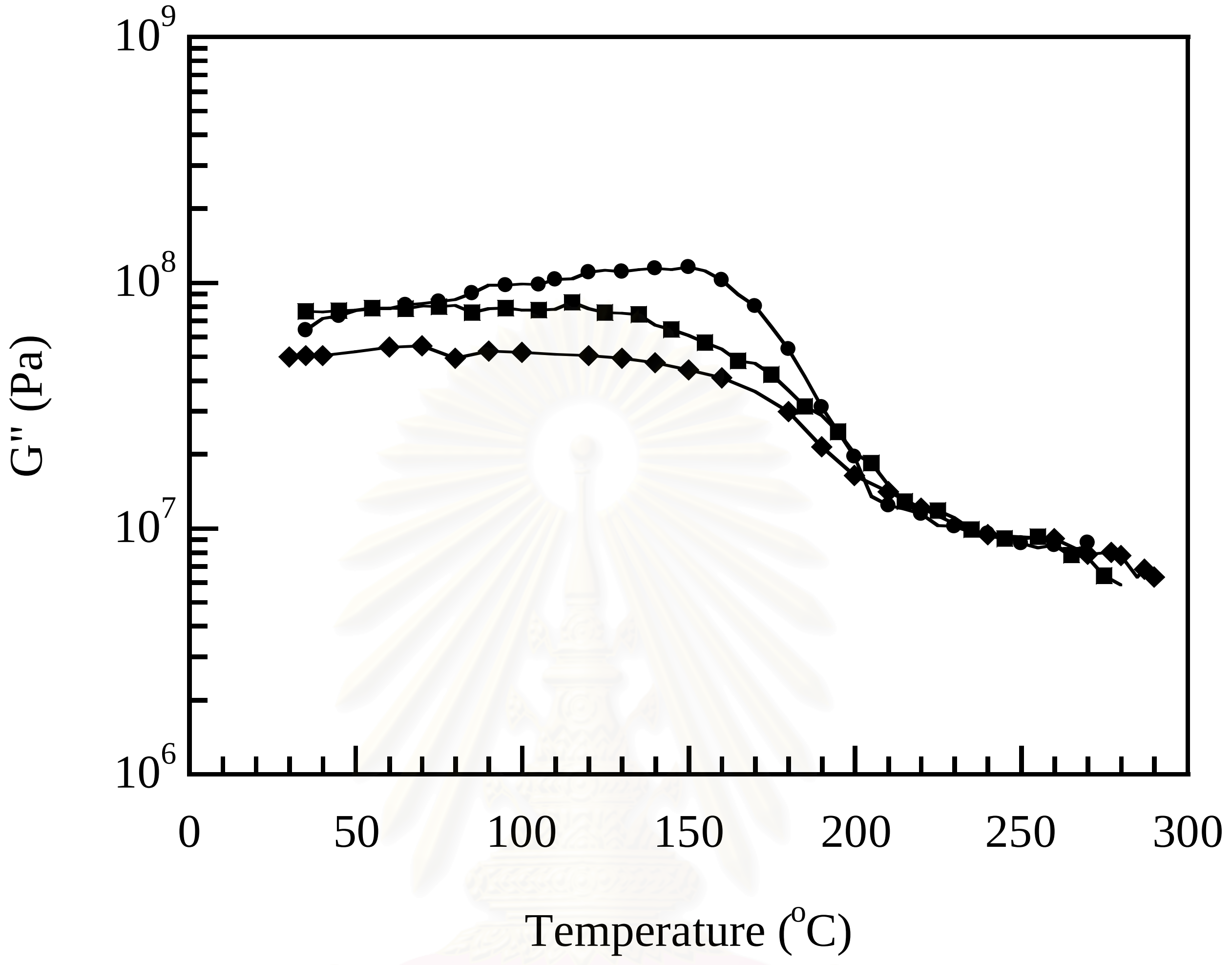

**Figure 5.32** Loss modulus of BA/PU (Diol 1000) at various compositions: (●) 80/20, (■) 70/30, (◆) 60/40.

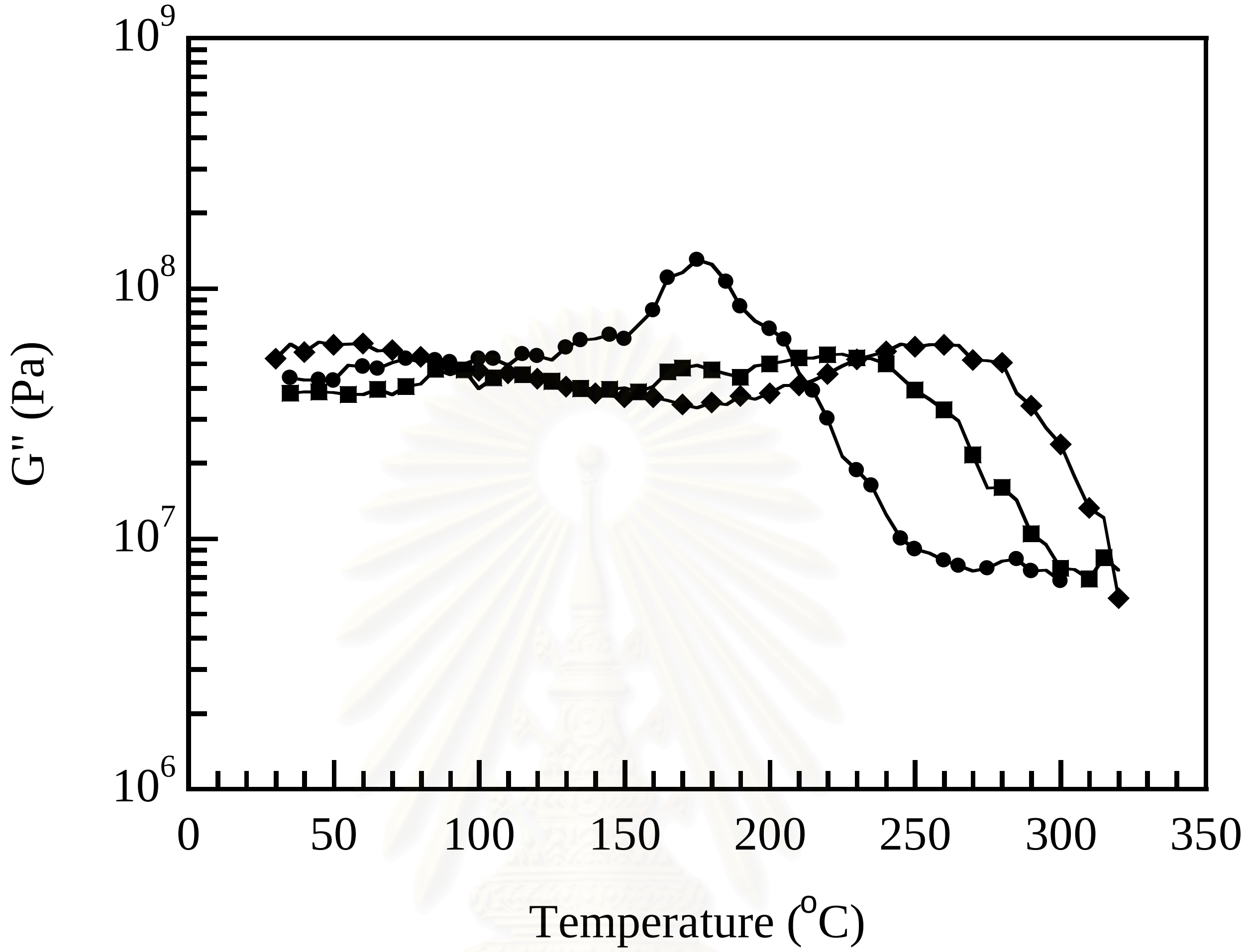

**Figure 5.33** Loss modulus of BA/PU (Diol 2000) at various compositions: (●) 80/20, (■) 70/30, (◆) 60/40.

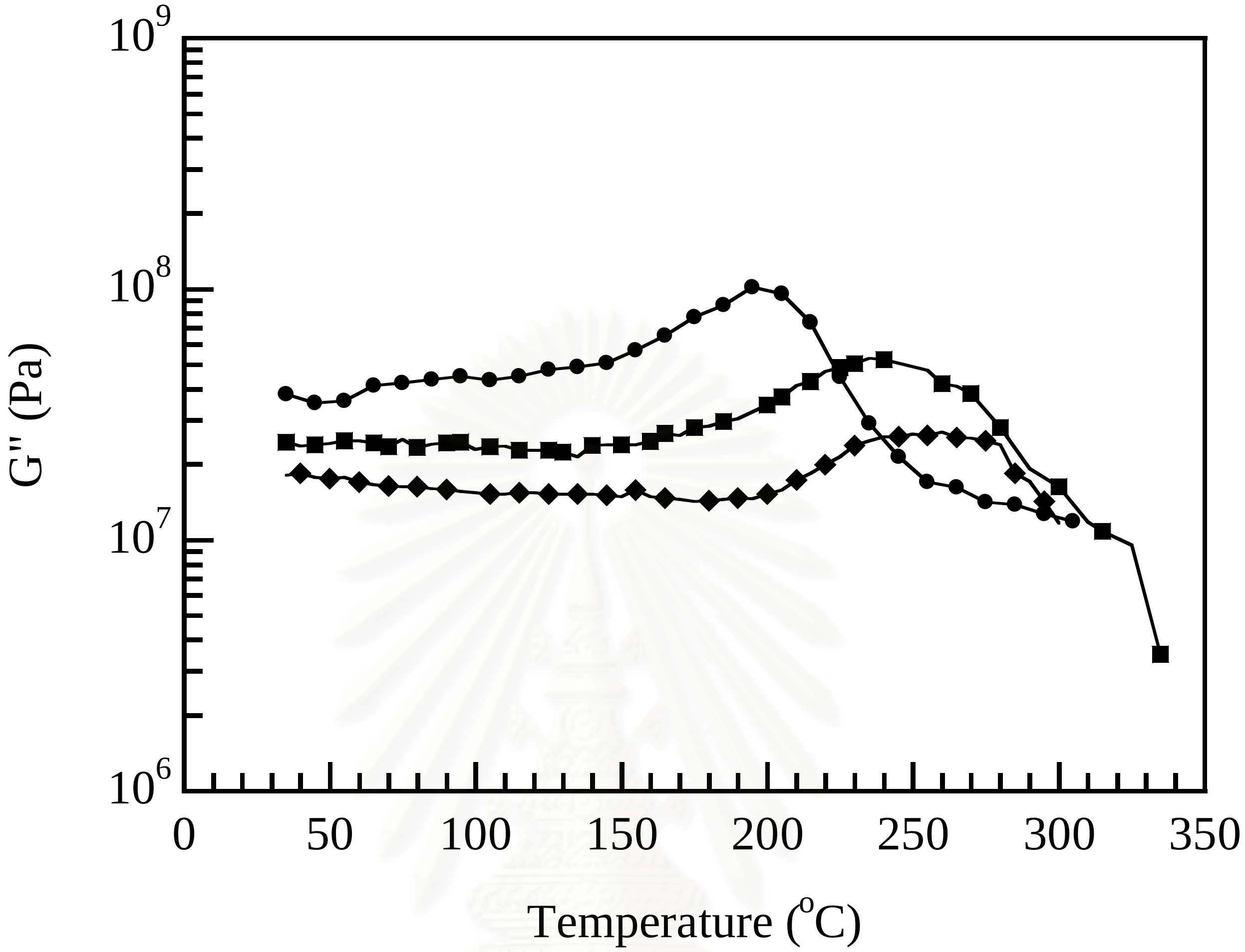

**Figure 5.34** Loss modulus of BA/PU (Diol 3000) at various compositions: (●) 80/20, (■) 70/30, (◆) 60/40.

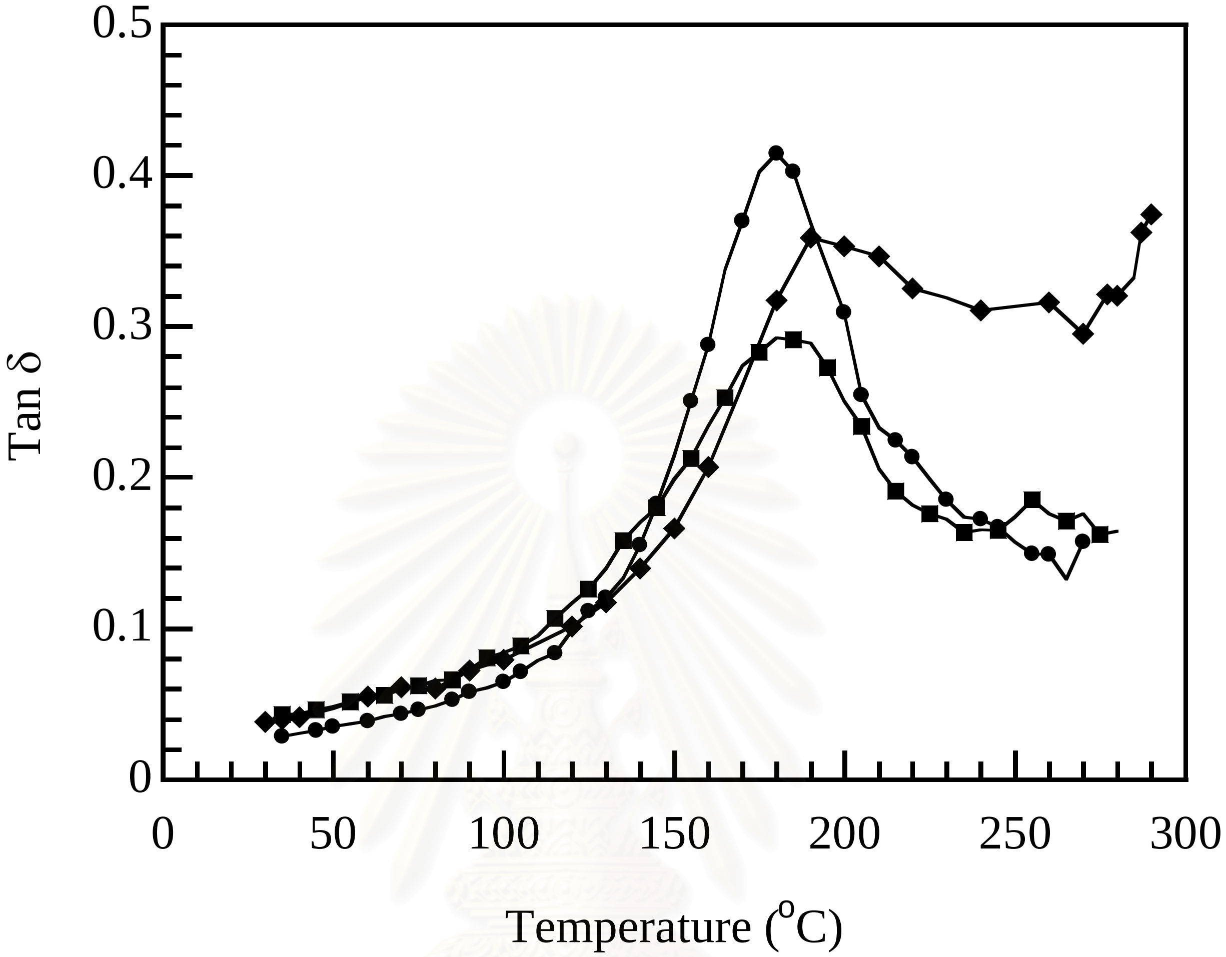

**Figure 5.35** Tan δ of BA/PU (Diol 1000) at various compositions: (●) 80/20, (■) 70/30, (◆) 60/40.

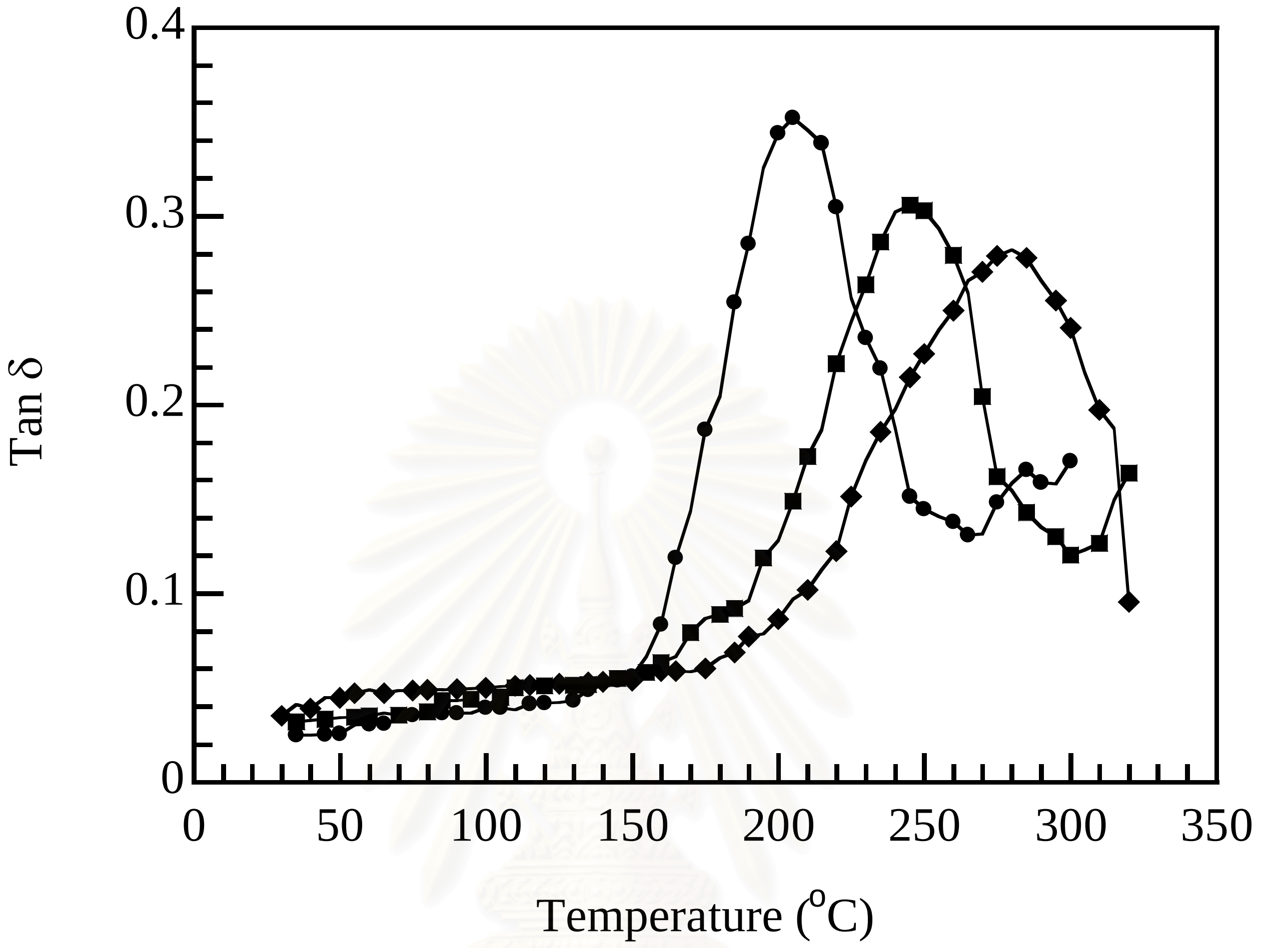

**Figure 5.36** Tan δ of BA/PU (Diol 2000) at various compositions: (●) 80/20, (■) 70/30, (◆) 60/40.

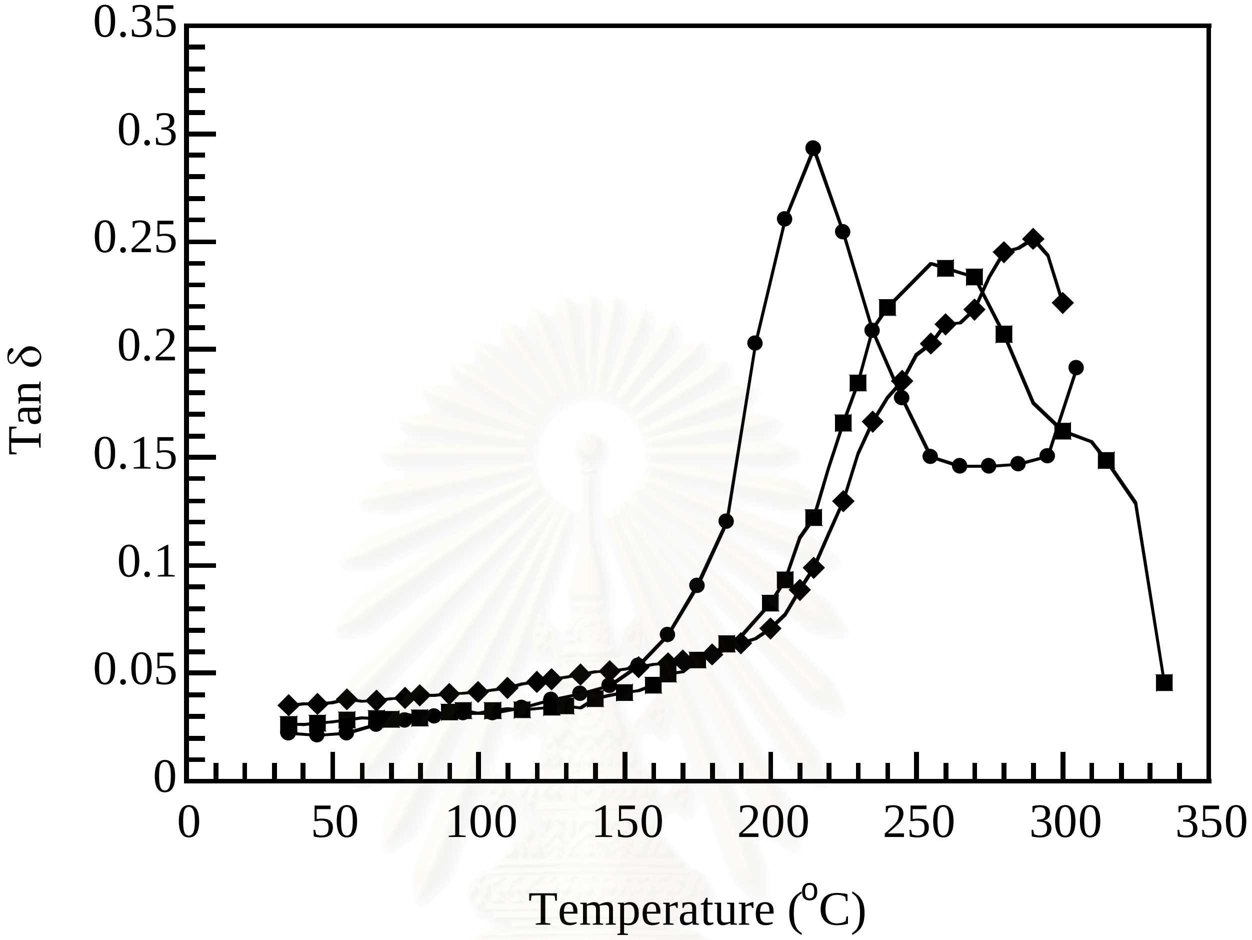

**Figure 5.37** Tan δ of BA/PU (Diol 3000) at various compositions: (●) 80/20, (■) 70/30, (◆) 60/40.

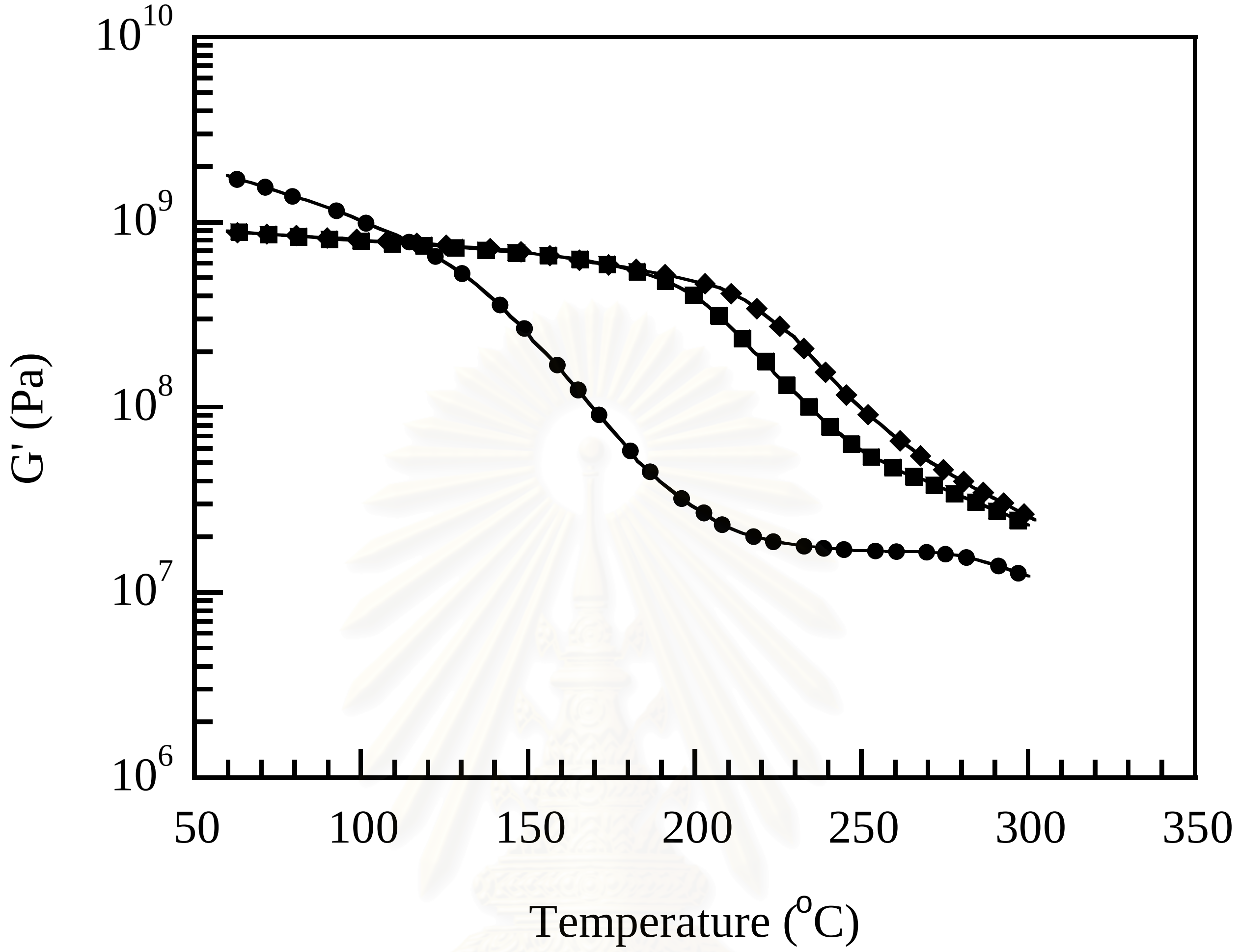

**Figure 5.38** Reproductive of storage modulus of BA/PU-70/30 at various molecular weight of PU: (●) Diol (mw 1000), (■) Diol (mw 2000), (◆) Diol (mw3000).

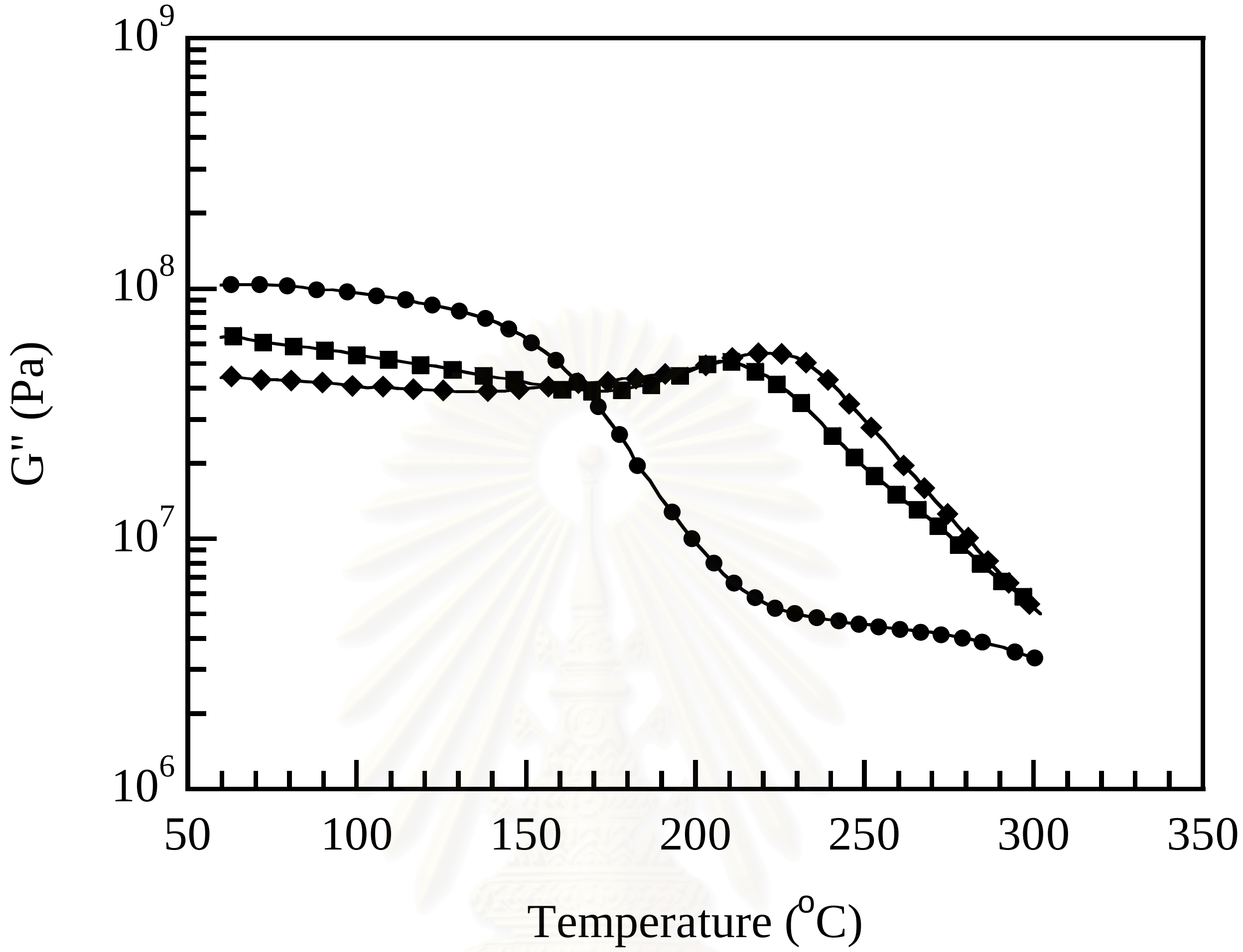

**Figure 5.39** Reproductive of loss modulus of BA/PU-70/30 at various molecular weight of PU: (●) Diol (mw 1000), (■) Diol (mw 2000), (◆) Diol (mw3000).

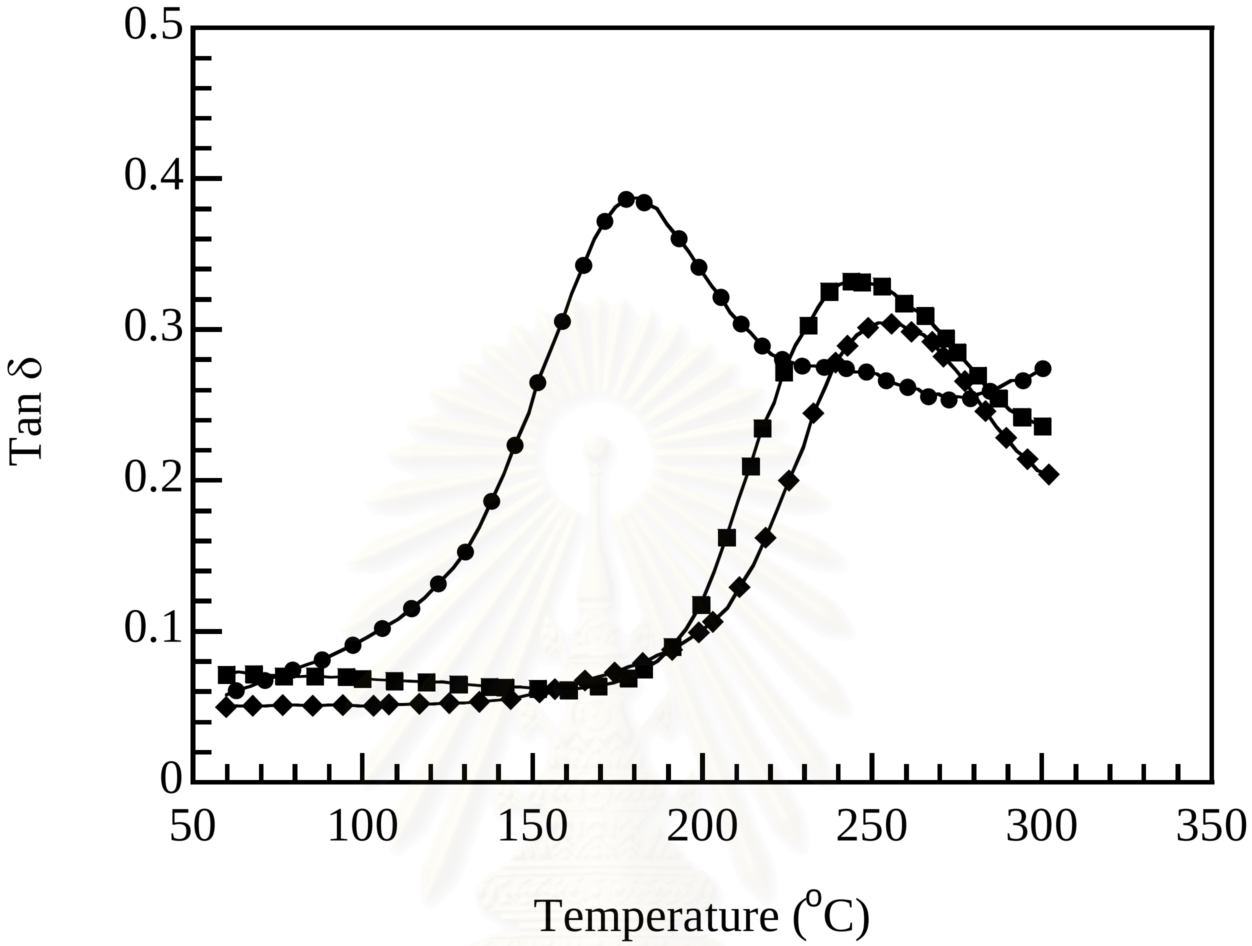

**Figure 5.40** Reproductive of tan δ of BA/PU-70/30 at various molecular weight of PU: (●) Diol (mw 1000), (■) Diol (mw 2000), (◆) Diol (mw3000).

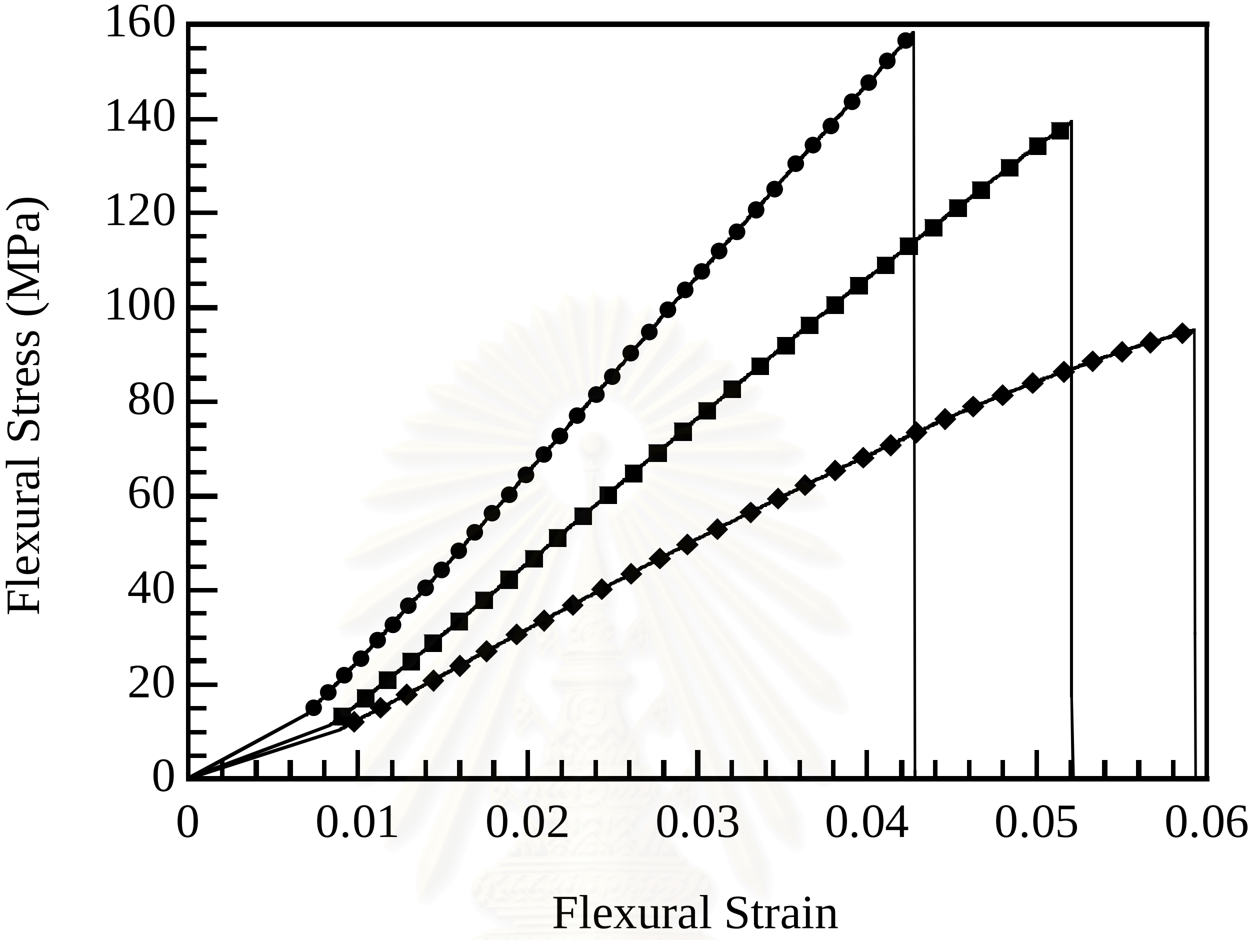

**Figure 5.41** Flexural stress & strain of BA/PU (Diol 1000) at various compositions: (●) 80/20, (■) 70/30, (◆) 60/40.

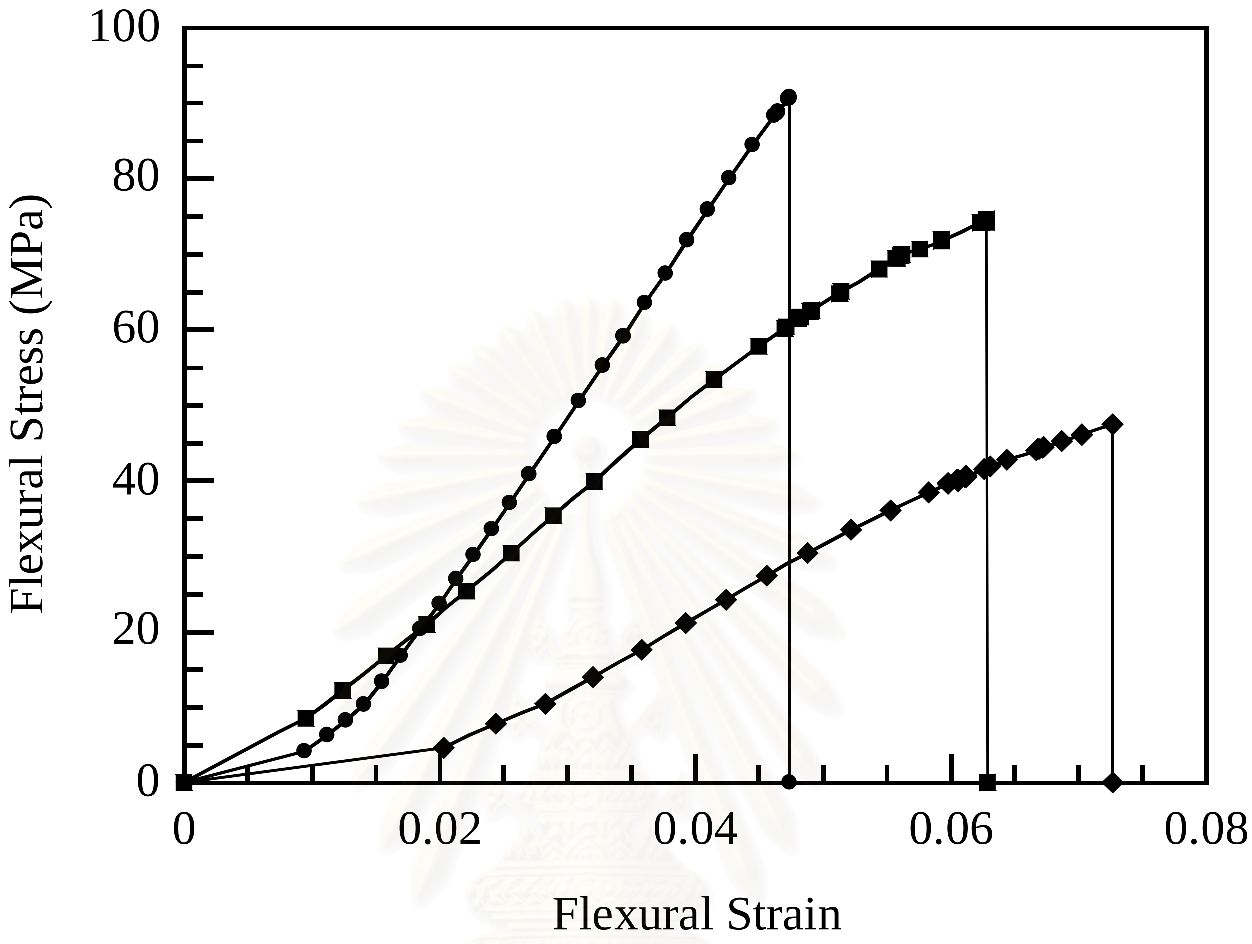

**Figure 5.42** Flexural stress & strain of BA/PU (Diol 2000) at various compositions: (●) 80/20, (■) 70/30, (◆) 60/40.

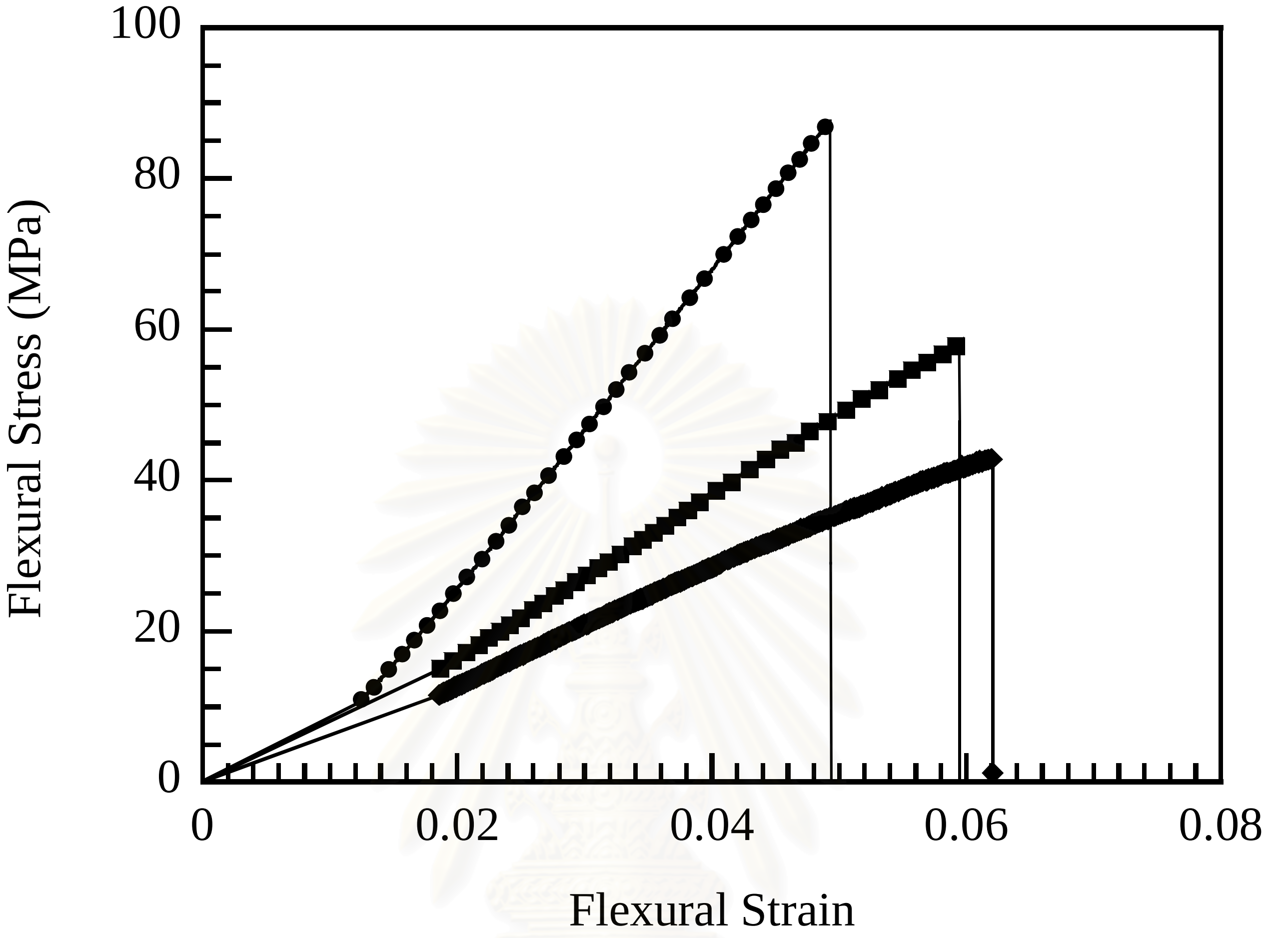

**Figure 5.43** Flexural stress & strain of BA/PU (Diol 3000) at various compositions: (●) 80/20, (■) 70/30, (◆) 60/40.

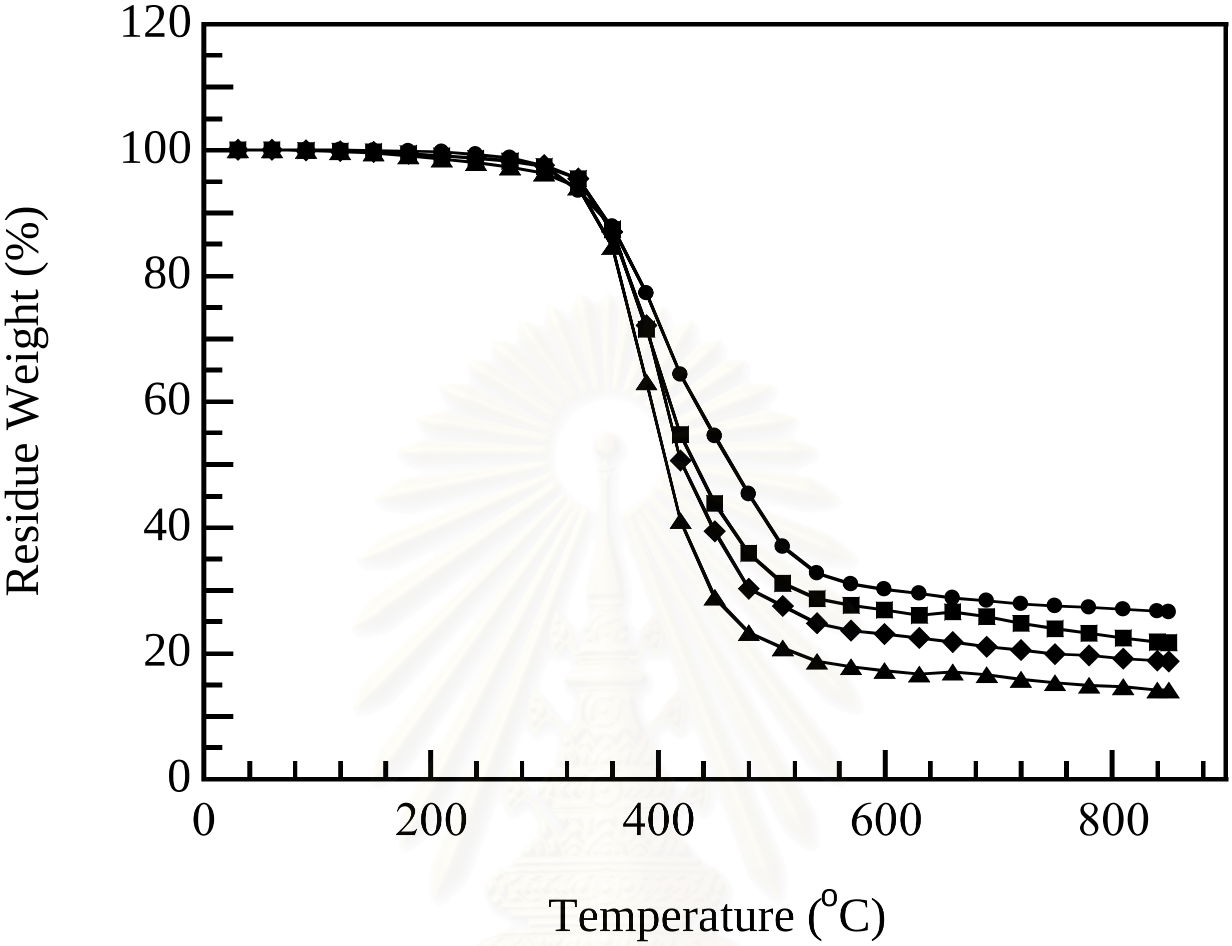

**Figure 5.44** TGA thermograms of BA/PU (Diol 1000) at various compositions: (●) 100/0, (■) 80/20, (◆) 70/30, (▲) 60/40.

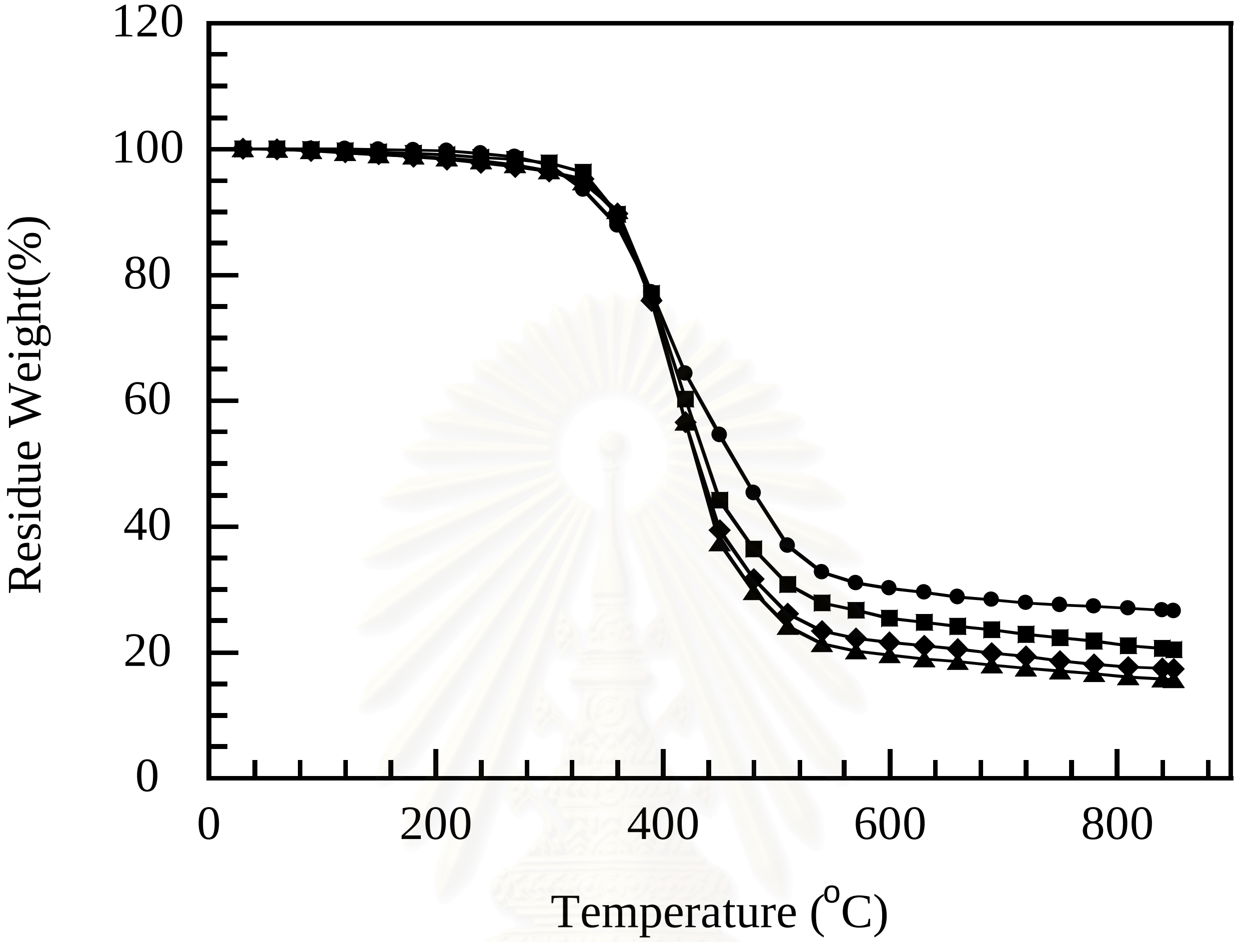

**Figure 5.45** TGA thermograms of BA/PU (Diol 2000) at various compositions: (●) 100/0, (■) 80/20, (◆) 70/30, (▲) 60/40.

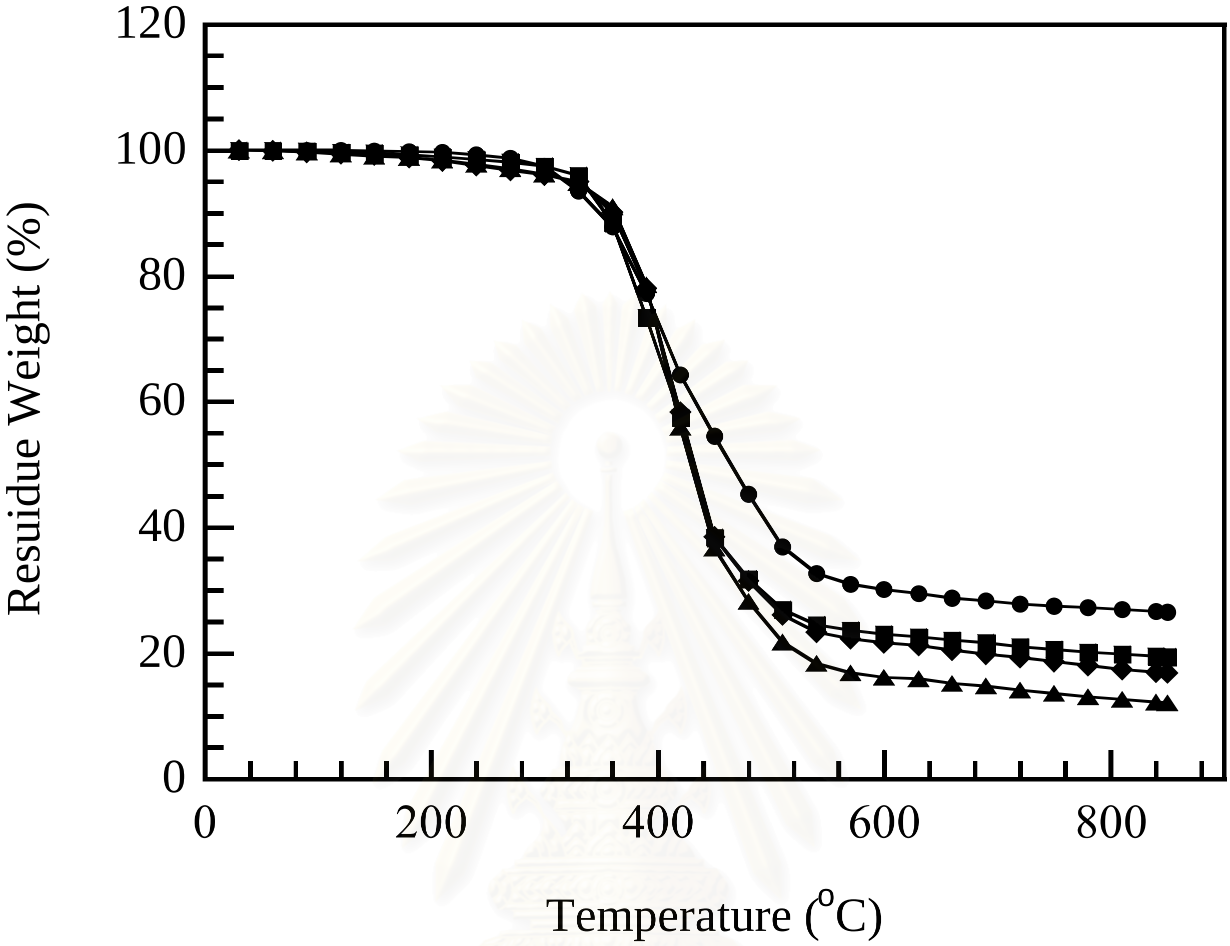

**Figure 5.46** TGA thermograms of BA/PU (Diol 3000) at various compositions: (●) 100/0, (■) 80/20, (◆) 70/30, (▲) 60/40.

# CHAPTER 6

# CONCLUSIONS

The elastomeric urethane prepolymers (based on Diol 1000, 2000 and 3000 and IPDI) and the flexible epoxy (EPO 732) were used to enhance flexibility of polybenzoxazine of bisphenol A/ aniline type. The resin mixture curing reaction was found to occur at higher temperature from the addition of both urethane prepolymer (Diol 1000, 2000 and 3000) and flexible epoxy.

The optimum compositions of BA/PU and BA/EPO 732 alloys to improve the flexural strength of materials are 90/10 and 70/30 mass fraction, respectively. This indicates that the rigid and brittle benzoxazine become the tough and ductile polymers. However,the flexural strain was found to increase with the mass fraction of PU or EPO 732.

Synergism in the glass transition temperature can be observed in the BA/PU alloys based on Diol 2000 and 3000. This phenomenon contributed by the addition of the urethane prepolymer was attributed to an improved crosslinked density from the PU incorporation. However, the flexible epoxy was found to reduce the degree of crosslinking thus loosens the network structure of BA/EPO 732 alloys resulting in the lowering of Tg with increasing the epoxy mass fraction.

The degradation temperature at 5 % weight loss is approximately 340 °C in all BA/PU alloy compositions using different molecular weights of Diol. However, the decreasing in the temperature at 5 % weight loss is observed in BA/EPO 732 system. The increasing in char yield of alloys depends on the increasing amount of BA due to the high char yield of the based polybenzoxazine.

The polybenzoxazine alloys with improved toughness and thermal properties have been developed. We suggest that the BA/PU (based on Diol 2000) alloys at the composition of 70/30 is the most optimum alloy which can enhance the flexibility and thermal properties of the polybenzoxazine.

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# Appendix A

## Microhardness test of benzoxazine/urethane prepolymer and benzoxazine/flexible epoxy alloys

Table A.1 Hardness of benzoxazine/urethane prepolymer alloys

| Compostion of alloys | Hardness | |
|---|---|---|
| | Upper | Lower |
| BA/PU 100/0 | 38.4 | 38.5 |
| | 38.7 | 38.4 |
| | 39.5 | 38.7 |
| BA/PU 90/10 | 34.4 | 33.4 |
| | 35.7 | 34.3 |
| | 33.8 | 32.3 |
| BA/PU 80/20 | 29.7 | 28.7 |
| | 27.6 | 30.0 |
| | 26.4 | 27.4 |
| BA/PU 70/30 | 19.7 | 20.0 |
| | 18.7 | 18.6 |
| | 17.4 | 19.5 |
| BA/PU 60/40 | 13.4 | 13.0 |
| | 12.6 | 11.8 |
| | 13.5 | 12.5 |
| BA/PU 50/50 | 4.8 | 4.9 |
| | 5.0 | 4.8 |
| | 4.9 | 4.8 |

Table A.2 Hardness of benzoxazine/flexible epoxy alloys

| Compostion of alloys | Hardness | |
|---|---|---|
| | Upper | Lower |
| BA/EPO 732 100/0 | 38.4 | 38.5 |
| | 38.7 | 38.4 |
| | 39.5 | 38.7 |
| BA/EPO 732 90/10 | 40.8 | 41.5 |
| | 39.4 | 40.7 |
| | 41.2 | 41.0 |
| BA/EPO 732 80/20 | 41.2 | 39.8 |
| | 41.4 | 40.0 |
| | 42.0 | 41.5 |
| BA/EPO 732 70/30 | 41.4 | 42.0 |
| | 41.3 | 42.1 |
| | 39.8 | 40.0 |
| BA/EPO 732 60/40 | 30.8 | 32.2 |
| | 32.5 | 33.3 |
| | 31.4 | 32.1 |
| BA/EPO 732 50/50 | 15.2 | 14.7 |
| | 15.5 | 15.5 |
| | 15.0 | 13.2 |

# VITAE

Mr. Surasak Pirstpindvong was born in Bangkok, Thailand on October 8, 1978. He graduted at the second level in 1993 from Yothinburana School and the high school level in 1995 from Satree Nontaburi School. In 2000, he received a Bachalor’s Degree of Chemical Engineering from the Faculty of Engineering, King Mongkut’s University of Technology Thonburi. After graduation, he pursed his graduate study from a Master Degree of Chemical Engineering, the Faculty of Engineering, Chulalongkorn University.