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EFFECT OF PROCESSING CONDITIONS ON PROPERTIES OF BENZOXAZINE-URETHANE COPOLYMERS

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มานพ สุดจิตต์จูล: ผลของภาวะการขึ้นรูปต่อสมบัติของเบนซอกซาซีน-ยูรีเทนโคพอลิเมอร์ (EFFECT OD PROCESSING CONDITIONS ON PROPERTIES OF BENZOXAZINE-URETHANE COPOLYMERS) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร.ศราวุธ ริมดุสิต, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: ดร. จันจิรา จับศิลป์, 96 หน้า.

งานวิจัยนี้มีจุดมุ่งหมายเพื่อพัฒนาสมบัติของเบนซอกซาซีน โดยอัลลอยกับยูรีเทนอิลาสโตเมอร์ที่มีความยืดหยุ่นสูง ซึ่งสามารถพัฒนาคุณสมบัติให้เบนซอกซาซีนมีความยืดหยุ่นเพิ่มมากขึ้น อีกทั้งในงานวิจัยนี้ได้มีการขึ้นรูปพอลิเมอร์อัลลอย ระหว่างเบนซอกซาซีนกับพอลิยูรีเทน ภายใต้ภาวะการขึ้นรูป 2 วิธี คือ การบ่มแบบดั้งเดิม (Traditional cure method) โดยการให้ความร้อนทันที และการบ่มแบบตามลำดับ (Sequential cure method) โดยสร้างพอลิยูรีเทนด้วยไอน้ำก่อนตามด้วยการให้ความร้อน เพื่อศึกษาอิทธิพลของภาวะการขึ้นรูปต่อสมบัติทางกลและทางความร้อน รวมถึงการหาสัดส่วนที่เหมาะสมระหว่างเบนซอกซาซีนและยูรีเทนพรีพอลิเมอร์จากการบ่มด้วยทั้งสองวิธี จากการทดลองพบว่าช่วงอุณหภูมิในการขึ้นรูปของเรซินผสมเบนซอกซาซีน/ยูรีเทนมีค่ากว้างมากขึ้นเมื่อทำการเพิ่มปริมาณของยูรีเทน โดยเฉพาะอย่างยิ่งการเกิดงานร่วม (synergy) ของอุณหภูมิการเปลี่ยนสถานะคล้ายแก้วของทั้งสองภาวะการขึ้นรูปสามารถเห็นได้อย่างชัดเจน นั่นคือ อุณหภูมิการเปลี่ยนสถานะคล้ายแก้วของระบบเบนซอกซาซีน/ยูรีเทน ที่ได้จะมีค่าสูงกว่าของพอลิเบนซอกซาซีน (186 องศาเซลเซียส) และ ยูรีเทน (-61 องศาเซลเซียส) และอุณหภูมิการเปลี่ยนสถานะคล้ายแก้วของระบบเบนซอกซาซีน/ยูรีเทนจะเพิ่มมากขึ้นตามปริมาณยูรีเทน พรีพอลิเมอร์ โดยค่าสูงสุดของอุณหภูมิการเปลี่ยนสถานะคล้ายแก้วพบที่ 260 ภายใต้สภาวะการบ่มแบบตามลำดับ และ 252 องศาเซลเซียส ภายใต้สภาวะการบ่มแบบดั้งเดิม ในสัดส่วนของระบบเบนซอกซาซีน/ยูรีเทน ที่ 60/40 นอกจากนี้อุณหภูมิการสลายตัวทางความร้อนของทั้งสองภาวะการขึ้นรูปเพิ่มขึ้นเล็กน้อยถึงปริมาณพอลิยูรีเทน 40 % โดยค่าสูงสุดของอุณหภูมิการสลายตัวทางความร้อนที่ 5% ของน้ำหนักที่หายไปพบที่ 329 องศาเซลเซียส ภายใต้สภาวะการบ่มแบบตามลำดับ และ 348 องศาเซลเซียส ภายใต้สภาวะการบ่มแบบดั้งเดิม ในสัดส่วนของระบบเบนซอกซาซีน/ยูรีเทน ที่ 60/40 มากไปกว่านั้นยังพบว่าปริมาณเถ้าของทั้งสองภาวะการขึ้นรูปจะสูงขึ้นตามสัดส่วนของเบนซอกซาซีน นอกจากนี้ พบว่าการมีโครงสร้างของเบนซอกซาซีนอยู่ในพอลิยูรีเทน สามารถช่วยลดการบวมตัวและการแตกโครงสร้างพอลิของยูรีเทนในคลอโรฟลอม สุดท้ายนี้ พบว่าภาวะการขึ้นรูปทั้งสองของระบบเบนซอกซาซีน-ยูริเทนอัลลอย ไม่ได้มีผลกระทบอย่างสำคัญต่อสมบัติดังที่กล่าวมา อย่างไรก็ตามอิทธิพลที่หลักต่อสมบัติของระบบเบนซอกซาซีน-ยูริเทน อัลลอย คือ สัดส่วนระหว่างเบนซอกซาซีนต่อยูรีเทนพรีพอลิเมอร์ในชิ้นงาน

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MANOP SUDJIDJUNE: EFFECT OF PROCESSING CONDITIONS ON PROPERTIES OF BENZOXAZINE-URETHANE COPOLYMERS. THESIS ADVISOR: ASSOC. PROF. SARAWUT RIMDUSIT, Ph.D., THESIS CO-ADVISOR: CHANCHIRA JUBSILP, D. Eng., 96 pp.

The purpose of this research is to improve performance of polybenzoxazine by alloying with an excellent flexible urethane elastomer which can enhance the flexibility of polybenzoxazine. The polymer alloys of polybenzoxazine and polyurethane was prepared by processing conditions in two methods i.e. Traditional cure method by immediate using thermal treated and Sequential cure method by firstly, moisture in order to produce urethane network following thermal treated. The effects of processing methods were investigated in term of thermal and mechanical properties. In addition, to determine suitable alloy compositions between benzoxazine and urethane resins based on the above processing techniques. The experimental results revealed that the processing window of the BA-a/PU resin mixtures was widened with the amount of the urethane prepolymer. Especially, the synergistic behavior of glass transition temperatures (T_g) of BA-a/PU alloys under both processing conditions is clearly observed. T_g's of the BA-a/PU alloys under both processing conditions were significantly greater than those of the neat resins, i.e. BA-a (T_g = 186°C) and PU (T_g = -61°C). T_g's of the BA-a/PU alloys increase with the mass fraction of the PU. The highest value of glass transition temperature was 260 °C under sequential cure method and 252 °C under traditional cure method at BA-a/PU 60/40. Furthermore, the degradation temperature was also about the same up to the PU content of 40 % by weight. The highest value of initial decomposition temperature at 5% weight was 329 °C under sequential cure method and 348 °C under traditional cure method at BA-a/PU 60/40. Moreover, the char yield of the alloys under both processing condition was enhanced with increasing amount of the benzoxazine mass fraction. In addition, the incorporate of benzoxazine structure with polyurethane can reduce their swollen and broken network in chloroform. Finally, the processing conditions of BA-a/PU alloys have no significant effect on above properties. On the other hand, the composition of BA-a/PU in alloys should be considered as the mainly influence.

Department : Chemical Engineering   Student's Signature Manop Sudjidjune.
Field of Study : Chemical Engineering   Advisor's Signature
Academic Year : 2009   Co-Advisor's Signature Chanchira Jubsilp

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CHAPTER I

INTRODUCTION

1.1 Overview

Recently, polybenzoxazine are a newly developed class of phenolic resins. These novel types of phenolic resins have not only the characteristics of traditional phenolic resins such as excellent thermal properties, flame retardance and high char yield, but also unique characteristics such as molecular design flexibility, very low moisture absorption, near zero shrinkage upon polymerization, low melt viscosities, and low dielectric constant [1]. Polybenzoxazine can be synthesized using the patented solventless technology to yield a clean precursor without the need for solvent elimination or monomer purification, which no creates serious threats to environment and human health [2]. Moreover, polybenzoxazine have been produced and developed in many chemical industries. For example, benzoxazine monomer was synthesized in laboratory of Shikoku Chemical Operation [3]. Epsilon™ Products in Henkel Corporation [4] produce polybenzoxazine for aerospace applications. The benzoxazine chemistry used in Epsilon™ offers several clear advantages over a high performance epoxy system:

- Low moisture absorption
- High temperature performance
- High hot/wet property retention
- High compression strength and modulus
- Good adhesion to fibers
- Excellent FST performance.

Moreover, Huntsman Corporation [5] produces polybenzoxazine for aerospace applications because it has many advantages. Polybenzoxazine with different backbones are available. Several products have been developed for Laminating and Structural Composite application. Sales are growing in Electronic applications. In addition, benzoxazine resins are also promising candidates for aerospace composites due to their performance such as high glass transition temperature, excellent mechanical properties, low moisture absorption and flame retardancy.

Figure1.1. The Epsilon™ benzoxazine family of resins has a unique orange color [4].

However, a number of shortcomings are also related with these materials that include brittleness, poor shelf life, usage of acid or base catalysts, release of by products, formation of micro voids during cure, and so forth [6]. Another shortcoming is the difficulty to process into thin film from the typical monomer because most monomers are usually powder. Moreover, the formed polymers are brittle as a consequence of the short molecular weight of the network structure. So, addition or alloying of elastromeric materials to brittle resins is a well-known approach to improve the flexibility. In this thesis, the toughness of the polybenzoxazines was improved by alloying with polyurethane.

Polyurethane was excellent flexibility, outstanding resistance, high abrasion resistance but low resistance to moisture and poor thermal stability [7]. Moreover, urethane prepolymer is formed network by reaction with water present in the atmosphere. So, there are many studies of sequential IPNs with urethane. For example, **S.B. Pandit, and V.M. Nadkarni** [8] synthesized sequential interconnected interpenetrating polymer networks of polyurethane and polystyrene by cured at room temperature to complete the PU network formation, followed by a postcure with thermal to complete the polymerization of styrene. **J. Yang et al.** [9] prepared polyurethane - polyacrylate interpenetrating networks with three types of urethane-acrylate IPN’s, two sequential and one simultaneous. The one types of sequential IPN prepared from PU network gelled then kept at room temperature allow the urethane polymerization to complete the PU network.

Figure 1.2. Polyurethane applications [10].

There have been numerous studies on the combinations of urethane and benzoxazine resins for improvement of mechanical properties and thermal stability. For example, **T. Takeichi et al.** [11] reported combinations of polyurethane(PU) that was synthesized from 2,4-tolylene diisocyanate (TDI) and polyethylene adipate polyol (MW ca. 1000) in 2 : 1 molar ratio and benzoxazine (BA-a) show only one glass transition temperature (Tg). The Tg increased with the increase of BA-a content. Furthermore, thermal stability of PU was greatly enhanced even with the incorporation of a small amount of Ba. **S. Rimdusit et al.** [12] reported the comparison of benzoxazine alloying with isophorone diisocyanate (IPDI)-based urethane prepolymers and with flexible epoxy. Alloying with urethane prepolymer can improve the flexibility of the rigid polybenzoxazine. Interestingly, the positive deviation on the glass transition temperature (Tg) of the benzoxazine–urethane alloys was clearly observed, i.e. Tg of the benzoxazine–urethane alloys were significantly greater (Tg beyond 200^{o}C) than those of the parent polymers (Tg of polybenzoxazine = 160^{o}C; Tg of urethane = -70^{o}C). Moreover, the Tg of benzoxazine–urethane alloy was found to increase with an increase of the urethane content. **H. Yeganeh et al.** [13] improved thermal stability of Polybenzoxazine Modified Polyurethanes .The result showed that thermal stability and flammability of the samples, which considerably improved in comparison to common thermoset polyurethanes, was depended on BA-a content of blends and increased with increasing of BA-a content. In addition, BA-a/EPU (50/50) sample showed the most favor amount of dissipation factor and the least favored value of dielectric constant (DC). Low moisture uptake and excellent solvent resistance of these blends were other fascinating factors that increase the merit of this new class of materials for application as electrical insulator.

The many research were not interested in the effect of processing condition on properties of combinations of urethane and benzoxazine resins. So, in this study, we prepared polymer alloys of polyurethane and polybenzoxazine, which processing conditions in two methods (traditional step cure and sequential cure). The curing behavior, mechanical properties and thermal stability of copolymer are investigated.

1.2 Objectives

1. To study effects of processing methods i.e. traditional step cure and sequential cure, on thermal and mechanical properties of benzoxazine-urethane polymer alloys.
2. To determine suitable alloy compositions between benzoxazine and urethane resins based on the above processing techniques.

1.3 Scopes of Research

1. Synthesis of benzoxazine resin by solventless synthesis technology.
2. Synthesis of urethane prepolymer by diol (MW = 2000) using toluene diisocyanate (TDI).
3. Preparation of polymeric alloys between the benzoxazine resin and urethane prepolymers at various weight ratios (BA-a: PU) i.e. 100:0, 80:20, 60:40, 40:60, 20:80 and 0:100.
4. Processing condition in two methods (Traditional step cure and Sequential cure).
5. Evaluation of the curing condition and behaviors of the copolymers.
    - Determining functional groups by FT-IR.
    - Finding curing condition by DSC and Rheometer.
6. Studying the effect of processing conditions on mechanical properties of Benzoxazine-Urethane copolymers**.**
    - Dynamic mechanical analysis (DMA).
7. Investigate the effect of processing conditions on thermal properies of the Benzoxazine-Urethane copolymers.
    - Thermogravimetric analysis (TGA).
8. Studying the effect of processing conditions on degradation in chloroform of the Benzoxazine-Urethane copolymers**.**
    - Swelling degree and Gel content.

CHAPTER II

THEORY

2.1 Benzoxazine Resin

These new materials, belong to the addition cure phenolics family were developed to combine the thermal properties and flame retardance of phenolics and the mechanical performance and molecular design flexibility of advanced epoxy systems.

The polybenzoxazines overcome several shortcomings of conventional novolac and resole-type phenolic resins, while retaining their benefits. benzoxazine resins are expected to replace traditional phenolics, polyesters, vinyl esters, epoxies, BMI, cyanate esters and polyimides in many respects. The molecular structure of polybenzoxazine offers superb design flexibility that allows properties of the cured material to be controlled for specific requirements of a wide variety of individual requirements. The physical and mechanical properties of these new polybenzoxazines are shown to compare very favorably with those of conventional phenolic and epoxy resins. The resin permits development of new applications by utilizing some of their unique features such as [14]

- Near zero volumetric change upon polymerization
- Low water absorption
- Tg much higher than cure temperature
- Fast mechanical property build-up as a function of degree of polymerization
- High char-yield
- Low CTE
- Low viscosity
- Excellent electrical properties

However, there are some shortcomings for polybenzoxazines. These include the brittleness of the cured resin, which is a common problem for thermosets, and relatively high temperature (ca. 200 ^{o}C) needed for the ring-opening polymerization, although acidic catalyst is effective to lower the cure temperature. Another shortcoming is the difficulty to process into thin film from the typical monomers because most monomers are powder and the polymers are brittle [15]. Benzoxazine monomer can be synthesized using the patented solventless technology to yield a clean precursor without the need for solvent elimination or monomer purification, which no creates serious threats to environment and human health [2].

Benzoxazine monomers are typically synthesized using phenol, formaldehyde and amine (aliphatic or aromatic) as starting materials either by employing solution or solventless methods. Various types of benzoxazine monomer can be synthesized using various phenols and amines with different substitution groups attached [16].

In this work, we use Bifunctional benzoxazine monomer which synthesized from bisphenol-A, formaldehyde, aniline [17] in our laboratory (show in figure 2.1). Upon heating, Bi-functional benzoxazines form a high molecular weight polymer via a ring opening mechanism (show in figure 2.2). It has been proposed that, the ring-opening initiation of benzoxazine results the formation of a carbocation and an iminium ion which in equilibrium [18]. Polymerization proceeds via the electrophilic substitution by the carbocation to the benzene ring. This transfer occurs preferentially at the free ortho and para position of the phenol group. The stability of the iminium ion greatly affects the propagation rate because carbocation is responsible for propagation. Though, several authors have proposed different mechanism of thermal curing of benzoxazine [6].

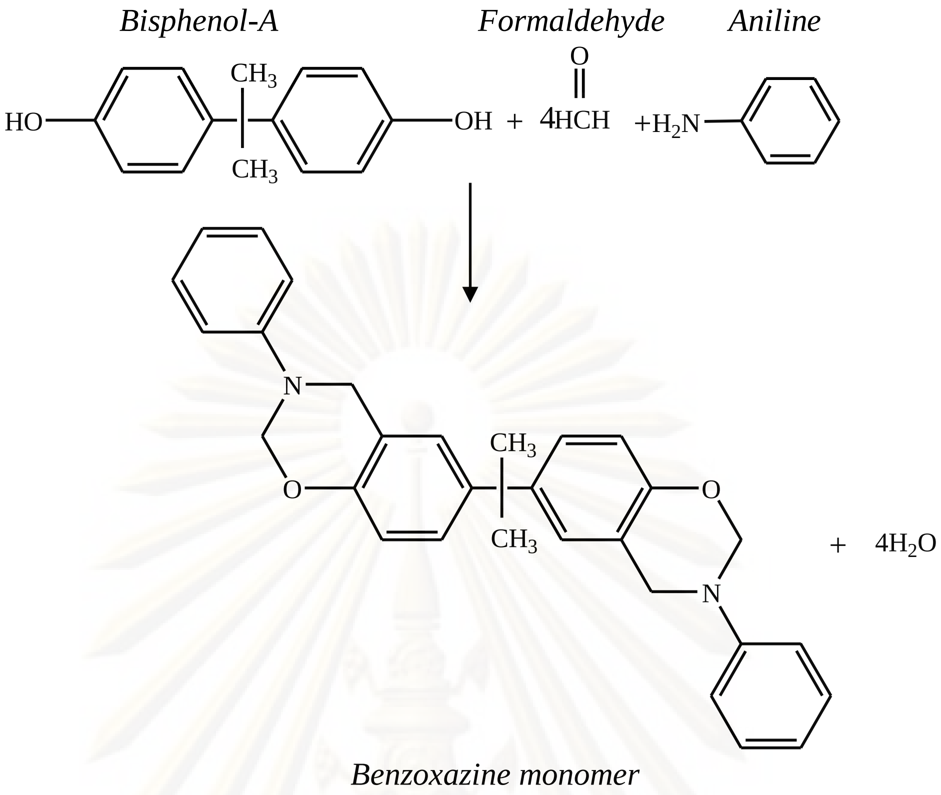


Figure 2.1. Synthesis of bifunctional benzoxazine monomer based on bisphenol A.

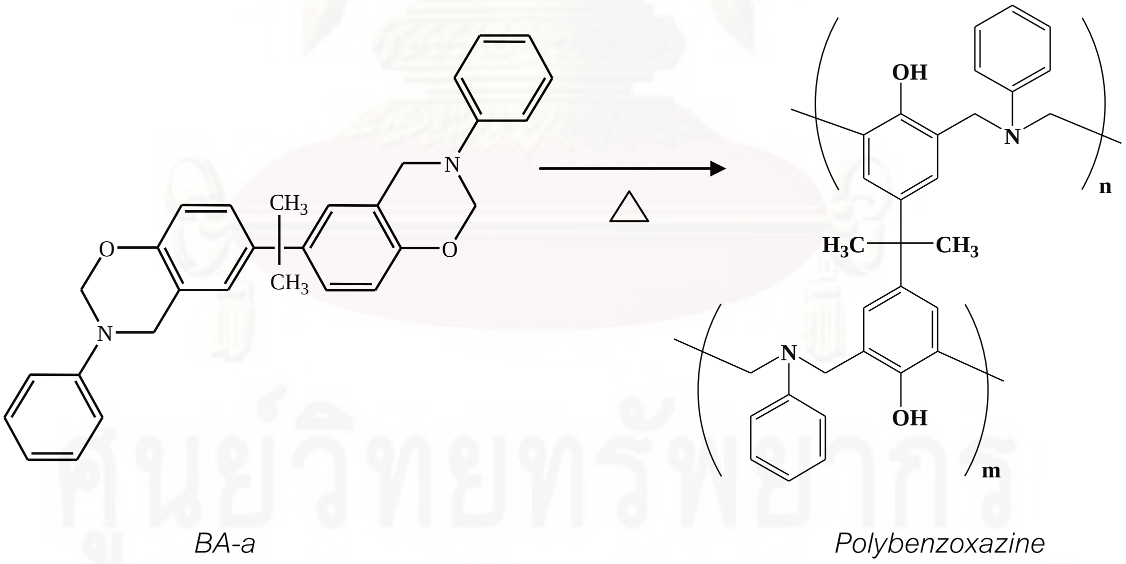


Figure 2.2. Ring-opening polymerization of bifunctional benzoxazine [11].

2.2 Polyurethane

Polyurethane are defined as polymers which contain urethane groups (-NH-CO-O-) in the main polymer chain. The urethane group results from the interaction of an isocyanate and a hydroxyl compound (see Equation 2.1).

$$\text{R-NCO} + \text{HO-R'} \longrightarrow \text{R-NH-CO-O-R'} \qquad (2.1)$$

It will be apparent that this reaction leads to polyurethane when multifunctional reactants are used. When a diisocyanate and a diol react together a linear polyurethane is obtained whilst a diisocyanate and a polyhydric compound (polyol) lead to a cross-linked polymer[19]. Polyurethane have excellent flexibility, outstanding resistance, high abrasion resistance but low resistance to moisture and poor thermal stability. Polyurethane is used in many applications such as automotive, forniture, construction, thermal insulation and footwear [7].

2.3 Polyurethane Prepolymer Technique [20]

Prepolymers are formed by the reaction of a diisocyanate with an oligo-polyol, at the molar ratio [diisocyanate]/[OH group] of 1/1, in fact only one group of diisocyanate reacts with one hydroxyl group of the polyol. A structure with free terminal -NCO groups called 'prepolymer' is produced (see Equation 2.2):

$$\underset{\text{Diisocyanate}}{\text{2OCN-R-NCO}} + \underset{\text{Oligo-diol}}{\text{HO}\sim\sim\sim\text{OH}} \xrightarrow{70\text{-}90\ ^{\circ}\text{C}} \underset{\text{Prepolymer}}{\text{OCN-R-NHCOC}\sim\sim\sim\text{OCNOCH-R-NCO}} \quad (2.2)$$

By the reaction of a prepolymer with a chain extender such as: ethylene glycol, diethylene glycol, 1,4 butane diol or a diamine, the high molecular weight polyurethanes are formed (see Equation 2.3).

$$\underset{\text{Prepolymer}}{\text{OCONH-R-NHCOO}\sim\sim\sim\text{OCONH-R-NCO}} + \underset{\text{Oligo-diol}}{\text{HO-R'-OH}} \longrightarrow \qquad (2.3)$$

$$\underset{\text{Polyurethane}}{[\text{-O-R'-O-OCONHRNHCOO}\sim\sim\sim\text{OCONHRNCOO-R'-O-}]_n}$$

This 'prepolymer' technique is frequently used in the manufacture of polyurethane elastomers, coatings, sealants, flexible foams, monocomponent polyurethanes, etc.

In the special case of monocomponent polyurethanes, the single partner of the reaction is the prepolymer. The prepolymer is extended to a high MW polymer by reaction with water present in the atmosphere. Water, is in fact, a chain extender and the resulting high MW polymer has both bonds: urethane and urea bonds (see Equation 2.4 or show in figure 2.3).

$$\underset{\text{Prepolymer}}{\text{n OCONH-R-HNCOO}\sim\sim\sim\text{OCONH-R-NCO}} + \underset{\text{Water}}{\text{n H-O-H}} \longrightarrow \qquad (2.4)$$

$$\underset{\text{Polyurethane}}{[\text{-OCONH-R-HNOCN-R-HNCOO}\sim\sim\sim\text{OCONH-R-HNCONH-R-HNCOO-}]_n}$$

If a prepolymer derived from an oligo-triol or an oligo-polyol, having three or more terminal NCO groups is used, if it is in contact with atmospheric humidity, crosslinked polyurethanes are obtained.

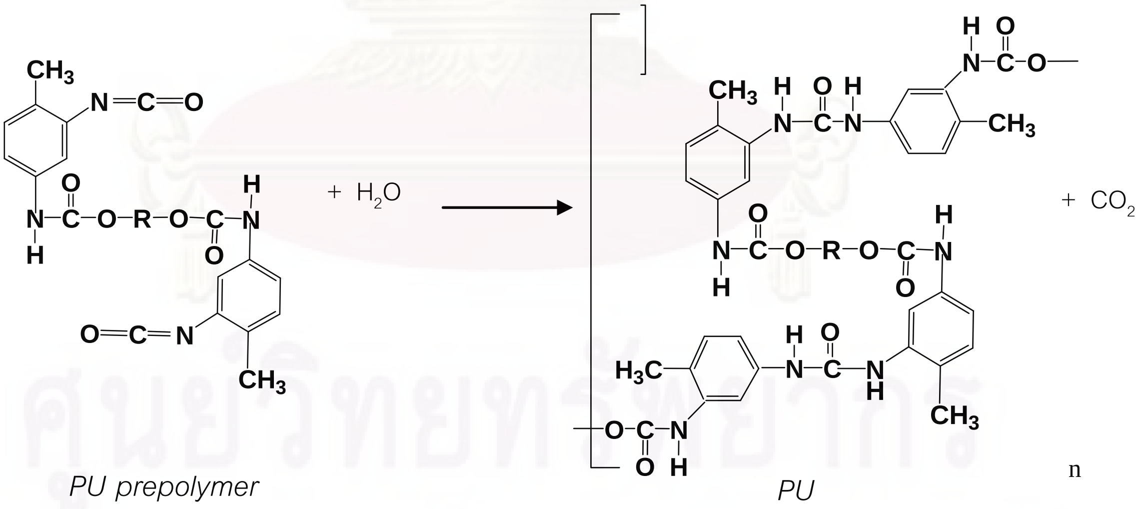


Figure 2.3. Polymerization of PU prepolymer by reaction with water.

2.4 Raw Materials

2.4.1 For synthesis bifunctional benzoxazine monomer based on bisphenol A

2.4.1.1 Bisphenol A

Bisphenol A is produced by reacting phenol with acetone in the presence of an acid catalyst (show in figure 2.4). Common catalyst are aqueous acids or acid clays. Promoters such as thioglycolic acid and resorcinol are also used [21].

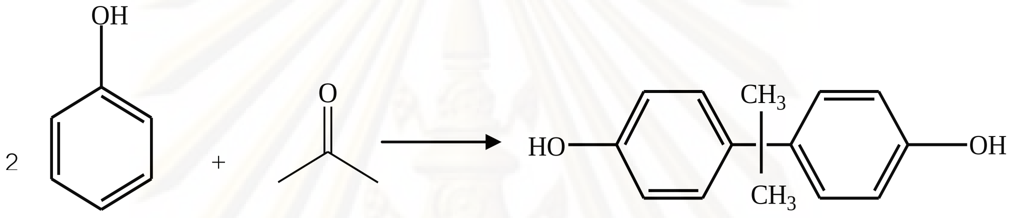


Figure 2.4. Synthesis of bisphenol A.

2.4.1.2 Formaldehyde

Formaldehyde is an unstable colorless gas, which is commercially supplied in 37% aqueous solution, as a solid cyclic trimer (trioxan), and as a solid polymer (paraformaldehyde) which used in this work. Almost all formaldehyde produced is derived from methanol either by oxidative dehydrogenation using silver or copper catalyst (see Equation 2.5), or by oxidation in the presence of Fe_2O_3 and MoO_3 (see Equation 2.6) [21].

$$CH_3OH \xrightarrow{\text{Cat}} HCHO + H_2 \qquad (2.5)$$

In the oxidative dehydrogenation, the generated hydrogen is oxidized to water upon addition of air.

$$CH_3OH + 0.5O_2 \xrightarrow{\text{Cat}} HCHO + H_2O \qquad (2.6)$$

2.4.1.3 Aniline

The classical method of systhesis of aniline is the reduction of nitrobenzene with hydrogen in the vapor phase using a copper/silica catalyst (show in figure 2.5). Nitrobenzene is produced in the nitration of benzene using a mixture of nitric acid and sulfuric acid [21].

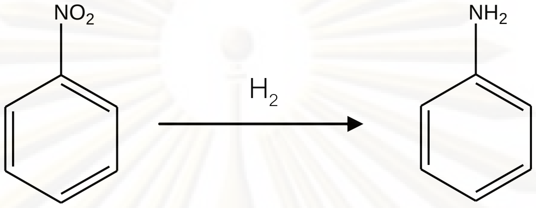


Figure 2.5. Synthesis of aniline by nitrobenzene.

Recently Aristech Chemical compoleted a 90,000-ton aniline plant using plant using phenol as the feedstock. This technology was deverloped by Halcon, and it is also used by Mitsui Toatsu in Japan. The amination of phenol is conducted in the vapor phase using an alumina catalyst, and yield are very high.

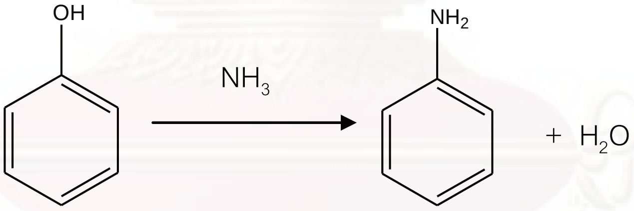


Figure 2.6. Synthesis of aniline by phenol.

2.4.2 For synthesis polyurethane

2.4.2.1 Isocyanates

In this work, We use toluene diisocyanate (TDI) which is an aromatic diisocyanate. Most of the TDI used is a mixture of the 2,4- and 2,6-isomers. The structure formulae of toluene diisocyanate (TDI) are shown in Figure 2.7.

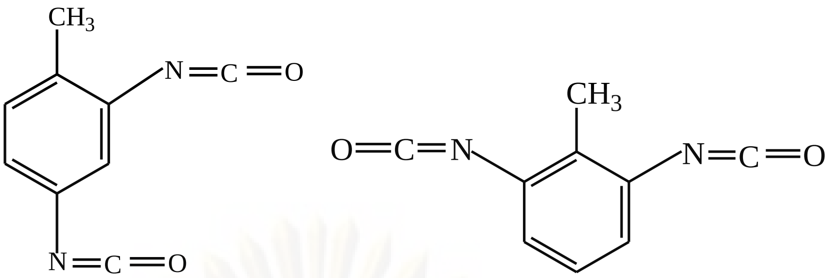


Figure 2.7. Structure of 2,4 toluene diisocyanate and 2,6 toluene diisocyanate (TDI) [7].

Toluene diisocyanate is prepared by direct nitration of toluene to give a 80:20 mixture of the 2,4- and 2,6-di-nitro derivatives, followed by hydrogenation to the corresponding diaminotoluene. Though toluene diisocyanate (TDI) is stable with a relatively high-flash point, it can be reacted with water, acid, base, organic, and inorganic compounds. The specifications of toluene diisocyanate are shown in Table 2.1.

Table 2.1. The specification of toluene diisocyanate [7].

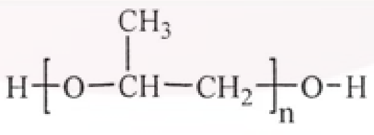
Properties	**Value**
Molecular weight	174.16
NCO content (% by weight)	48.3
Purity (% by weight)	99.5
Melting point (^oC)	19-22
Boiling point (^oC)	251
Density (g/cm^3)	1.22 at 20 ^oC
Viscosity (mPa.s)	3.2 at 20 ^oC
Vapor pressure (Pa)	3.3 at 25 ^oC

2.4.2.2 Polyol

The polyols that are used to make polyurethanes have been developed to possess the required reactivity with commercially available isocyanates and to produce polyurethanes with specific properties. A wide range of polyols is used in polyurethane manufacturing. Most of the polyols used, however, fall into two classes: hydroxyl-terminated polyethers, or hydroxyl-terminated polyesters.

The structure of the polyol plays an important role in determining the properties of the final urethane polymer. The molecular weight and functionality of the polyols are the main factors, but the structure of the polyol chains is also important. In this work, we used polyether polyols with the fixed molecular weight of 2000 to synthesize our urethane prepolymer.

Polyether polyols contain the repeating ether linkage –R–O–R– and have two or more hydroxyl groups as terminal functional groups. They are manufactured commercially by the catalyzed addition of epoxies (cyclic ethers) to an initiator. The most important types of the cyclic ethers by far are propylene oxide and ethylene oxide, with smaller quantities of butylene oxide also being consumed. These oxides react with active hydrogen-containing compounds (called initiators), such as water, glycols, polyols and amines; thus, a wide variety of compositions of varying structures, chain lengths and molecular weights is theoretically possible. By selecting the proper oxide (or oxides), initiators, and reaction conditions and catalysts, it is possible to synthesize a series of polyether polyols that range from low-molecular-weight polyglycols to high-molecular-weight resins. Most polyether polyols are produced for polyurethane applications; however, other end uses of the polyols range from synthetic lubricants and functional fluids to surface-active agents. In this work, the polyol used for the synthesis of our urethane prepolymer is polypropylene glycol (MW = 2000). The structure formulae of the polypropylene glycol are shown in Figure 2.8.



$$H\!\left[O-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-CH_2\right]_n\!O-H$$

Figure 2.8. Structure of polypropylene glycol.

2.5 Interpenetrating polymer network (IPN)

A polymer comprising two or more networks which are at least partially interlaced on a molecular scale but not covalently bonded to each other and cannot be separated unless chemical bonds are broken. A mixture of two or more preformed polymer networks is not an IPN [22].

Sperling L.H. [23], IPNs produced by different methods may be distinguished as follows:

(i) Sequential IPNs, where polymer network I is prepared first. Network I swells in monomer II and cross-linking agent and is then polymerized in situ. Thus, in sequential IPNs the synthesis of one network follows the synthesis of the other.

(ii)Simultaneous IPNs, where the monomers or prepolymers and crosslinking agents for synthesis of both networks are mixed together. The reactions are carried out simultaneously. It is important that the crosslinking reaction should proceed according to different mechanisms to avoid chemical interaction between macromolecules of two networks. Usually these mechanisms are polyaddition and radical polymerization.

In cases (i) and (ii), chain transfer via polymerization may take place and grafted IPNs may be formed. Another very important class of IPNs is semi-IPNs, namely, systems in which one of the components is a linear polymer. Semi-IPNs may be characterized as sequential or simultaneous IPNs depending on the way the linear polymer is introduced. Various types of IPNs may also be classified by the mechanism of phase separation proceeding during IPN formation. These mechanisms are nucleation and growth, and spinodal decomposition. Differences in the conditions of phase separation predetermine the physical and morphological features of IPNs.

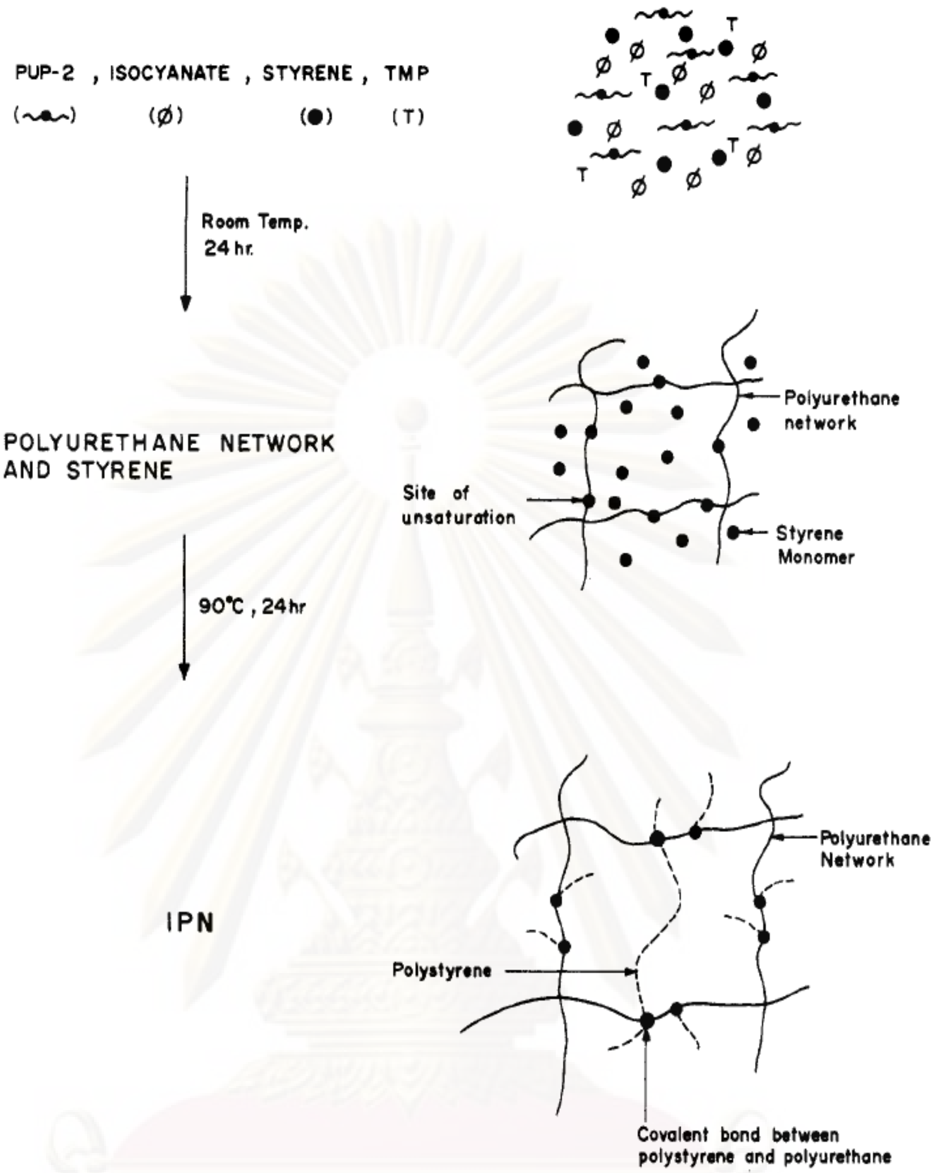


Figure 2.9. Interconnected IPN formation of polyurethane and polystyren by sequential IPNs method [8].

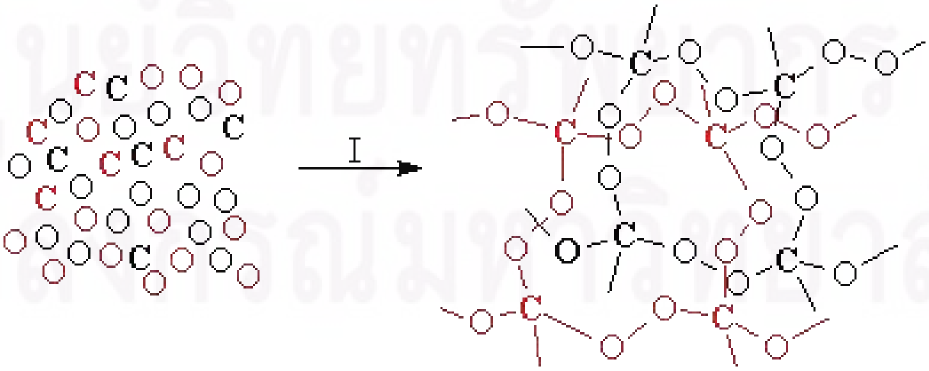


Figure 2.10. Model of IPN formation by simultaneous IPNs method [24].

2.6 Network Formation between Benzoxazine Resin and Urethane Prepolymer

T. Takeichi et al [11]. studied about the synthesis and characterization of poly(urethane-benzoxazine) flims. The poly(urethane-benzoxazine) films as novel polyurethane (PU)/phenolic resin alloys were prepared by blending a benzoxazine monomer (BA-a) and TDI-polyethylene adipate polyol (MW = 1000) based PU prepolymer. The mechanism of benzoxazine-urethane alloys was proposed by model reaction of monofunctional benzoxazine monomer, 3,4-dihydro-3,6-dimethyl-2H-1,3-benzoxazine (CM) and phenyl isocyanate (show in figure 2.11). From FT-IR results of benzoxazine-urethane alloys confirm that the main structures in benzoxazine-urethane alloys are considered to be urethane formation via a crosslinking between NCO of the PU prepolymer and phenolic OH from ring-opening polymerization of BA-a, and the allophanate formation via the intermolecular reaction of the PU prepolymer.

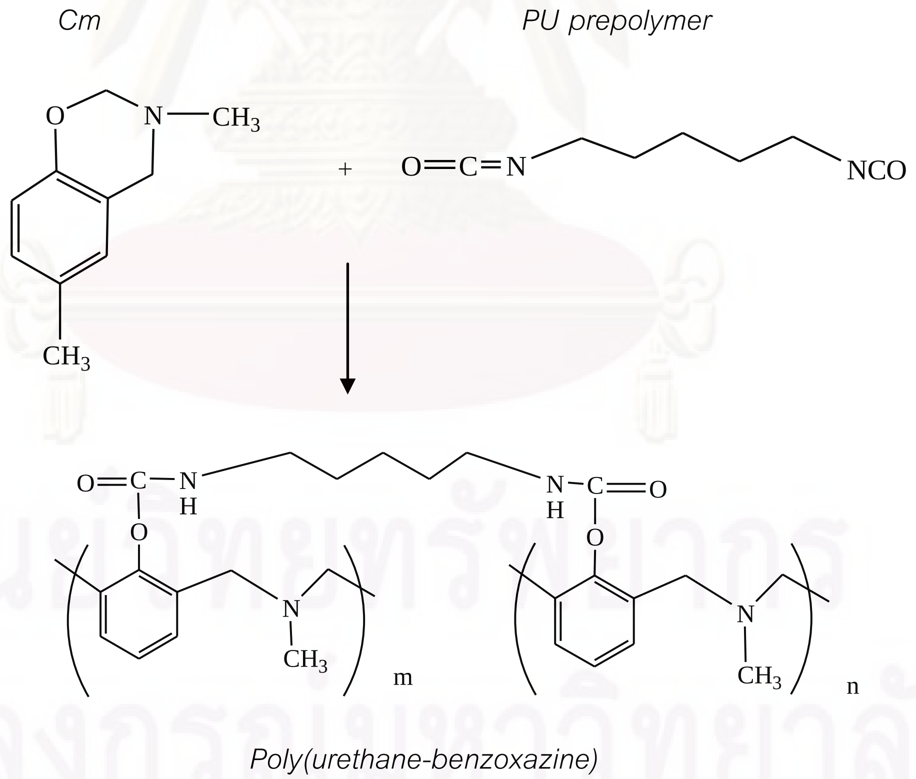


Figure 2.11. Reaction of the Cm-type polybenzoxazine and PU prepolymer.

CHAPTER III

LITERATURE REVIEWS

3.1 Preparation IPNs of Polyurethane

S.B. Pandit, and V.M. Nadkarni, 1994 [8] synthesized sequential interconnected interpenetrating polymer networks of polyurethane and polystyrene by cured at room temperature for 24 h to complete the PU network formation, followed by a post cure at 90 ^{o}C for 20 h and at 120 ^{o}C for 6 h to complete the polymerization of styrene. The results of the swelling studies, wide angle X-ray diffraction, and the solid state ^{13}C NMR spectroscopy, it is proposed that the network cage structures would represent the interconnected IPNs.

J. Yang et al., 1996 [9] prepared polyurethane - polyacrylate interpenetrating networks with three types of urethane-acrylate IPN’s, two sequential and one simultaneous types. Example, sequential IPN $PU_{g15,75\%}PA\ (EHA)_{100\%}PU_{100\%}$ prepared from PU network gelled in ca. 15 min. Gelation was noted as a rapid change in the sample from a fluid to a rubbery state. After 2 h at room temperature (ca. 75% PU conversion), these samples were photolyzed for 10 min with 3000 Å lamps in a Rayonet photochemical reactor, conditions sufficient to cause complete polymerization of the acrylate. The sample was kept at 22 °C for at least another 46 h to allow the urethane polymerization to go to completion before any measurement on the system was carried out. And sequential IPN $PA\ (EHA)_{100\%}PU_{100\%}$ was photolyzed immediately for 20 min at 3000 Å and then placed in an oven at 60°C for 4 h to complete the PU network formation.

3.2 Benzoxazine-Urethane Alloys

T. Takeichi et al., 2000 [11] prepared poly(urethane-benzoxazine) films as novel polyurethane/phenolic resin composites from blending a benzoxazine monomer (Ba) and urethane prepolymer (PU) that was synthesized from 2,4-tolulene diisocyanate (TDI) and polyethyleneadipate polyol (MW ca. 1000) in 2:1 molar ratio.

The progress of the curing of PU/BA-a films was followed by IR. Figure 3.1 shows an example taken from PU/BA-a films at each curing stage, along with the spectra of BA-a [Fig. 3.1(a)] and PU prepolymer [Fig. 3.1(b)]. All the characteristic absorbances are clearly observed in PU/BA-a films treated at 100 °C for 1 h [Fig. 3.1(c)]. It is obviously noticed that the disappearance of absorbance at 2275 cm^{-1} after 150 °C/1 h cure cycle [Fig. 3.1(d)], indicating the reaction of NCO groups in the PU prepolymer. Moreover, the absorptions at 948 and 1499 cm^{-1} assigned to the tri-substituted benzene ring in BA-a have been weakened with the curing progress, which suggests a decrease in the tri-substituted benzene rings, indicating the ring-opening polymerization.

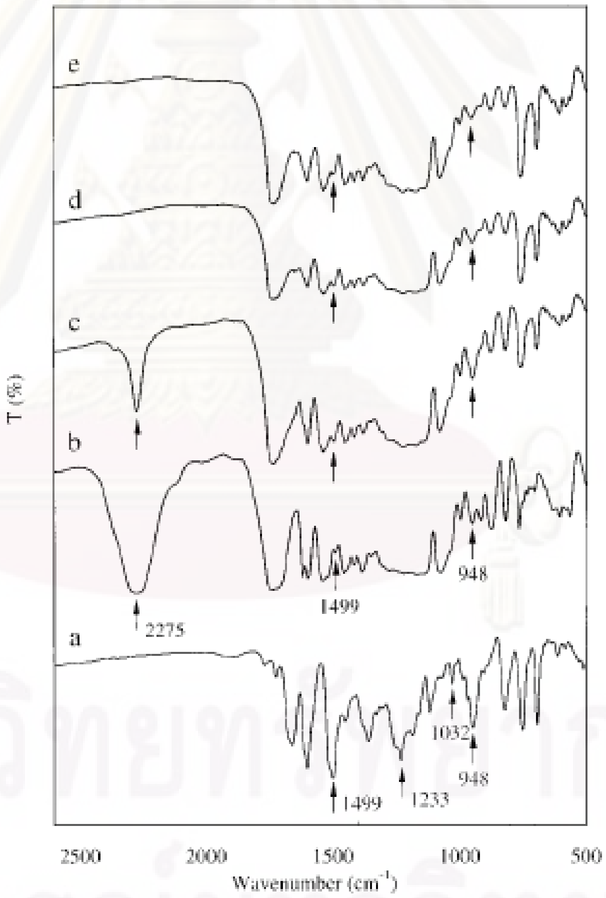


Figure 3.1. IR spectra of: (a) BA-a; (b) PU prepolymer; and Pu/BA-a-85/15 treated at: (c) 100 °C/1 h; (d) 150 °C/1 h; and (e) 190 °C/1 h.

For more investigation of the curing behavior of benzoxazine monomer in the presence of the PU prepolymer, DSC measurement was recorded. Examples of DSC are shown in Figure 3.2 in the case of PU/BA-a (90/10). Exotherm due to the ring opening of BA-a is clearly seen. The exothermic quantity upon curing decreases from 6.2cal/g to 3.8cal/g as the curing temperature is increased from 100 to 150 °C, suggesting that the partial ring-opening of Ba occurred at 150 °C, affording polybenzoxazine containing phenolic OH groups.

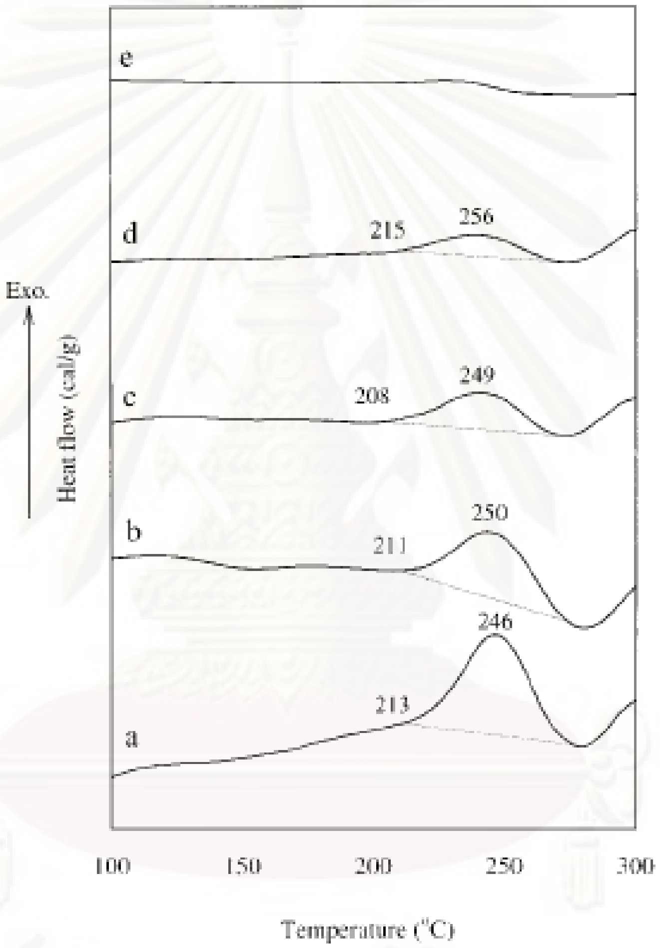


Figure 3.2. DSC thermograms of PUB/BA-a (90/10) film treated at various temperatures: (a) 100 °C/1 h; (b) 150 °C/1 h; (c) 170 °C/1 h; (d) 190 °C/1 h; and (e) 200 °C/1 h.

Thermal properties were investigated by thermogavimetric analysis (TGA). Figure 3.3 shows TGA profile of PU/Pa films. The results show that initial decomposition temperatures (5% weight loss) of PU/Pa films are higher than that of the PU itself and increasing the BA-a contents to a higher decomposition temperature. Thus, incorporating polybenzoxazine into PU can open an effective way to an improvement on the thermal stability of PU.

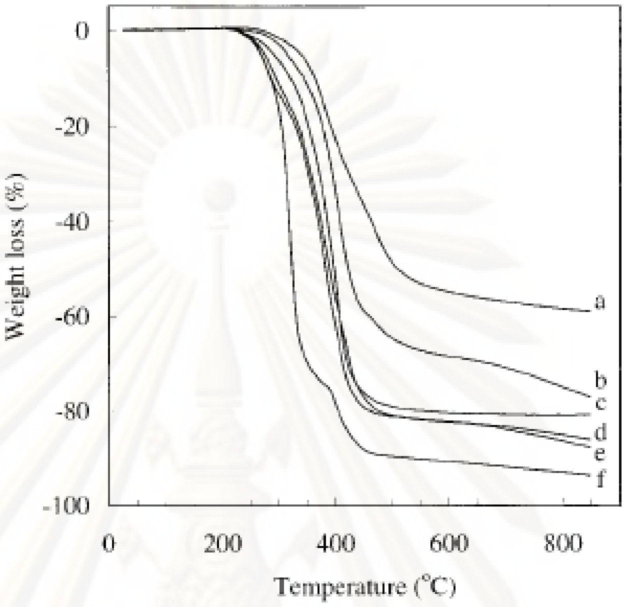


Figure 3.3. TGA analysis of PU/BA-a films: (a) PU/BA-a (0/100); (b) PU/BA-a (70/30); (c) PU/BA-a (80/20); (d) PU/BA-a (85/15); (e) PU/BA-a (90/10); (f) PU/BA-a (100/0).

S. Rimdusit et al., 2005 [12] improved the toughness of polybenzoxazine by alloying with urethane prepolymer (PU) from blending a benzoxazine monomer (BA-a) and urethane prepolymer (PU) that was synthesized from isophorone diisocyanate (TDI) and polyester polyol (MW ca. 2000) in 2:1 molar ratio.

The transition temperature was determined using DMA. The T_g of the polyurethane elastomer and polybenzoxazine(BA-a) based polybenzoxazine were reported to be about -70 to -20°C and 160 to 170°C, respectively. The T_g of BA-a/PU binary systems were found to increase with the mass fraction of PU. The effects of the urethane prepolymer (PU) on the flexural properties are show in figure 3.4. The flexural strength of the BA-a/PU at a 90/10 weight ratio was slightly higher than that of the polybenzoxazine homopolymer. The flexural strength then decreased with the mass fraction of the PU when the amount of the PU was greater than 20 wt%. The flexuaral modulus of these alloy; decrease monotonically with the amount of the PU, whereas, the toughness of the BA-a/PU increased with the mass fraction of PU.

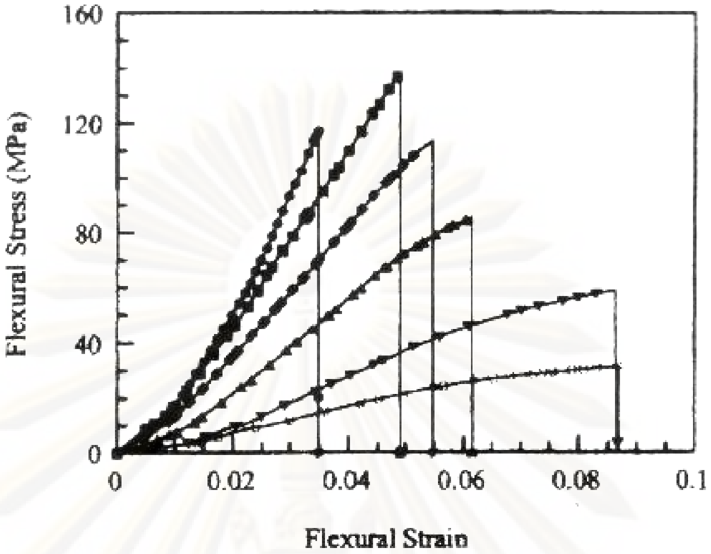


Figure 3.4. Flexural stress and strain of BA-a/PU alloys at various compositions.
: (•) 100/0, (■) 90/10, (◆) 80/20, (▲) 70/30, (▼) 60/40 and (⊙) 50/50.

H. Yeganeh et al., 2008 [13] improved thermal stability of Polybenzoxazine Modified Polyurethanes as a New Type of Electrical Insulators. Epoxy-Terminated Polyurethane Prepolymer (EPU) was prepared from CAPA210, HDI, and glycidol and benzoxazine was prepared from Bisphenol-A (47.01 g, 0.2 mol), aniline (37.20, 0.4 mol), and paraformaldehyde (25.26, 0.8 mol).

The thermogram of the benzoxazine monomer (Fig. 3.5a) showed a curing exotherm with a peak located at about 228 °C, which is the characteristic of the thermal curability of this resin. At DSC thermogram of EPU (Fig. 3.5b) melting of EPU was observed as an endothermic peak at about 55 °C. The DSC thermogram for binary system of EPU and Ba (Fig. 3.5c) showed two successive curing exothermic peaks centered at about 190 and 248 °C. The first peak is related to the reaction of urethane NH and epoxy groups of EPU and second exotherm is related to the reaction of BA-a with BA-a.

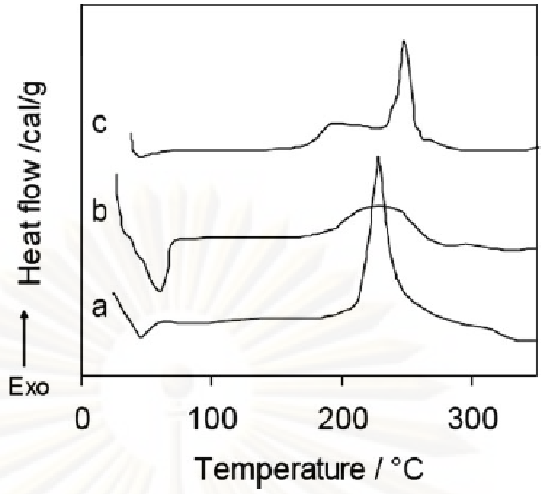


Figure 3.5. DSC thermograms for curing reaction of (a) Ba, (b) EPU, and (c) Ba/EPU (50/50).

Figure 3.6 shows FTIR spectra of BA-a, EPU, and Ba/ EPU (50/50) mixture before and after thermal treatment. In Fig. 3.6a, the spectrum also contains a peak at 1496 cm^{-1} attributed to the tri-substituted benzene ring. Upon heating, IR absorbances at 943, 1027, and 1231 cm^{-1} disappeared resulting from the opening of oxazine rings. Also, the shift of trisubstituted benzene ring absorbance at 1496–1474 cm^{-1}, which is attributed to tetra-substituted benzene ring, indicated the formation of network. Appearance of a broad peak at about 3400 cm^{-1} because of the formation of phenolic hydroxyl groups was another indication for ring opening reaction of BA-a upon thermal treatment. FTIR spectrum of EPU (Fig. 3.6c) showed the characteristic bonds of urethane groups at 3370 cm^{-1} (N-H stretching), 1730 cm^{-1} (NHCOO stretching combined with ester COO stretching), and 1530 cm^{-1} (C-N stretching, combined with N-H out of plane bending). The bands of epoxy groups were presented as a doublet at 864 and 913 cm^{-1}. Upon thermal treatment of EPU, urethane NH groups can act as a nucleophile and attack to epoxy rings, therefore, new allophanate bonds and hydroxyl groups can be generated. Investigation of FTIR spectrum of EPU after curing reaction showed nearly complete reaction of epoxy groups, which was indicated by the disappearance of epoxy peaks at 864 and 913 cm^{-1}. Broadening of peaks at about 3400 and 1730 cm^{-1} due to the formation of new hydroxyl and allophanate bonds can be supportive for reaction pathway.

FTIR spectroscopy that a blend of BA-a and EPU (Fig. 3.6e) contained absorption characteristic of both the benzoxazine resin and epoxy modified polyurethane, such as the peaks at 943 and 1231 cm^{-1} from the benzoxazine species and that of 1730 cm^{-1} from urethane carbonyl and of 864 and 913 cm^{-1} from epoxy rings. After the completion of curing reaction, the disappearance of absorbances at 864 and 913 cm^{-1} indicated the reaction of epoxy groups at EPU. The absorptions at 943 and 1496 cm^{-1} assigned to the trisubstituted benzene ring in BA-a, were also disappeared. This could be related to the ring opening polymerization reaction of BA-a.

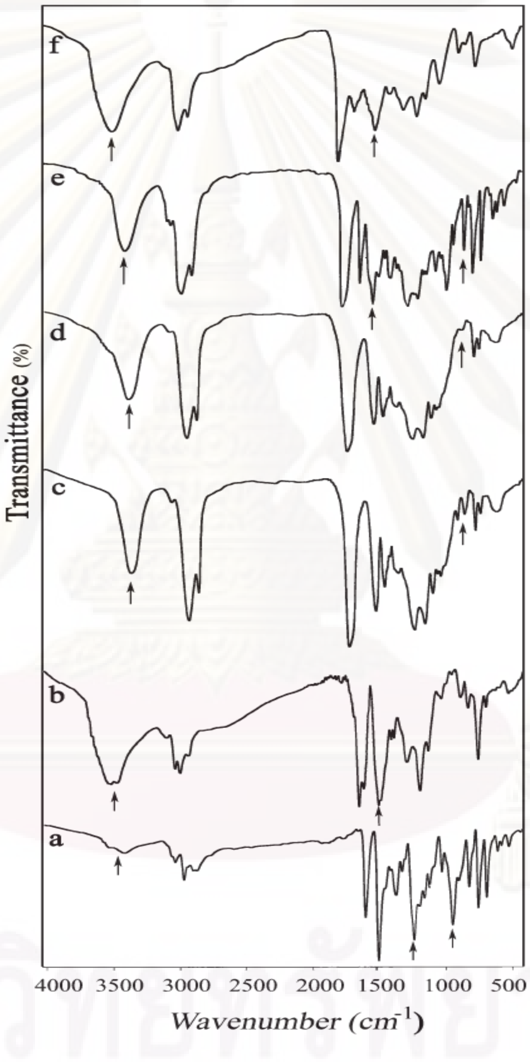


Figure 3.6. FTIR spectra of (a) BA-a monomer, (b) polybenzoxazine, (c) EPU, (d) EPU after thermal treatment, (e) BA-a/EPU(50/50) before thermal treatment, and (f) BA-a/EPU(50/50) after thermal treatment.

Mechanical properties were determined from stress-strain curves with an Instron 6025 instrument and Dynamic mechanical testing (DMTA) .Result showed that the better mechanical property of sample BA-a/EPU(50/50) in comparison to other blends, could be attributed to the existence of more extensive inter and intramolecular interactions of polybenzoxazine and polyurethane components.

TGA experiment was carried out as a means for evaluation of thermal stability of the prepared polymers and blends.TGA curves are shown in Fig. 3.7. The results show that initial decomposition temperature (up to 10% weight loss) and maximum decomposition temperature of the blends are higher than that of pure polyurethane sample and lower than pure polybenzoxazine sample. Investigation of TGA curves show that the rate of polymer decomposition is lower for the samples with higher concentration of BA-a. Also incorporation of polybenzoxazine into polyurethane resulted in considerable enhancement in char yield percent.

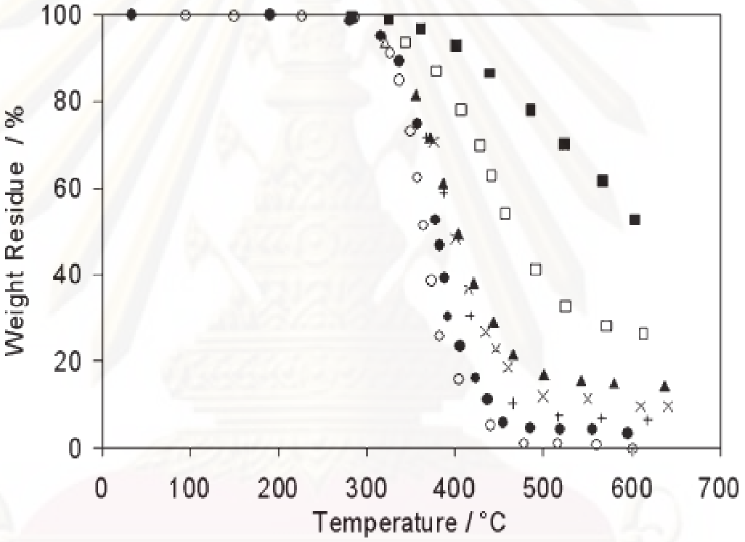


Figure 3.7. TGA curves of the BA-a/EPU (100/0) (■), BA-a/EPU (75/25) (□), BA-a/EPU (50/50) (▲), BA-a/EPU (35/65) (×), BA-a/EPU (25/75) (+), BA-a/EPU (15/85) (●), BA-a/EPU (0/100) (○).

S. Rimdusit et al., 2008 [25] study effects of Polyol Molecular Weight on Properties of Benzoxazine–Urethane Polymer Alloys. The materials used in this research are benzoxazine resin and urethane resin. The urethane prepolymer terminated with isocyanate group was prepared from TDI and poly(propylene glycol) at a molar ratio of 2:1 using various Mn of the poly(propylene glycol), i.e., 1000, 2000, 3000, and 5000 g/mol. The result of this research is

Gel Permeation Chromatography

The most of chain lengths of all types of polyol molecules used were nearly equal.

Fourier Transform Infrared Spectroscopy

The chemical structures of neat resins and their formation reactions were studied by FT-IR spectroscopic technique. At 1729 cm^{-1} (C=O stretching of urethane) and 2274 cm^{-1} (N=C=O stretching of unreacted-isocyanate group). It can be observed that the peak height at 1729 cm^{-1} trended to decrease with increasing the molecular weight of polyol based on the same mass of the resin. All spectra of the prepolymer indicated that the C=O absorption peak of urethane increased whereas the N=C=O peak significantly decreased with the progress of the reaction to form the urethane prepolymer.

Differential Scanning Calorimetry

The DSC experiment revealed the fully cured condition of binary mixture to be at 160^{o}C, 170^{o}C, 180^{o}C, and 200^{o}C for 2 h at each temperature. The Tg of the binary mixture increased with increasing the urethane mass ratio. Moreover, the Tgs were unaffected by the molecular weights of the urethane polyol comparing based on the same BA:PU mass ratio.

Thermogravimetric Analysis

The degradation temperatures of the BA: PU polymer alloys were found to be similar to the neat polybenzoxazine. Moreover, the char yield of the polymer alloys was found to decrease with increasing the PU fraction in the binary system but increase with the molecular weights of the polyol.

Flexural Property Measurement

The modulus of the binary systems tended to decrease following the rule of mixture. On the other hand, the effects of the number average molecular weights of the polyol on the flexural moduli of the alloys were not significant. The strength of the binary systems exhibited the synergistic behavior with the maximum at the BA: PU ratio of 90:10 for all molecular weights of the polyol.

Solvent Extraction

The BA: PU2K ratio of 70:30 was found to change from its original state (The color of chloroform was changed from colorless to deep yellow) whereas the solvent of the other three compositions remained colorless throughout the whole evaluation period. The swelling degree of the edges of this specimen increased with number average molecular weight of the polyol.

3.3 Benzoxazine-Urethane IPNs

Y.Cui et al., 2003 [26] prepared polyurethane / polybenzoxazine-based interpenetrating polymer networks (IPNs) from a benzoxazine monomer (BA-a) and polyurethane network that was synthesized from diphenylmethane diisocyanate (MDI), Poly(ethylene glycol) (PEG) of average molecular weight 1000g mol^{-1} ,1,4-butanediol (BD) and 1,1,1-trimethylolpropane (TMP). The nomenclature of the samples is listed in Table 1. The FTIR spectra of the resulting IPNs indicate that all bands in the spectrum of PU/PBA-a IPN can be found in that of the component polymers. Therefore, it is inferred that there are no apparent graft reaction between the two component networks during the formation of IPN.

Fig. 3.8 shows the surface morphology of IPNs with different compositions. Although exhibiting a transparent appearance, PU/PBA-a IPNs showed phase separation to a certain level regardless of composition. By comparing Fig 3.8(a and b), the molecular size of PBA-a in the lower tri-functional crosslinker formed PU-based IPN is higher than in the more crosslinked PU-based IPN. The difference observed between another series of PU/PBA-a ratios (Fig 3.8(c, d)) well confirms this change. The result of the TEM studies perfectly coincided with what was obtained from SEM studies. As shown in Fig 3.8 (e and f), two networks exhibit good entanglement and interpenetrating behaviour as expected. The size of the PBA-a network, the dark phase, decreased with increasing crosslinker in the PU composition

Table 3.1. Nomenclature and formulations of samples.

Sample code	**MDI/PEG/BD/TMP/ by molar ratio**	**PU/Ba by weight**
PBa	-	0/1
PU 10	3.05/1/1.8/0.2	1/0
PU 10-50	3.05/1/1.8/0.2	1/1
PU 10-66	3.05/1/1.8/0.2	2/1
PU 10-75	3.05/1/1.8/0.2	3/1
PU 20-50	3.05/1/1.6/0.4	1/1
PU 20-75	3.05/1/1.6/0.4	3/1

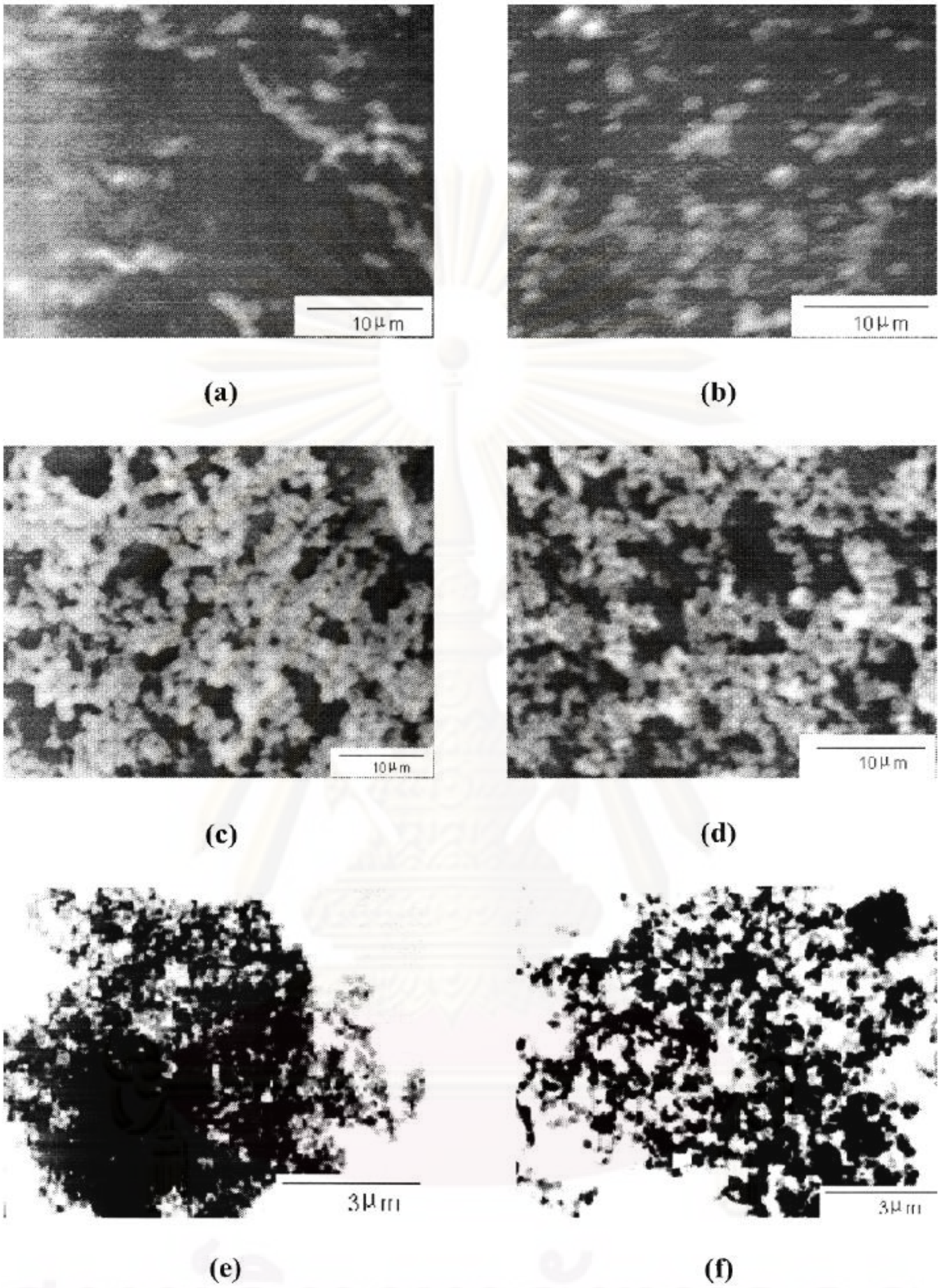


Figure 3.8. SEM and TEM photographs of IPNs. SEM photographs: (a) PU10-75, (b) PU20-75, (c) PU10-50, (d) PU20-50. TEM photographs: (e) PU10-50, (f) PU20-50.

CHAPTER IV

EXPERIMENTAL

4.1 Raw Materials

Raw Materials used in this research are benzoxazine resin, urethane prepolymer. In this work, we use Bifunctional benzoxazine is based on bisphenol-A. Bisphenol-A (polycarbonate grade) was supplied by Thai Polycarbonate Co.,Ltd. (TPCC). Para-formaldehyde (AR grade) was purchased from Merck Co. and aniline (AR grade) was from Fluka Chemicals Co. The polyurethane prepolymer was synthesized from polypropylene glycol polyol at a molecular weight of 2000 and 2, 4-tolulene diisocyanate (TDI). Toluene diisocyanate was obtained from the South City Group whereas polypropylene glycol polyol at a molecular weight of 2000 was kindly supplied by IRPC Co., Ltd. Dibutyltin dilaurate (DBTL) is the catalyst for a synthesis of urethane prepolymer.

4.2 Synthesis of Benzoxazine Monomer

Benzoxazine resin (BA-a) was synthesized from bisphenol-A, Para-formaldehyde, and aniline at a molar ratio of 1:4:2. The mixture was heated to 110°C in an aluminum pan and was mixed rigorously for about 30 minutes to yield a light yellow solid monomer product, according to the patented solventless method [2]. The product was then ground into fine powder and can be kept in a refrigerator for future-use.

4.3 Synthesis of Urethane Prepolymer

The urethane prepolymer was synthesized from polypropylene glycol polyol at a molecular weight of 2000 and 2, 4-tolulene diisocyanate (TDI) in a 1:2 molar ratio. Tolulene diisocyanate and polypropylene glycol polyol were mixed together in a four-necked round-bottomed flask and dibutyltin dilaurate was added at 0.075% by weight. The mixture was then stirred under a nitrogen stream at 70°C for 2 hour. The urethane prepolymer obtained transparency viscous were cooled to room temperature and kept in a nitrogen-purged, closed container.

4.4 Preparation of Benzoxazine-Urethane Alloys

The benzoxazine monomer (BA-a) was blended with various amount of urethane prepolymers (BA-a: PU) i.e. 100:0, 80:20, 60:40, 40:60, 20:80 and 0:100. The mixtures were typically heated to about 110°C in an aluminium pan and mixed thoroughly until clear homogeneous resin mixtures were obtained. The molten resin mixture was poured into an aluminium mold for sample thickness 3 mm that is used for phase seperation behavior testing and cast onto aluminiam sheet by docter blade for Benzoxazine-Urethane film. Prepare copolymers between benzoxazine resin and urethane prepolymer in two processing methods. Firstly, the polymer mixtures were processed under sequential cure methods at room temperature (90% humidity) to firstly complete the urethane network formation (24 hour for film and 48 hour for sample thickness 3 mm) followed by thermal curing in an air-circulated oven to polymerize the benzoxazine resin portion (120°C 1 hr, 150°C 1 hr, 170°C 1 hr, and 180°C 5 hr for specimen in aluminium mold and fully cure step at 130°C 1 hr, 150°C 1 hr, 180°C 1 hr, 190°C 1 hr and 200°C 4 hr for films that cast onto aluminium sheet). Secondly, traditional cure methods, immediately thermal curing steps in an air-circulated oven at the same conditions. All the specimens were finally left to cool down to room temperature and then ready for sample characterizations. Whereas, the neat polyurethane was prepared by casting onto glass plate.

4.5 Sample Characterizations

4.5.1 Fourier Transform Infrared Spectroscopy (FT-IR)

The chemical structure and network formation behavior of sample was studied by a Fourier transform infrared spectroscopy (FTIR). Fourier transform infrared spectra of all samples were required by using a Spectrum GX FT-IR spectometer from Perkin Elmer with an ATR accessory. All spectra were taken as a function of time with 64 scans at a resolution of 4 cm^{-1} and a spectral range of 4000-650 cm^{-1}. For urethane prepolymer, a small amount of a viscous liquid sample was casted as thin film on a potassium bromide (KBr) window.

Moreover, phase separation behavior of sample was studied by a homemade slide-on diamond µIRE which consists of two parts as shown in Figure 4.1. The first part is the slide-on housing, which contained quick-released spring loaded that designed for fixing the slide-on diamond µIRE, which is employed for adjusting the still location of the slide-on diamond µIRE in order to obtain a high energy throughput. The second part is the slide-on diamond µIRE that equipped with a gem-quality round brilliant cut diamond IRE (0.1005 ct type IIA natural diamond) which mounted in a stainless steel supporting. The homemade slide-on housing was fixed on the 15X Schwarzschild-Cassegrain infrared objectives and the slide-on diamond µIRE was slid into slide-on housing as shown in figure 4.2. The incident infrared radiation from the infrared microscope is coupled onto the table facet of the diamond µIRE. The amount of light was controlled by the aperture of the microscope. The infrared radiation was focused at the culet of the diamond µIRE. The contact area of the slide-on diamond µIRE was ~30 µm in diameter. Due to the small contact area of the diamond µIRE and the easily operation of the microscope stage (i.e., moving stage up and down), ATR FT-IR spectra of small sample size can be observed. This technique is non-destructive and has short analysis time.

4.5.2 Rheological Properties Measurement

Rheological properties of each resin mixture were investigated using a Rheometer (Haake Rheo Stress 600, Thermo Electron Cooperation) equipped with parallel plate geometry. The processing window was determined under an oscillatory shear mode at a frequency of 1 rad/s. The testing temperature was ramped at a heating rate of 2^{o}C/min to a temperature beyond the gel point of each resin and the dynamic viscosity was recorded.

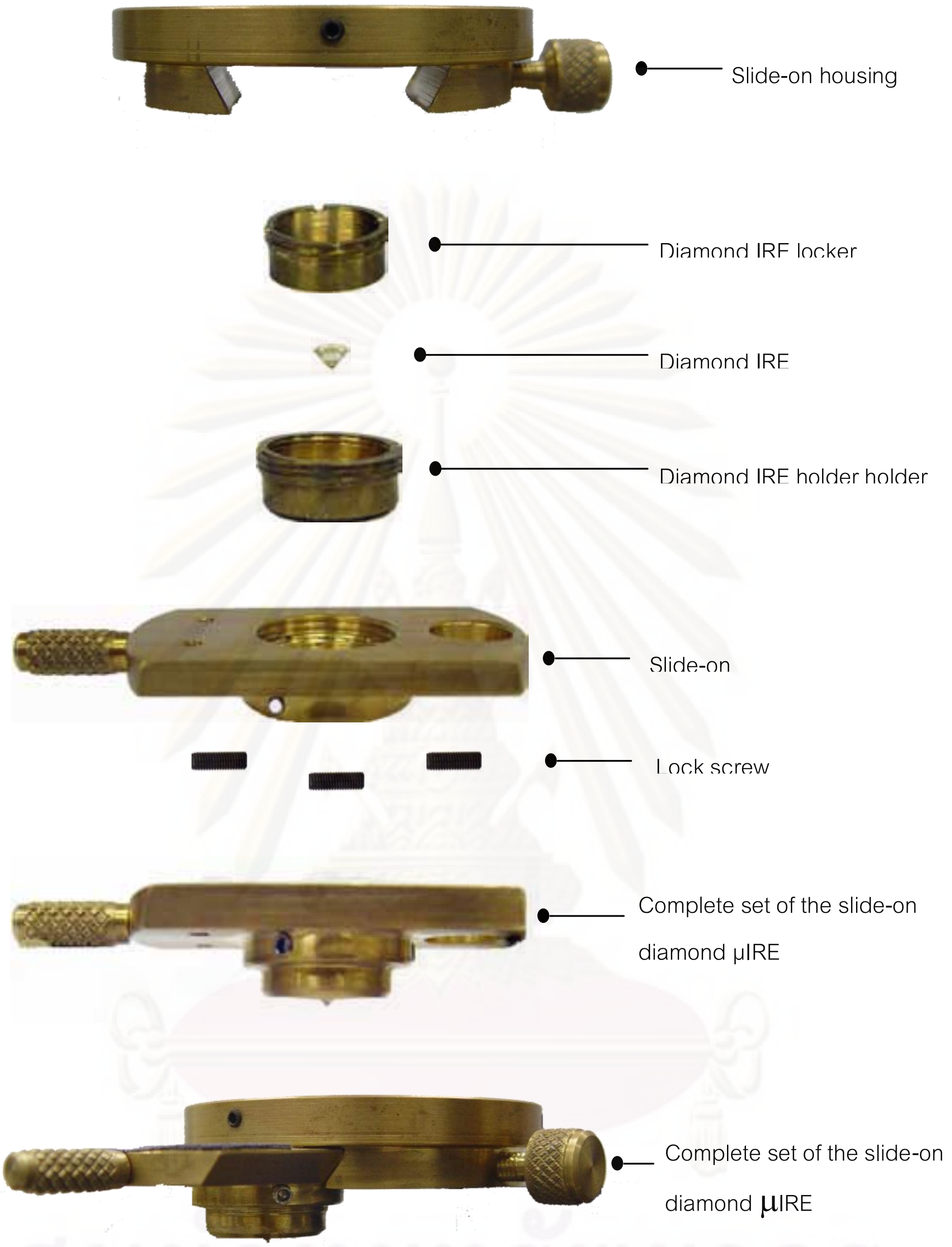


Figure 4.1. The homemade slide-on diamond µIRE accessory.

Figure 4.2. The homemade slide-on diamond μIRE was fixed on the 15X Schwarzschild-Cassegrain infrared objectives: (A) picture of Nicolet 6700 equipped with infrared microscope, (B) slide-on diamond μIRE was fixed on infrared microscope, (C) slide-on diamond μIRE was fixed on infrared microscope and aligned to high energy throughput, and (D) infrared microscope.

4.5.3 Differential Scanning Calorimetry (DSC)

A differential scanning calorimeter (DSC) model 2910 from TA Instruments was used to study the curing behavior of BA-a/PU resin mixtures. All samples were put in aluminum pans with lids. The DSC thermogram was obtained using a heating rate of 10^{o}C/min from temperature at 30^{o}C to 300^{o}C under a constant flow of nitrogen of 50 ml/min. The sample with a mass in a range of 3-5 mg was sealed in an aluminum pan.

4.5.4 Dynamic Mechanical Analysis (DMA)

The dynamic mechanical analyzer (DMA) model DMA242 from NETZSCH was used to investigate the dynamic mechanical properties and relaxation behaviors of BA-a/PU polymer alloys obtained from two processing method. The BA-a/PU film was performed in a tension mode. The temperature was scanned from -130 °C to the temperature beyond the glass transition temperatures (Tg) of each specimen with a heating rate of 2°C /min under nitrogen atmosphere. The glass transition temperature was taken as the maximum point on the loss modulus or loss tangent curves.

4.5.5 Thermogravimetric Analysis (TGA)

The degradation temperature (Td) and char yield of the benzoxazine alloys at various mass fractions of urethane prepolymers of two processing method were studied using a Thermogravimetric analyzer (TGA). The thermogravimetric analyses were determined using a Perkin Elmer Instrument Technology SII Diamond TG/DTA thermogravimetric analyzer. The testing temperature program was ramped at a heating rate of 20°C/min from room temperature to 800°C under nitrogen purging at 100 ml/min. Weight loss of the samples was measured as a function of temperature. The degradation temperatures (Td) of BA-a/PU polymer alloys were reported at their 5% and 10% weight loss. Moreover, the char yield of all sample were also reported at 800°C**.**

4.5.6 Density Measurement

The densities of BA-a/PU alloys of both processing method were determined by water displacement method according to ASTM D 792-00 (Method A) [27]. All measurements were performed at room temperature. The density of the specimen was calculated by a following equation:

$$\rho = (\frac{A}{A-B}) \times \rho_o \qquad (4.1)$$

where ρ = Density of the specimen, g/cm^3.

A = Weight of the specimen in air, g.

B = Weight of the specimen in liquid, g.

ρ_o= Density of the liquid at the given temperature, g/cm^3.

$$Theoretical.density = (\rho_B.X_B) + (\rho_U.X_U) \tag{4.2}$$

where

ρ_B = density of benzoxazine, g/cm^3

ρ_U = density of urethane prepolymer, g/cm^3

X_B = benzoxazine weight fraction

X_U = urethane prepolymer weight fraction

The measurement was run 3 times for each specimen and the average value of the sample volume was obtained.

4.5.7 Swelling Degree and Gel Content

Volumetric swelling degree and gel content of BA-a/PU alloys of both processing method were determined by immersion in chloroform at room temperature for 1 week. They were calculated using the following formulae [28]:

$$\text{Volumetric swelling degree: } Q = 1 + \frac{\rho_2}{\rho_1} \times \left(\frac{m_s}{m_t} - 1 \right) \tag{4.3}$$

$$\text{Gel content (\%)} = \frac{m_g}{m_t} \times 100 \tag{4.4}$$

where ρ_1 = Density of chloroform (ρ_1 =1.489 g/cm^3).

ρ_2 = Density of BA-a/PU alloys, g/cm^3.

m_s = Weight of swollen specimen, g.

m_g = Dried weight after swelling, g.

m_t = Initial weight of specimen, g.

The measurement was run 3 times for each specimen and the average value of the sample volume was obtained.

4.5.8 Microhardness Testing

Microhardness of compressed specimens was measured utilizing a Vickers microhardness tester (model FM-700) from Future-Tech. A pyramidal diamond was applied to the surface of the composite under a load of 10 g for top surface and 50 g for bottom surface with in 15 s. Diagonal length of the indentation was measured through a micrometric eyepiece with an objective lens (50x magnifications). Each sample was measured repeatedly for ten times. The hardness value of the specimen was calculated by a following equation [29]:

$$HV = 1.854 \frac{L}{d^2} \tag{4.5}$$

where HV = Vicker hardness value (Kg/m^2)

L = Load (Kg)

d = Arithmetic mean of the two diagonals (m)

Figure 4.3. Microhardness tester model FM-700 [30].

CHAPTER V

RESULTS AND DISCUSSION

5.1 Fourier Transform Infrared Spectroscopy Investigation

The chemical structures of benzoxazine resin, urethane resin and their network formation reactions were studied by Fourier transform infrared spectroscopy (FTIR). The FT-IR spectra of benzoxazine resin (BA-a) and polybenzoxazine are shown in Figure 5.1. Characteristic absorption bands of the BA-a monomer were found at 934 and 1230 cm^{-1} both assigned to C-O-C stretching mode of benzoxazine ring and 1496 cm^{-1} assigned to tri-substituted benzene ring (Figure 5.1 a). As the curing process proceeded characteristic absorption bands at 934 and 1230 cm^{-1} disappeared due to the opening of oxazine rings. Moreover, the shift of tri-substituted benzene ring absorbance at 1496 cm^{-1} to tetra-substituted benzene ring at 1475 cm^{-1} and the formation of a broad peak at about 3397 cm^{-1} due to the formation of phenolic hydroxyl groups indicated the occurrence of polybenzoxazine network (Figure 5.1 b). Polymerization mechanism of benzoxazine resin observed in this work was in good agreement with the previous reports by Dunkers et al. [31], Takeichi et al. [1, 11] and Rimdusit et al. [12, 25].

In this research, urethane prepolymer was prepared by reacting poly propylene glycol polyol (Molecular Weight = 2000) with toluene diisocyanate (TDI). The important functional group of urethane prepolymer is NH-COO group which suggested the existence of the reaction between isocyanate groups (NCO) with hydroxyl group of the polyol (OH) in order to form a urethane linkage. The urethane prepolymer could produce a crosslink network by reacting with atmospheric moisture and the reaction was also investigated by FT-IR. The spectra are illustrated in Figure 5.2. Figure 5.2a presents FT-IR spectra of urethane prepolymer and the characteristic band was observed at 2268 cm^{-1} (NCO-terminated group) and at 1730 cm^{-1} (NH-COO). Figure 5.2 b exhibits urethane prepolymer which was cured by moisture. The characteristic absorption band of urea linkage at 1638 cm^{-1} (C=O) and 3300 cm^{-1} (NH stretching vibrations) were clearly observed. The disappearance of NCO-terminated group indicated that urethane prepolymer had been converted to polyurethane.

In this work, the network formation between benzoxazine resin and urethane prepolymer using two different curing schemes was examined i.e. the sequential cure method and the traditional cure method. The sequential cure method consisted of two steps (i.) moisture cure to induce polyurethane network formation first and followed by (ii.) thermal cure for BA-a/PU and BA-a/BA-a reactions. Figure 5.3 illustrates FT-IR spectrum of a BA-a/PU 20/80 mixture under a moisture cure step at various times. FT-IR results revealed that the moisture cure reaction at room temperature proceeded with time. The decrease of the characteristic absorption band at 2264 cm^{-1}indicated that NCO-terminated group reacted with atmospheric moisture to produce a crosslink network. The observed urea bonds as characterized absorption bands at 1639 and 3291 cm^{-1} in the obtained network which was shown in Figure 5.2b. The time to complete PU network formation from the real time plot of FT-IR spectra was determined to be at least 48 hours when a specimen thickness 3 mm was used. Moreover, we observed that the moisture cure method merely completed the urethane network formation but did not influence the network formation of the benzoxazine monomer because the characteristic absorption bands of benzoxazine curing (see Figure 5.1) were not altered by moisture curing step.

Figure 5.4a-5.4c illustrates FT-IR spectrum of a BA-a/PU (20/80) mixture under a moisture cure step. From the FT-IR spectra, it can be observed that the disappearance of NCO-terminated group suggested the progress of inter or intra molecular reaction of the isocyanate group with moisture to produce the urea linkage. However, NCO-terminated group was found to reappear at higher temperature i.e. after 150^{o}C thermal cured that see in Figure 5.4a'-5.4d'. This phenomenon was possibly due to because of the breakage R-NHCO- bond of biuret and allophanate, it transformed to be NCO-terminated group. The biuret and allophanate in this system was produced from the excess isocyanate in side reactions [32-33]. The mechanism of reverse NCO at high temperature is described in Figure 5.5. Urethane groups may be considered hydrogen active compounds, due to the hydrogen atom linked to the nitrogen atom. By reaction of an isocyanate with a urethane group an allophanate is formed. Similarly to the allophanate formation, the –N-H groups of ure react with isocyanates to generate a biuret. Moreover, the phenomenon of NCO reappearance was also observed in traditional curing method as illustrated in Figure 5.6. This phenomenon was possibly due to because of the breakage R-NHCO- bond of allophanate.

The FT-IR spectra of network formation of BA-a/PU alloys (20/80) using sequential cured, were summarized in Figure 5.7. Figure 5.7 reveals the FT-IR spectra of BA-a/PU 20/80 resin mixture (Figure 5.7a), resin mixture after moisture cure step (Figure 5.7b) and polymer alloy (Figure 5.7c) in sequential cure method. From the Figure 5.7b, the decrease of characteristic absorption band at 2272 cm^{-1} indicated that NCO-terminated group reacted with moisture to produce a crosslink network. The moisture cure reaction produced urea linkages at characteristic absorbtion band at 1640 and 3300 cm^{-1}. After heating, from the Figure 5.7c, the characteristic absorption bands at 928 and 1226 cm^{-1} both assigned to C-O-C stretching mode of benzoxazine ring almost disappeared as a result of the opening of oxazine rings. Furthermore, the shift of tri-substituted benzene ring absorbance at 1496 cm^{-1} to tetra-substituted benzene ring at 1474 cm^{-1} and the appearance of a broad peak at about 3314 cm^{-1} due to the formation of phenolic hydroxyl groups indicated the occurrence of polybenzoxazine network. The absorbance peaks attributed to the chemical shifts of BA-a due to its ring opening polymerization (Figure 5.1) were not clearly seen from the FT-IR because the absorbances of benzoxazine are superposed by the absorbances of polyurethane. Moreover, isocyanate group from the reversible of biuret and allophanate might be reacted with phenolic hydroxyl groups from the ring-opened structure of the benzoxazine resin same as traditional cure method.

In addition, Figure 5.8 reveals the FT-IR spectra of BA-a/PU (20/80) resin mixture (Figure 5.8a) and of the fully cured polymer alloy (Figure 5.8b) obtained by a traditional cure method. From Figure 5.8a, the spectrum of the BA-a/PU resin mixture exhibited the characteristic peaks at 934 and 1228 cm^{-1} which were the C-O-C stretching mode of the benzoxazine resin. The absorption band at 2272 cm^{-1} was assigned to the NCO-terminated group of an un-reacted isocyanate group. After heating, both absorption bands of C-O-C stretching band of the benzoxazine resin and NCO-terminated group of urethane prepolymer reduced while the broad absorption band of the phenolic hydroxyl groups was observed at about 3353 cm^{-1} as shown in Figure 5.8b. This observation suggested that the phenolic hydroxyl groups from the ring-opened structure of the benzoxazine resin then reacted with the NCO groups. The results are also in good agreement with the result previously reported by Takeichi et al. [1, 11]. Takeichi et al. proposed that the reaction between NCO in PU and phenolic hydroxyl groups in the BA-a polymer might have occurred, although not all the chemical changes can be confirmed by FT-IR due to the structure similarity of the PU and BA-a polymer.

5.2 Processing Windows of BA/PU Resin Determined by Rheometry

All BA-a/PU resin mixtures are miscible giving homogenous and transparent liquid mixtures after blended. The effect of the urethane prepolymer on the chemorheology of the BA-a/PU resin mixture is shown in Figure 5.9. In the the processing windows rheograms, the temperature of the resin mixture was ramped from about 30^{o}C up to the temperature beyond the gel point of each sample using a heating rate of 2^{o}C/min and the dynamic viscosity was recorded. On the left hand side of Figure 5.9, we can see that the liquefying temperature of the binary mixture as indicated by the lowest temperature that the viscosity rapidly approaches its minimum value significantly decreases with increasing the urethane prepolymer mass fraction. For consistency, the temperature at the viscosity value of 1000 Pa s was used as a liquefying temperature of each resin. Figure 5.9, it was observed that the increasing urethane prepolymer mass fraction in the resin mixtures led to the lowering of their liquefying temperatures. This is due to the fact that the urethane prepolymer used is liquid while the benzoxazine resin is solid at room temperature. The addition of the liquid urethane prepolymer in the solid BA-a resin yielded a softer solid at room temperature ranging from BA-a/PU (80/20) to BA-a/PU (60/40). Moreover, it can be investigated that mass fraction of urethane prepolymer was more than mass fraction of benzoxazine resins, no liquefying temperature was detected. It reveals the fact that with PU more than 50% by weight of the resin mixtures is liquid at room temperature. Therefore, the addition of the urethane prepolymer in the BA-a resin caused the shifting of the transition from solid state to liquid state at lower temperature. Lowering the liquefying temperature obviously enables the use of lower processing temperature of a compounding process, which is desirable in various applications.

In addition, at the end of the A-stage viscosity or at higher temperature, the resin mixtures underwent crosslinking reactions past their gel points, which was defined as a transition of liquid (sol) to solid (gel), (i.e. the right side of the rheograms), resulting in a sharp increase in their viscosities. In this case, the maximum temperature at which the viscosity was rapidly raised above 1000 Pa.s was used as gel temperature of each resin [34-35]. On the right hand side of Figure 5.9, it can be seen that the gel point was found to increase with increasing the mass fraction of urethane prepolymer. These results suggested that the urethane prepolymer had retardation effect on the curing reaction of the benzoxazine monomers. These results are in good agreement with the behavior of the exothermic peaks in DSC thermograms (see in Figure 5.10). When the urethane prepolymer was mixed into the benzoxazine resin, the exothermic peaks in DSC thermograms were found to shift to higher temperature confirming a curing retardation effect of the urethane prepolymer. Furthermore, the processing windows of the BA-a/PU resin mixtures, defined by temperature ranges from liquefying temperature to gelation temperature, were clearly widened with an addition of the urethane prepolymer. For example, the processing window for BA-a/PU at 60/40 was approximately 50^{o}C to 218^{o}C compared to the range of 68^{o}C to 195^{o}C for the neat benzoxazine resin. This behavior provides BA-a/PU resins with sufficiently broad processing windows for a typical compounding process in a composite manufacturing.

5.3 Differential Scanning Calorimetry (DSC) for Curing Behavior Investigation

The curing behavior of the binary mixtures of benzoxazine resin and urethane prepolymer at various compositions by differential scanning calorimetry using a heating rate of 10^{o}C/min at a temperature range of 30-300 ^{o}C is shown in Figure 5.10. From the DSC thermograms, it can be seen that only a single dominant exothermic peak of the curing reaction in each resin composition was observed. The phenomenon suggested that the reactions to form a network structure of these binary mixtures took place simultaneously at about the same temperature. Moreover, we see that the curing reaction of these binary systems was observed to proceed without the need of any catalyst or curing agent. In the Figure 5.10, when the urethane prepolymer was mixed into the benzoxazine resin, the exothermic peak was observed to shift to higher temperature. For example, the positions of exothermic peak of BA-a/PU resin mixtures at 100/0, 80/20, 60/40, 40/60, 20/80 mass ratio were found to be 232 ^{o}C, 242 ^{o}C, 250 ^{o}C, 253 ^{o}C and 255 ^{o}C, respectively. This can be explained by the dilution effect of the benzoxazine monomers with the presence of the urethane prepolymer since the curing retardation was more pronounced when the amount of urethane prepolymer increased. The shifting to high temperature of the exothermic peaks of the mixtures also showed a similar trend to the gelation temperature of the resin mixtures. The graph also revealed a decrease of the area under the exothermic peak with increasing mass fraction of the urethane prepolymer most likely due to a decrease in the number of moles of the reacted functional groups of each resin mixture with the amount of the urethane prepolymer. This is due to the fact that urethane prepolymer cannot form a network by heat and requires BA-a as its crosslinker. Thus the lower the BA-a fraction, the less curing exotherm was observed.

5.4 Effect of Processing Condition on Dynamic Mechanical Properties

The mechanical properties of BA-a/PU alloys processed by sequential cure and traditional cure methods were investigated by a dynamic mechanical analyzer (DMA). The experiment was performed under a tension mode from -120 to 300^{o}C. The evaluated polymer alloy compositions were ranging from 0-100% by weight of PU mass fraction. The dynamic mechanical properties of the BA-a/PU alloys using traditional heat cure method are shown in Figure5.11-5.13. From Figure 5.11, the storage modulus of a solid polymer at its glassy state tended to decrease with increasing PU mass fraction in the polymer alloys as a result of the more flexible PU compared to the polybenzoxazine. The storage modulus at room temperature of the neat polybenzoxazine and the polyurethane were determined to be 3.12 GPa and 0.00215 GPa whereas their alloys showed the storage modulus at room temperature of 1.51 GPa in BA-a/PU 80/20, 1.03 GPa in BA-a/PU 60/40, and 0.167 GPa in BA-a/PU 40/60 respectively. This result indicated that the addition of the more flexible PU in the polymer alloys make the materials more flexible thus broadened the useful properties of the polybenzoxazine. When benzoxazine was a major component, rubbery plateau modulus of polymer alloys was increased with urethane prepolymer mass fraction whereas opposite trend was observed in the modulus at room temperature. Crosslink density of a polymer network can be calculated from rubbery plateau modulus as suggested by Nielsen [36].

$$\log\left(\frac{E'}{3}\right) = 7.0 + 293(\rho_x) \qquad (5.1)$$

From Nielson’s equation above, E' is a storage modulus in a rubbery plateau region (dyn/cm^2), ρ_x is a crosslinked density that is the mole number of network chains per unit volume of the polymers (mol/cm^3).The crosslinked density of all polymer alloys that determined from equation 5.1 was found to increase with the mass fraction of the urethane prepolymer. In addition, when polyurethane was a major component, the rubbery plateau modulus of polymer alloys was increased with benzoxazine resin mass fraction when compared with the neat polyurethane. This clearly shows the increase of the crosslink density with the increase of benzoxazine content.

The glass transition temperature (T_g) of BA-a/PU alloys that obtained by the two processing conditions was determined from the peak maximum of the loss modulus (E") curves. Figure 5.12 shows the loss modulus curves of the BA-a/PU alloys obtained by a traditional cure method as a function of temperature. As T_g depends largely on the amount of the thermal energy required to keep the polymer chains moving, a number of factors which affect rotation about chain link, will also influence T_g. Those factors are (1) chain flexibility. (2) molecular structure (steric effect), (3) molar mass, and (4) branching and crosslinking [37]. When the BA-a was a major component, the BA-a/PU alloys films showed two peak maxima or two Tg’s in the loss modulus curve. The T_g at about -61^{o}C belonged to the polyurethane domain in the alloys while another peak at higher temperature was a T_g of BA-a/PU alloys. This suggested that BA-a/PU alloys films was a heterogeneous network that composed of polyurethane domain and benzoxazine domain in the alloy sample. From Figure 5.12, we can see that the T_g of the neat polybenzoxazine was determined to be 186°C whereas those of the polymer alloys were about 208°C in BA-a/PU (80/20), and 252°C in BA-a/PU (60/40). Therefore, adding urethane elastomer into polybenzoxazine can substantially increase the T_g of the polymer alloys. Moreover, the synergistic behavior of the T_g of the alloys was evidently observed that T_g’s of all alloys showed greater values than both of the polybenzoxazine and the polyurethane i.e. 186°C and -61°C, respectively. On the other hand, the BA-a/PU alloy films having PU as a major component, showed only one glass transition temperature at about -51°C which was the characteristic of an elastomeric material. The T_g of these alloys were slightly increase when compare with T_g of the neat polyurethane.

Effect of a crosslinked density on a T_g of the polymer network can be accounted for using the Fox-Loshaek equation [38].

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

where $Tg(\infty)$ is the glass transition temperature of infinite molecular weight linear polymer, k and k_x are the numerical constants, M_n is the number averaged molecular weight which equals infinity in the cross-linked system, therefore, this term can be neglected in our case and ρ_x is the crosslinked density. According to the Fox-Loshaek equation, the cross-linked density is one key parameter affecting T_g of the polymer networks. The T_g of the polymer network increased when its cross-linked density in the alloys increased. From those results, it can be concluded that an ability of the urethane prepolymer to enhance crosslinked density of the polybenzoxazine alloys was attributed to the observed synergy in glass transition temperatue as explained above.

The glass transition temperature and network charateristic of BA-a/PU alloy films were also examined in Tan δ curves, shown in Figure 5.13. The tan δ or loss tangent curves, obtained from the ratio of energy loss or viscous part (E") to storage energy or elastic part (E') of dynamic modulus of material. The T_g of the polymer alloys can also obtained from the peak temperature on the tan δ curve of each sample similar to that from the loss modulus curve. The T_g’s of the alloys were observed to shift to higher temperature when the urethane prepolymer content in the alloys increased same as those from the loss modulus curves. Moreover, the magnitude of the tan δ peak reflecting the large scale mobility associated with alpha relaxation. The peak height of the tan δ tended to decrease when the mass fraction of the urethane prepolymer increased. This suggested the reduction in chain’s segmental mobility with increasing crosslinked density as urethane prepolymer mass fraction in the polymer alloys increased. Furthermore, the width at half height of the tan δ corresponded to the network heterogeneity of the system. Furthermore, in Figure 5.13, the width at half height of the tan δ curves of BA-a/PU polymer alloys was broader with increasing urethane prepolymer mass fraction in the polymer alloys. This implied that a more heterogeneous network in the BA-a/PU polymer alloys was observed when the PU mass fraction increased.

In addition, the dynamic mechanical properties of the BA-a/PU alloys under sequential cure method are shown in Figure5.14-5.16. The storage modulus of a BA-a/PU alloys obtained by a sequential cure method in Figure 5.14 tended to decrease with increasing the PU mass fraction same as the storage modulus of a BA-a/PU alloys obtained by a traditional cure method in Figure 5.11. The storage modulus at room temperature of the neat polybenzoxazine and the polyurethane were determined to be 3.12 GPa and 0.00215 GPa whereas their alloys showed the storage modulus at room temperature of 1.57 GPa in BA-a/PU 80/20, 0.69 GPa in BA-a/PU 60/40, and 0.0215 GPa in BA-a/PU 40/60 respectively. The crosslinked density of all polymer alloys was found to increase with the mass fraction of the urethane prepolymer. Moreover, the glass transition temperature (T_g) of BA-a/PU alloys obtained by sequential cure method were shown in Figure 5.15. The BA-a/PU alloy films again showed two glass transition temperatures when BA-a was a major component in the network. The T_g of the BA-a/PU (60/40) showed single T_g at -57°C which was the characteristic of an elastomeric material. Moreover, the synergistic behavior of the T_g of the alloys were observed to be the same as that of the traditional cure method. From Figure 5.15, the T_g of the neat polybenzoxazine was determined to be 186°C whereas those of the polymer alloys were about 216°C in BA-a/PU (80/20), 260°C in BA-a/PU (60/40). The glass transition temperatures of BA-a/PU alloy films under sequential cure method obtained from Tan δ curves were illustrated in Figure 5.16. T_g's of the all alloys were observed to shift to higher temperature with urethane prepolymer content same as those from the traditional cure method. From the above results, it was evident that the specimens obtained from both processing methods yielded almost the same mechanical and thermal properties although they experienced different network formation schemes. It was likely that the thermal treatment which was used in both processing methods provided the final alloy network of similar characteristics. Under the thermal treatment (up to 200^{o}C for 4 hr.), most network linkages might undergo rearranging reaction from the reversible nature of most network linkages thus provided the final network structures with similar characteristics.

The storage modulus at room temperature of the samples from the two processing conditions was compared in Figure 5.17. The storage modulus of both processing method clearly decreased with increasing PU mass fraction in the polymer alloys. However, the storage modulus of the specimen from sequential cure method was lower than traditional cure method in BA-a/PU 60/40 and 40/60. This might be due to the fact that sequential cure method produced greater continuous network of polyurethane than traditional cure method. The crosslinked density of the two processing conditions was compared in Figure 5.18. From this figure, the crosslinked density of BA-a/PU alloys obtained by traditional cure method was slightly higher value than that of BA-a/PU alloys obtained by sequential cure method. This implied that the molecular motion in the BA-a/PU alloys obtained by traditional cure method was slightly more restricted than the BA-a/PU alloys obtained by sequential cure method. Moreover, the glass transition temperature of two processing condition were compared in Figure 5.19. The glass transition temperature of BA-a/PU alloys obtained by sequential cure method was observed to be slightly higher than BA-a/PU alloys obtained by traditional cure method. However, the values of the glass transition temperature were only about 5^{o}C different. The above results suggested that the two processing schemes had no significant effect on those major properties of the obtained alloys. The major factor that greatly influenced most properties of those BA-a/PU alloys was mainly the composition of the alloys.

5.5 Effect of Processing Condition on Thermal Stability

Thermal stability of BA-a/PU alloys under two processing conditions was investigated by thermogravimetric analysis (TGA) under N_2 atmosphere and the thermagram are shown in Figure 5.20 and 5.21. Figure 5.20 shows TGA thermogram of BA-a/PU alloys under traditional cure method at various urethane contents. The thermal stability of BA-a/PU alloys was indicated by the degradation temperature (T_d)

at 5% or 10% weight loss of the specimens. The thermal decomposition in each alloy was found to show a single stage weight loss. The T_d's of the neat polybenzoxazine and the polyurethane were determined to be 326°C and 274°C whereas their alloys showed the T_d values of 340°C in BA-a/PU 80/20, 348°C in BA-a/PU 60/40, 336°C in BA-a/PU 40/60 and 327°C in BA-a/PU 20/80 respectively. T_d's of the polymer alloys were found to marginally change with increasing urethane content but when mass fraction of urethane prepolymer was more than that of the benzoxazine resin, T_d's of the polymer alloys were found to decrease with the PU mass fraction. Therefore, the addition of the urethane prepolymer into the polybenzoxazine was able to maintain the thermal stability of the polybenzoxazine up to about 60% by weight of the PU. These results are in good agreement with the previous reports by Rimdusit et al. [12].

Figure 5.21 shows TGA thermogram of BA-a/PU alloys under sequential cure method at various urethane contents. The initial decomposition temperature of the specimens under sequential cure method showed similar trend as the specimens under traditional cure method. The T_d values of BA-a/PU 80/20, 60/40, 40/60, 20/80 were determined to be 329°C, 329°C, 327°C and 321°C respectively. The initial decomposition temperatures of different processing were compared in Figure5.22. This Figure show that the initial decomposition temperature of traditional cure method higher values than the initial decomposition temperature of sequential cure method. The maximum initial decomposition temperatures of all alloys were occurring at BA-a/PU 60/40 of both processing condition. These results might be due to crosslink density of the polymer alloys at traditional cure method higher than sequential cure method.

Furthermore, the char yield of BA-a/PU alloys under traditional cure method and sequential cure method, which reported at 800^oC under N_2 atmosphere, was illustrated. In Figure 5.20, the polybenzoxazine had higher char yield value of about 34% while the polyurethane was used no char residue. This is due to the fact that the chemical structure of the polyurethane composed of a less thermally stable aliphatic structure of the polypropylene glycol polyol compared to the prevalent benzene rings in the molecular structure of the polybenzoxazine. It can be observed that the residual weight of the BA-a/PU alloys was found to systematically decrease with increasing PU mass fraction. The char yields of BA-a/PU alloys value of 31 in BA-a/PU 80/20, 29 in BA-a/PU 60/40, 25 in BA-a/PU 40/60 and 12 in BA-a/PU 20/80 respectively. Because of, the polyurethane had much lower char forming ability than the polybenzoxazine. This result is also consistent with our previous reported [1, 11, 12]. In Figure 5.21, the char yields of BA-a/PU alloys value of 32 in BA-a/PU 80/20, 31 in BA-a/PU 60/40, 22 in BA-a/PU 40/60 and 11 in BA-a/PU 20/80 respectively. The char yields of different processing were compared in Figure5.23. From the results revealed that the both processing conditions have no effect on char yield. Because the char yield depend on compositions of benzoxazine resin more than network structure.

5.6 Effect of Processing Condition on Density

Density measurement of all BA-a/PU alloys was showed the presence of void in the specimens. Figure 5.24 illustrates the density of specimens with various urethane contents comparing with their theoretical density. The actual density of the polymer alloys was calculated using equation (4.1) and the theoretical density of the polymer alloys was calculated from equation (4.2) in experimental section. The theoretical density was calculated based on the densities of the polyurethane and polybenzoxazine were 1.06 g/cm^3[38] and 1.19 g/cm^3[39] respectively. In the result, the densities of the polymer alloys were observed to systematically decrease with increasing urethane prepolymer fraction suggesting that the theoretical and actual density of the BA-a/PU alloys followed the rule of mixture. The rule of mixture of theoretical densities were determined to be 1.164 g/cm^3 in BA-a/PU 80/20, 1.138 g/cm^3 in BA-a/PU 60/40, 1.112 g/cm^3 in BA-a/PU 40/60 and 1.086 g/cm^3 in BA-a/PU 20/80. Figure 5.24 observed that the actual densities were slightly lower than those of the theoretical densities of both processing condition. Because of the rather high melt viscosity of the urethane prepolymer, adding more urethane prepolymer directly affected on the mixing behavior and the obtained densities were normally slightly lower than the theoretical values.

5.7 Effect of Processing Condition on Swelling Degree and Gel Content in Chloroform

The BA-a/PU alloys of two processing condition were characterized in term of their degree of swelling in chloroform. Swelling is the process of dissolution of a polymer in a defined solvent. At first, the solvent molecules slowly diffuse into the polymer to produce a swollen gel. If the polymer–polymer intermolecular forces are high, thanks to crosslinking, crystallinity, or strong hydrogen bonding, this is all what happens. But, if these forces are overcome by the introduction of strong polymer–solvent interactions, a second stage, the dissolution of the polymer, can take place [40]. The process of swelling results actually from the balance between repulsive and attractive phenomena i.e. (i) the thermodynamic mixing between the net polymer and the solvent. (ii) Interaction between fixed charged groups and free ions as happens in proton-exchange membranes and (iii) the elastic force of the polymer and also inter-chain attractive forces. The relationship between the degree of swelling of BA-a/PU alloys and polyurethane content are illustrated in Figure 5.25. The film specimens can swell at different degree in chloroform. In this Figure, it is clearly observed that the volumetric swelling degree of the BA-a/PU alloys under both processing conditions increased along with polyurethane content. The same behavior was reported by Feng and Li [28]. They studied volumetric swelling degree of polyesterurethane (PULG) during degradation and before degradation in chloroform. They reported that the volumetric swelling degree of copolymer network increased along with degradation time. This indicated that the polymer chain between crosslink points broke down due to the scission effects of molecules, ions and radicals in the oxidative degradation solution. Pekel et al. [41] reported that volumetric expansion of the network reduced as a function of increasing crosslink density. Moreover, the volumetric swelling degree of BA-a/PU alloys increased rapidly from 3.5 (BA-a/PU 20/80) to 17 (neat polyurethane) because of their broken network in chloroform. Comparing the swelling values of neat benzoxazine to BA-a/PU 40/60, the volumetric swelling degree of the Ba-a/PU alloys slightly increased with increasing the polyurethane content. Therefore, the benzoxazine structure (more than 40% mass fraction) combined with polyurethane can obstruct their swollen and broken network of polyurethane in chloroform.

Gel content of BA-a/PU alloys of two processing condition in chloroform at various composition were presented in Figure 5.26. Gelation dose, at which is the amount of insoluble polymer in any solvent [42]. In this Figure, it is clearly seen that the gel fraction of the BA-a/PU alloys both processing conditions decreased with an increase of polyurethane content. The gel content was determined to be 96% of neat polybenzoxazine in one week. The gel content of the polyurethane can also be observed values at about 45%. Hence, gel content of the BA-a/PU alloys decreased with an increase of polyurethane mass fraction. This results was implied that mass fraction of polyurethane in films had significant effect on gel content of the BA-a/PU alloys. Therefore, to incorporate of benzoxazine structure with polyurethane can improve their network degradation of polyurethane in chloroform.

5.8 Phase Separation Behavior of BA-a/PU Alloys

Phase separation of BA-a/PU alloys were investigated using a homemade slide-on diamond µIRE in Nicolet 6700 equipped with infrared microscope and micro hardness tester. Figure 5.27 shows FT-IR spectrum of a BA-a/PU alloys (BA-a 80% weight ratio, cured at 180^{o}C 1 hour) at top surface (Figure 5.27a) and bottom surface (Figure 5.27b) respectively. From this figure, it can be observed that intensity of characteristic absorption band at 1730-1700 cm^{-1} which assigned to urethane bond (NH-COO) and the appearance of a broad peak at about 3500 cm^{-1} due to the formation of phenolic hydroxyl groups indicated the existance of polybenzoxazine network at top surface more than at bottom surface. This phenomenon suggested that on the top surface have urethane portion more than the bottom surface. Moreover, this result was confirmed by hardness test. Microhardness of compressed specimens was measured utilizing a vickers microhardness tester. Figure 5.28 exhibits surface hardness of BA-a/PU alloys on top surface and bottom surface at various curing temperature i.e. 180 ^{o}C 1 hour, 3 hour and 5 hour. From the figure, it can be noticed that surface hardness values of top surface exhibited lower than bottom surface in all curing condition. This result implied that the top surface have urethane portion more than bottom surface. Because of urethane is elastic material whereas polybenzoxazine is rigid material. Furthermore, the surface hardness values of top surface and bottom surface was increase with curing temperature. This phenomenon suggested that both of top and bottom surface also have benzoxazine network which influenced to hardness.

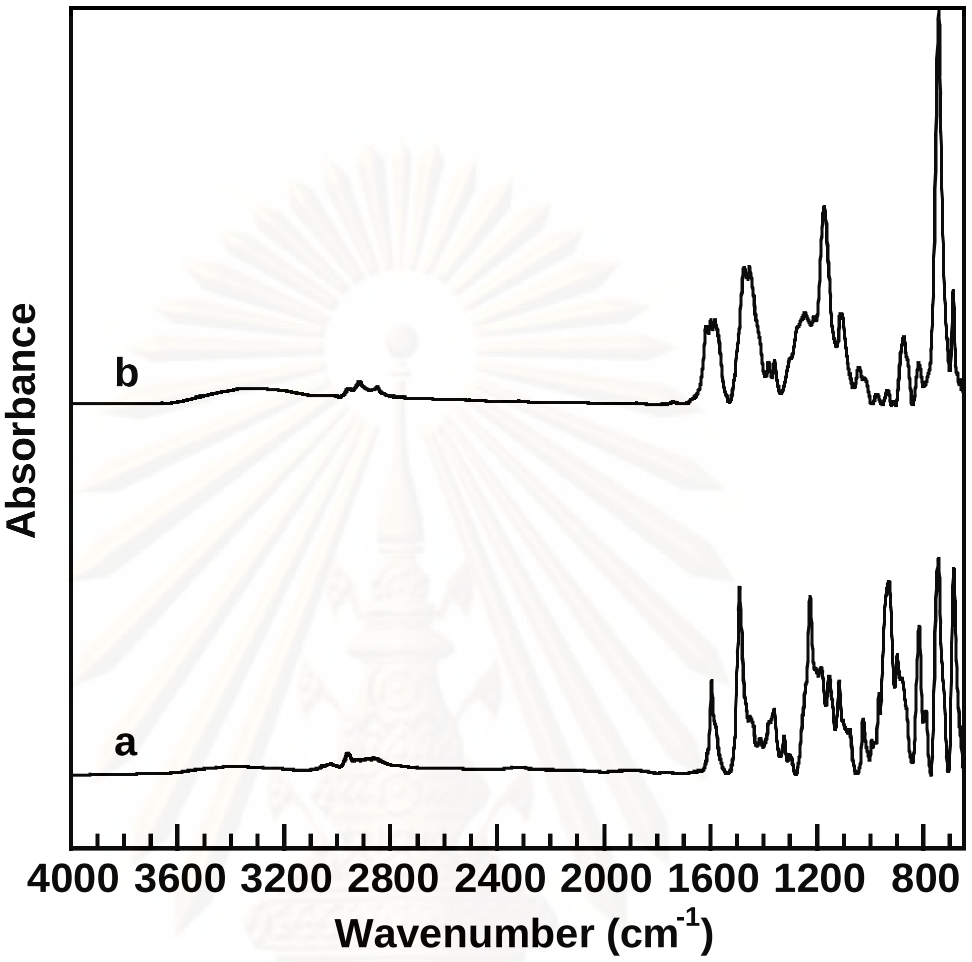


Figure 5.1. FT-IR Spectra of benzoxazine resin and its polymer: a) Benzoxazine monomer (BA-a); b) Polybenzoxazine (PBA-a).

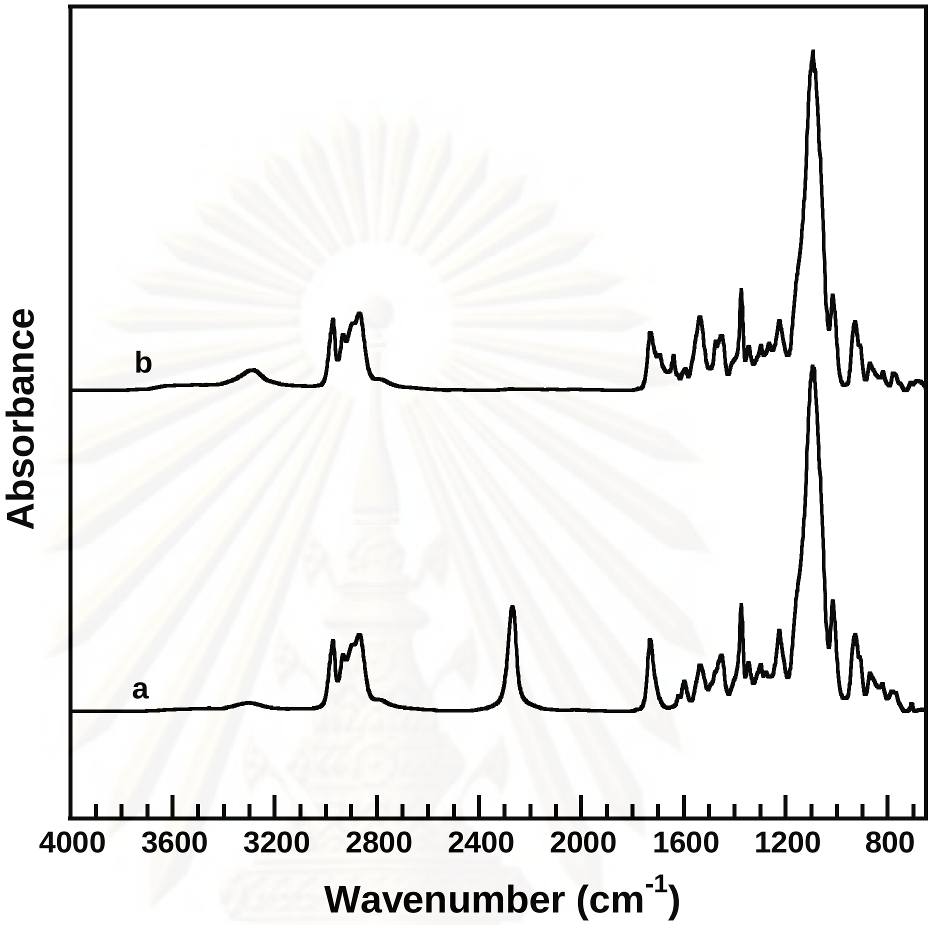


Figure 5.2. FT-IR Spectra of urethane prepolymer and its polymer:
a) Urethane prepolymer; b) Polyurethane.

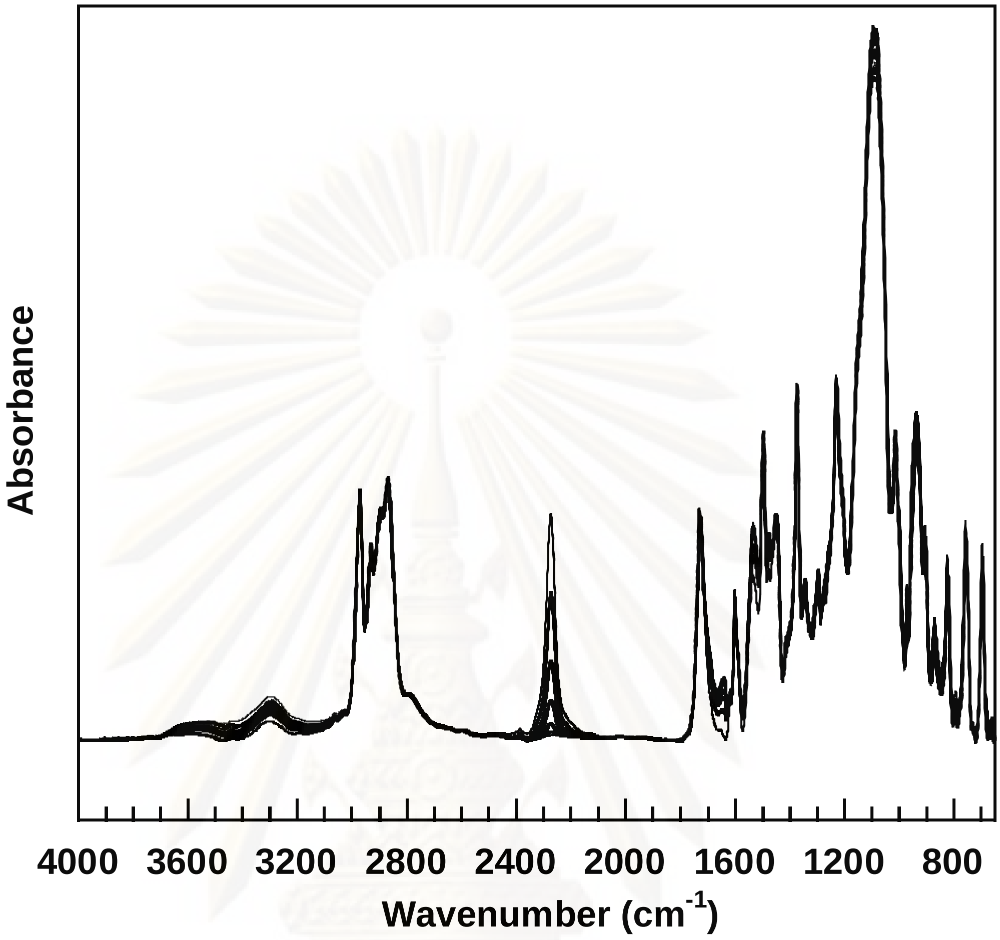


Figure 5.3. FT-IR spectra of BA-a/PU alloys (20/80) obtained by moisture cure method at various times.

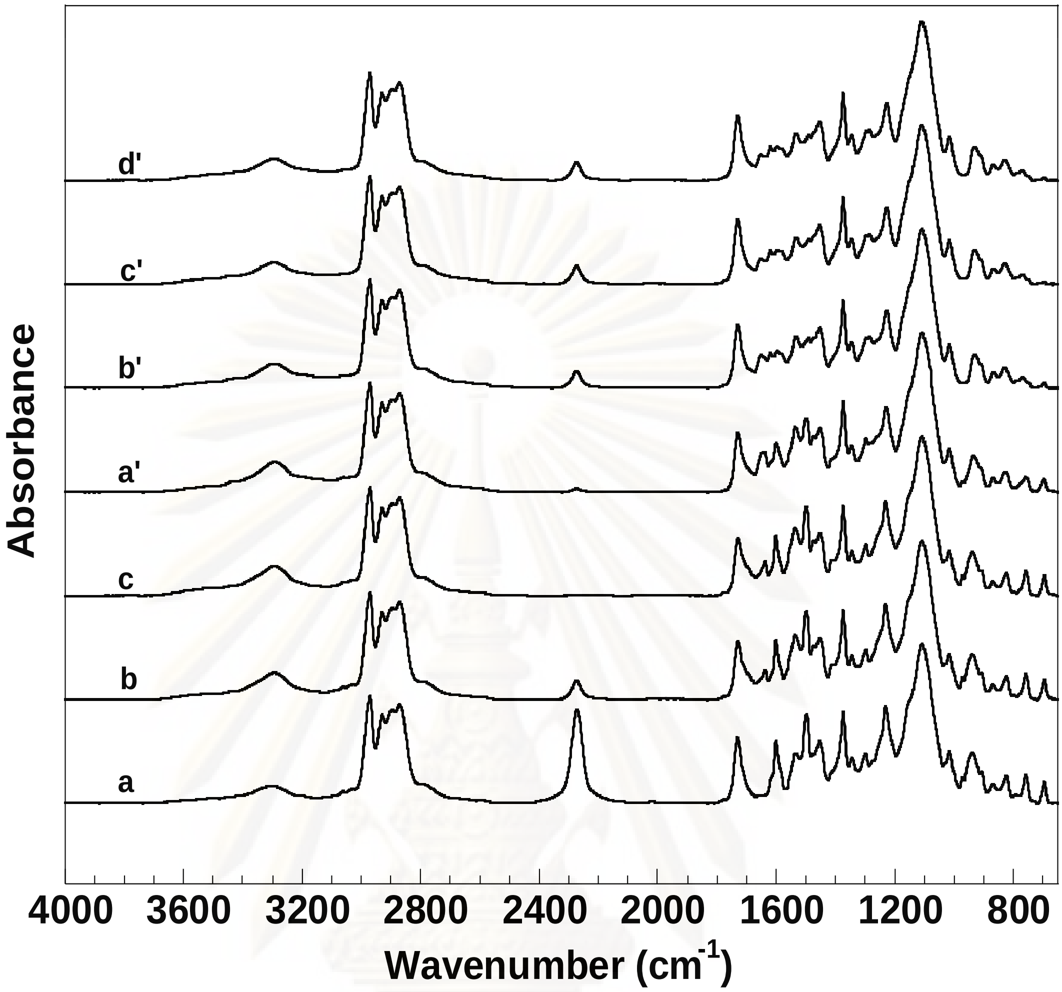


Figure 5.4. FT-IR spectra of BA-a/PU alloys (20/80) by moisture cured: a) 0 hr; b) 8 hr; and c) 12 hr) and thermal treated: a') 150 °C/1 hr; b') 180 °C/1 hr; c') 190 °C/1 hr and d') 200 °C/1 hr.

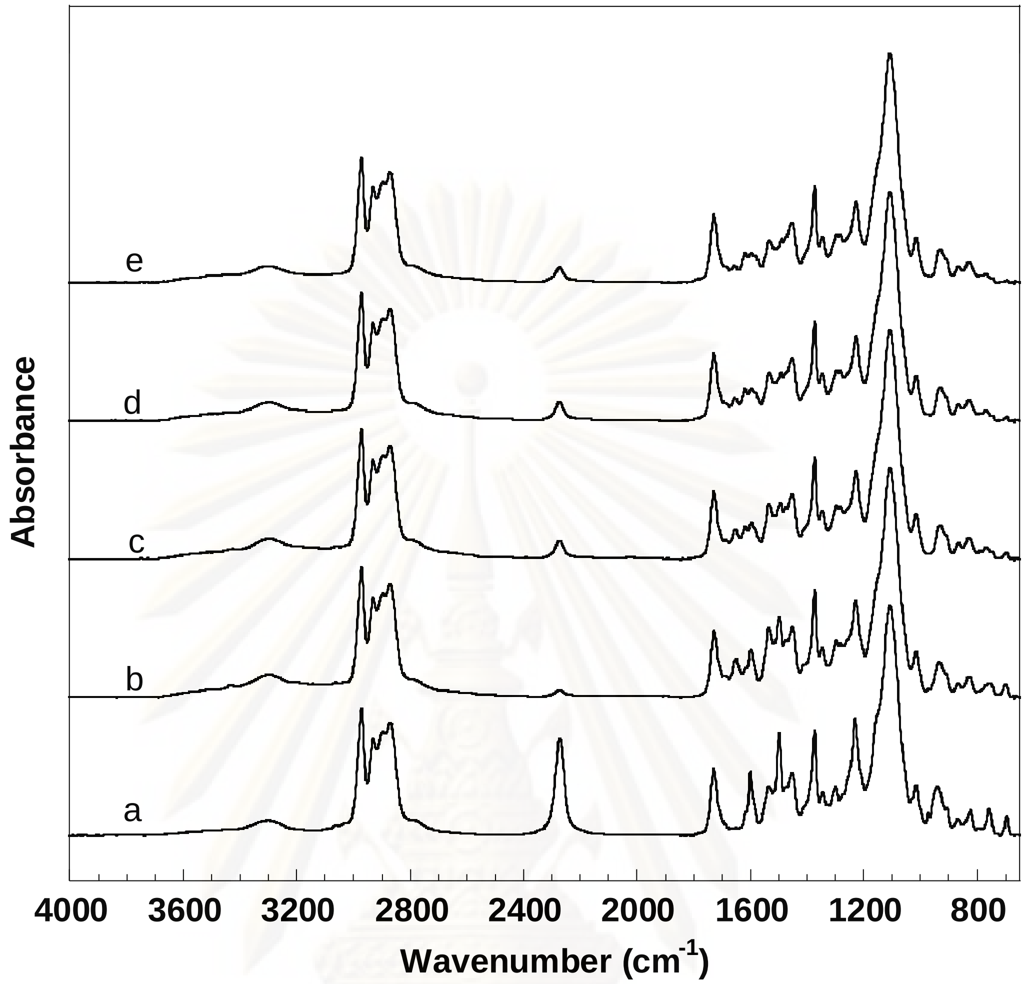


Figure 5.5. FT-IR spectra of BA-a/PU alloys (20/80) by thermal cured:
a) before treated; b) 150 ^{o}C/1 hr; c) 180 ^{o}C/1 hr; d) 190 ^{o}C/1 hr and e) 200 ^{o}C/1 hr.

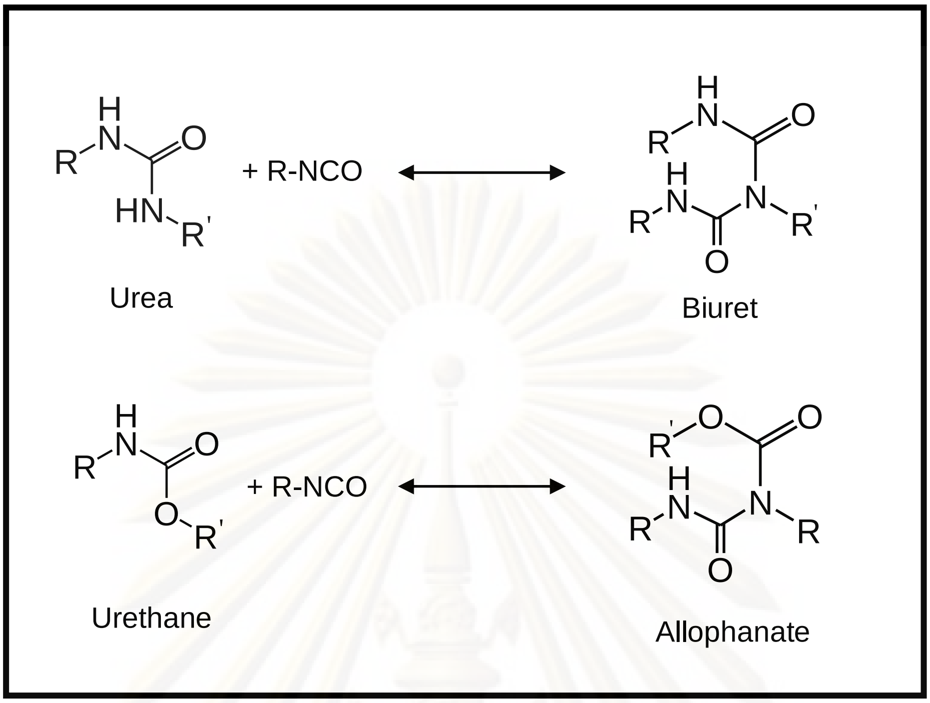


Figure 5.6. Formation of secondary isocyanate reaction products.

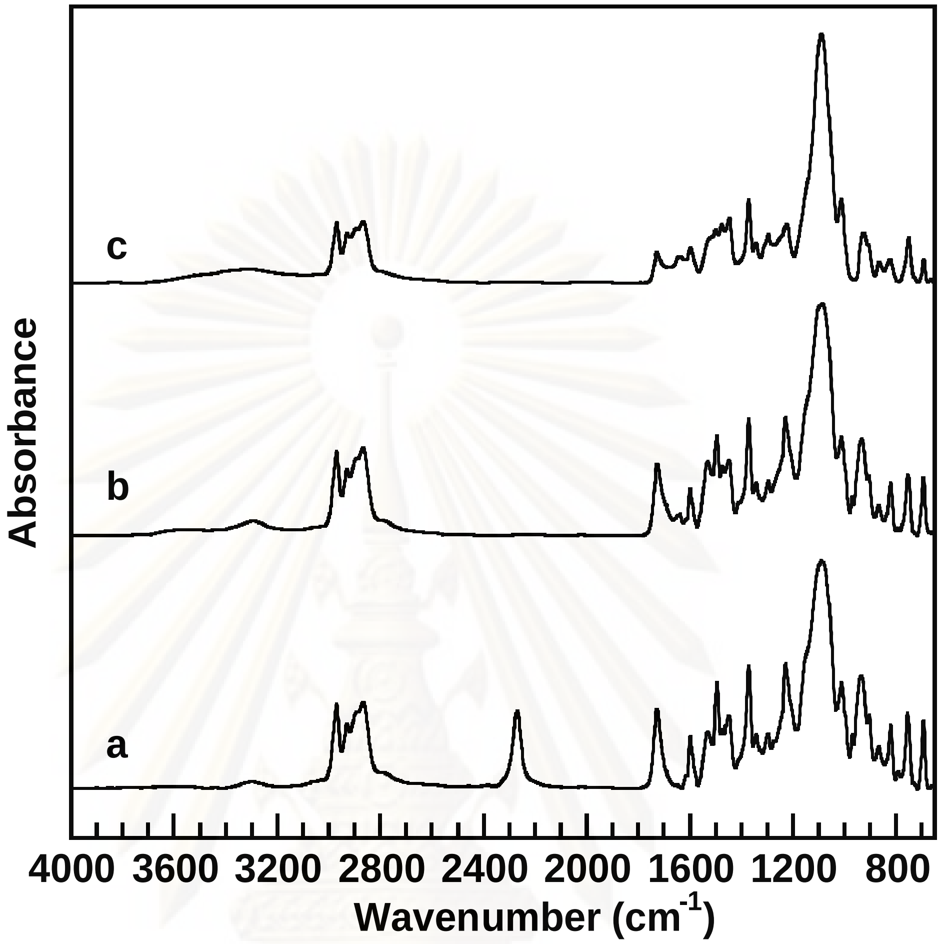


Figure 5.7. FT-IR spectra of BA-a/PU alloys (20/80) obtained by sequential cure method**:** a) BA-a/PU resins; b) moisture cured; c) thermal cured.

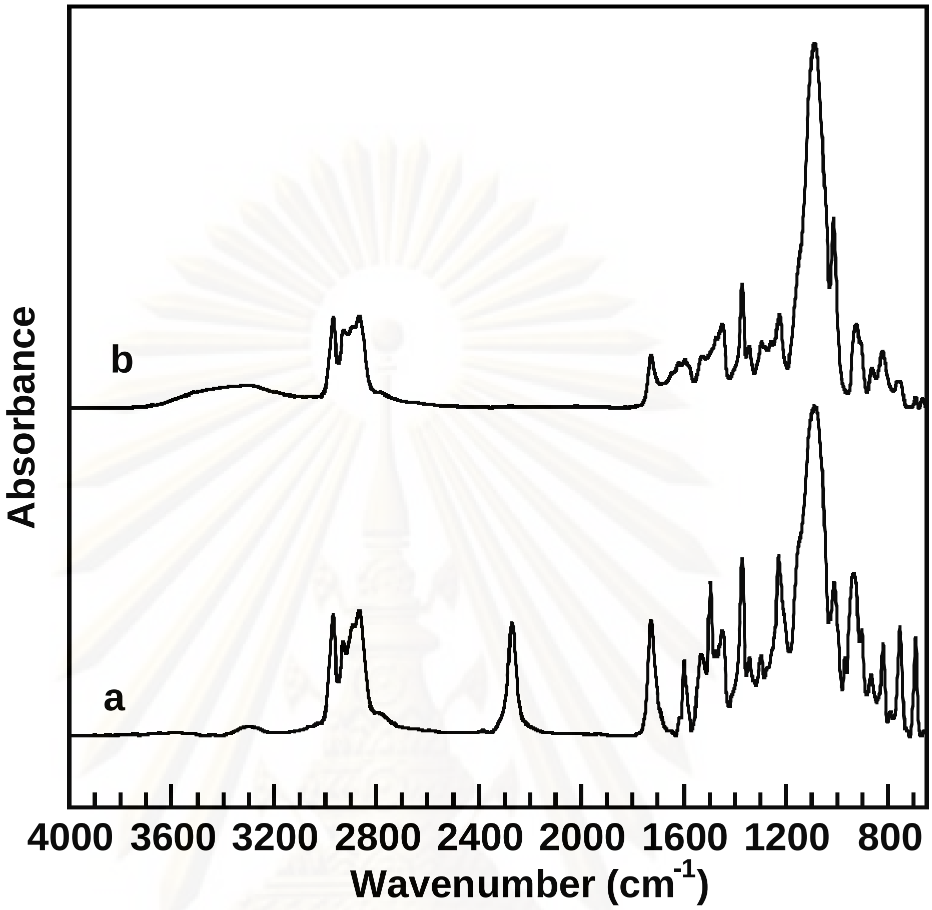


Figure 5.8. FT-IR spectra of BA-a/PU alloys (20/80) obtained by traditional cure method**:** a) BA-a/PU resins; b) thermal cured.

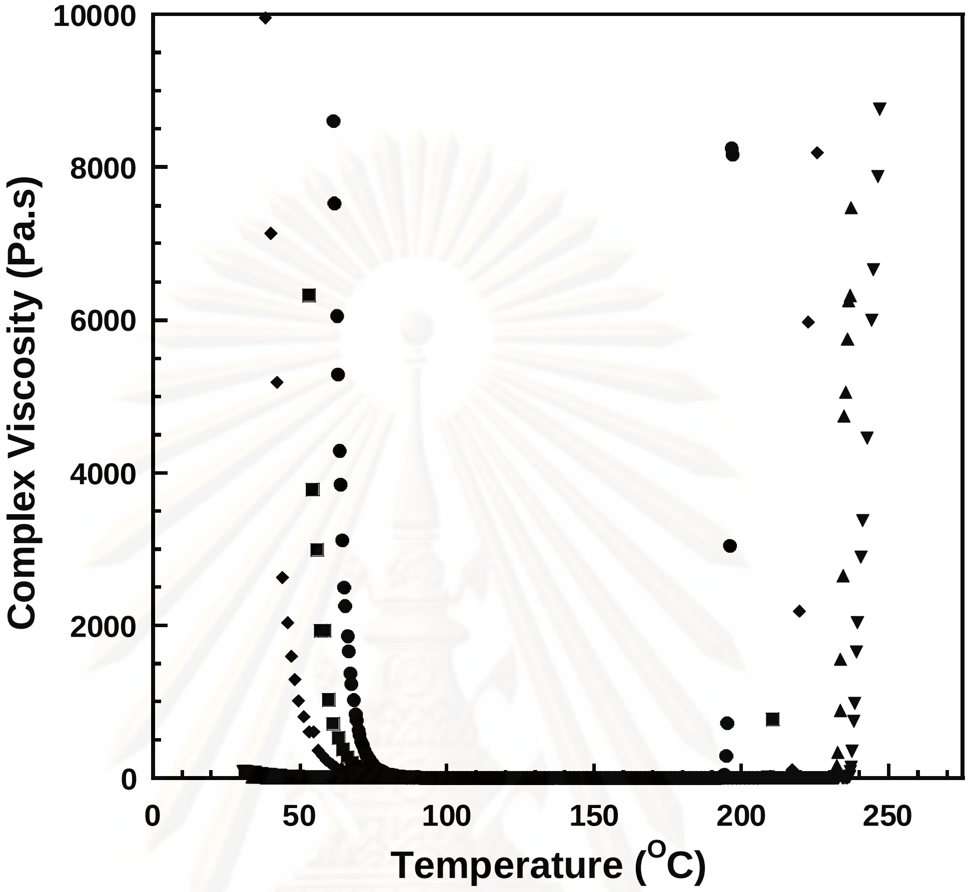


Figure 5.9. Processing windows of BA-a/PU resin mixtures at various compositions: (●) BA-a/PU 100/0, (■) BA-a/PU 80/20, (◆) BA-a/PU 60/40, (▲) BA-a/PU 40/60 and (▼) BA-a/PU 20/80.

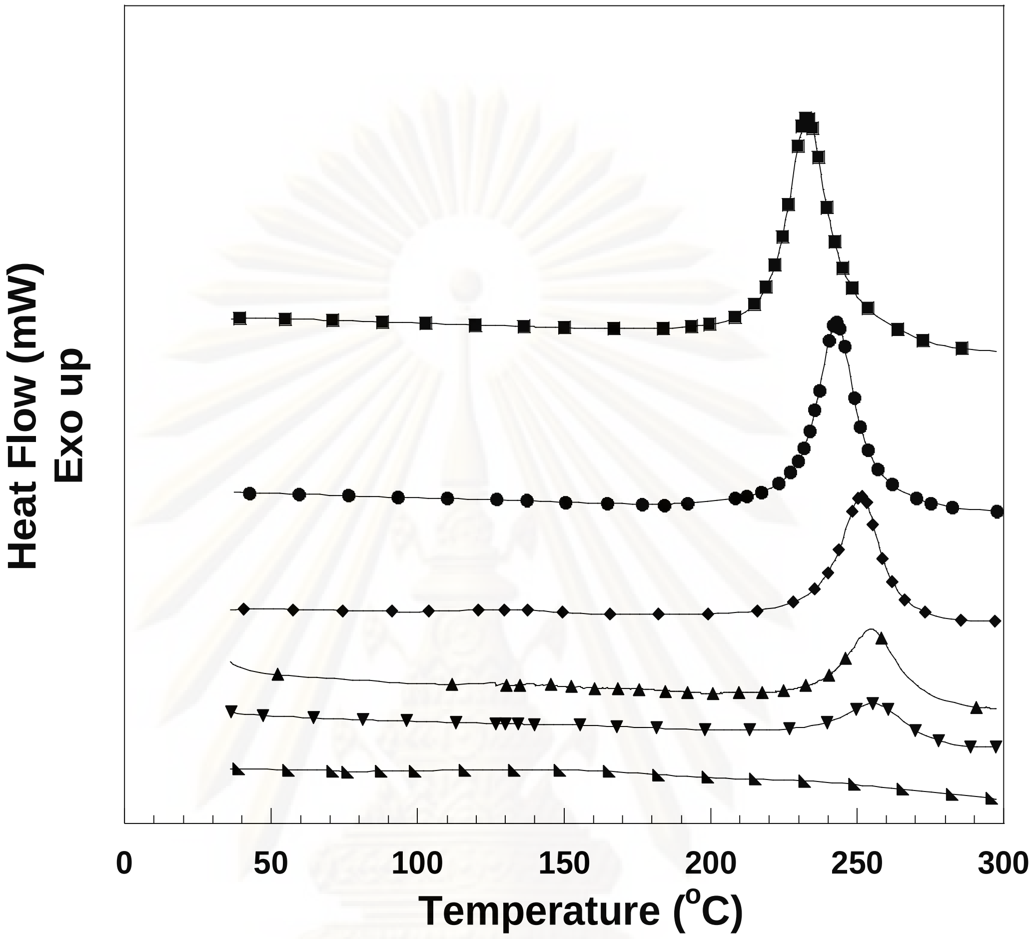


Figure 5.10. DSC thermograms of BA-a/PU resin mixtures at various compositions: (●) BA-a/PU 100/0, (■) BA-a/PU 80/20, (◆) BA-a/PU 60/40, (▲) BA-a/PU 40/60 (▼) BA-a/PU 20/80, and (◣) BA-a/PU 0/100.

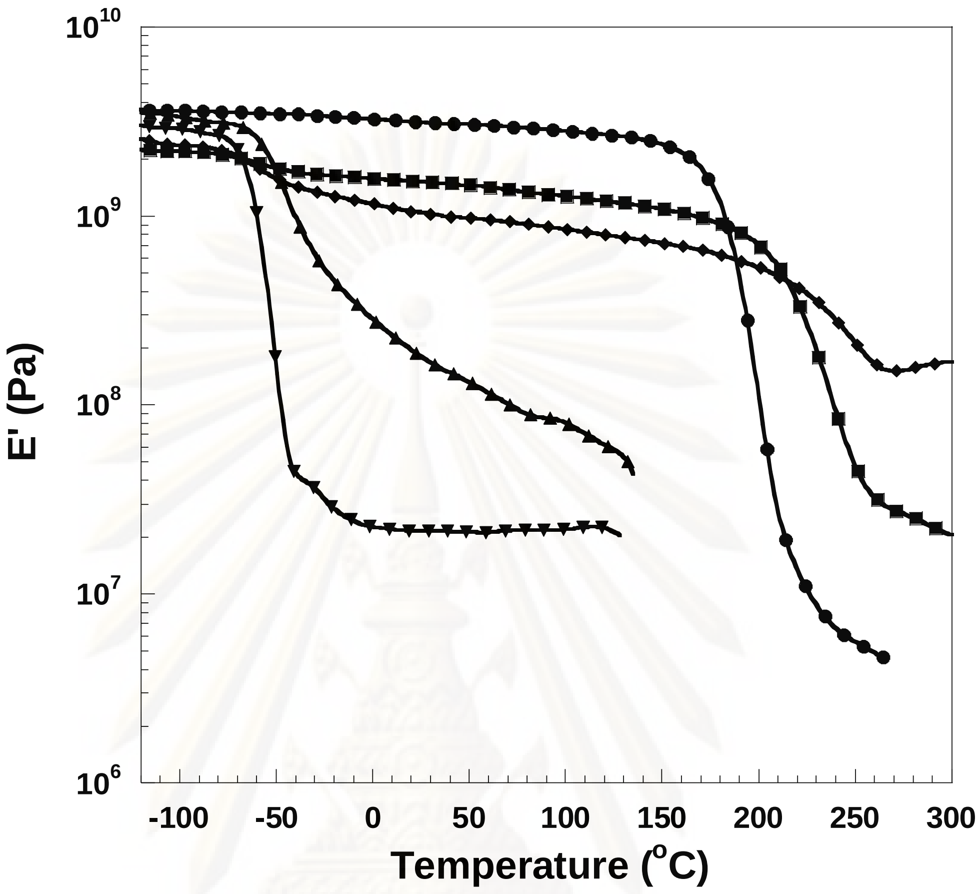


Figure 5.11. Storage modulus of BA-a/PU alloys obtained by traditional cure method at various PU compositions: (●) BA-a/PU 100/0, (■) BA-a/PU 80/20, (◆) BA-a/PU 60/40, (▲) BA-a/PU 40/60 and (▼) BA-a/PU 0/100*.

* BA-a/PU 0/100 obtained by moisture cure method.

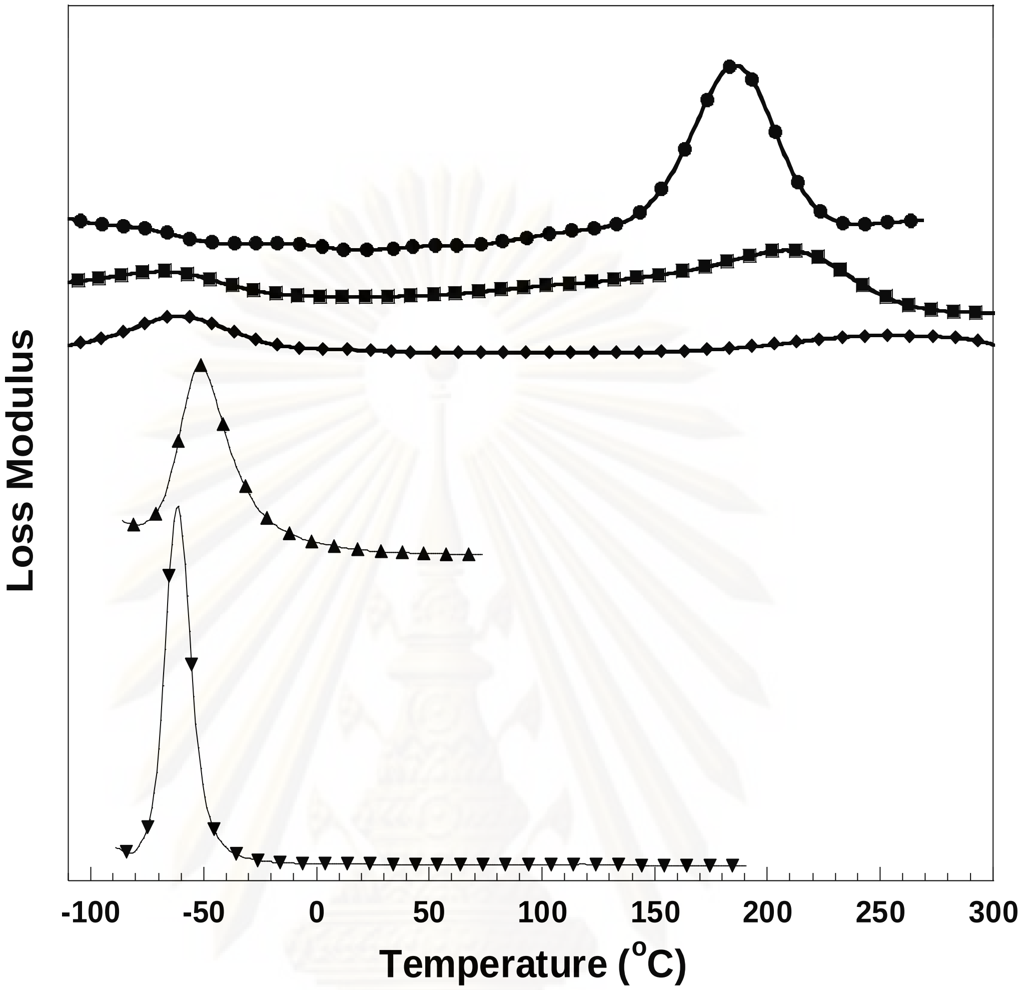


Figure 5.12. Loss modulus of BA-a/PU alloys obtained by traditional cure method at various PU compositions: (●) BA-a/PU 100/0, (■) BA-a/PU 80/20, (◆) BA-a/PU 60/40, (▲) BA-a/PU 40/60 and (▼) BA-a/PU 0/100*.

* BA-a/PU 0/100 obtained by moisture cure method.

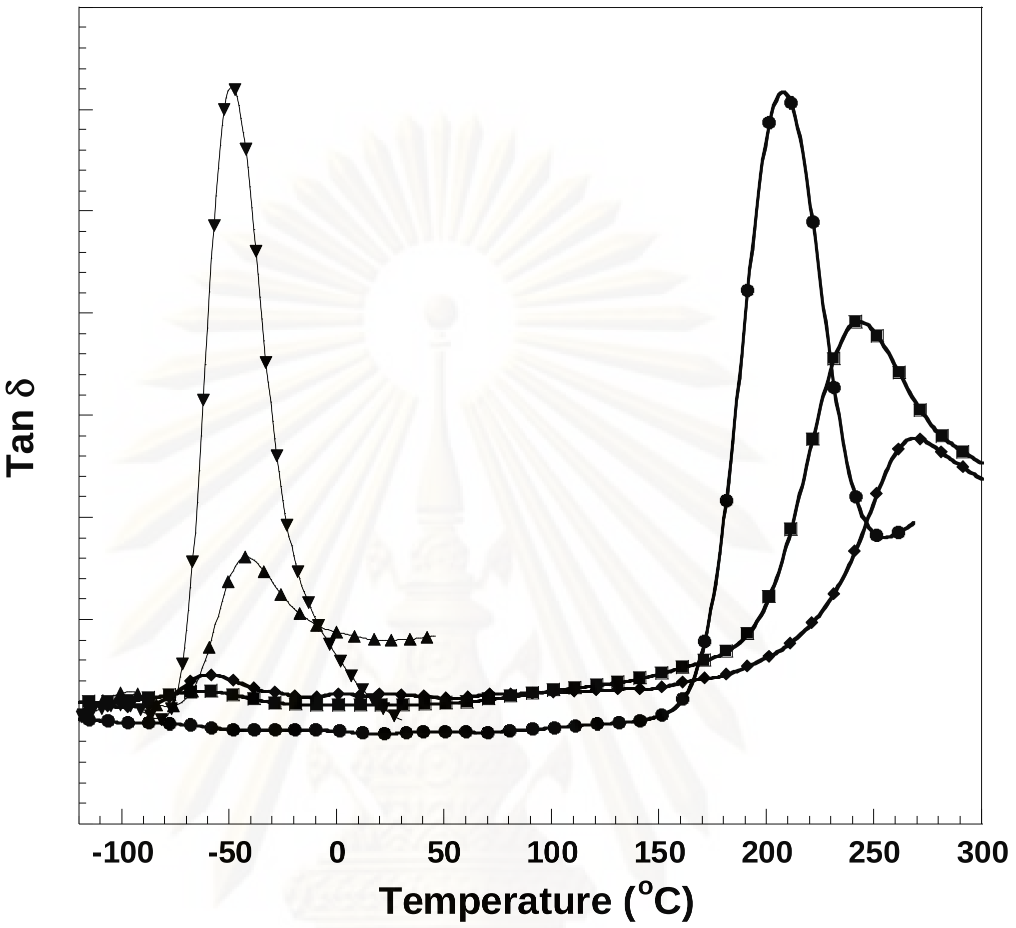


Figure 5.13. Tan δ of BA-a/PU alloys obtained by traditional cure method at various PU compositions: (●) BA-a/PU 100/0, (■) BA-a/PU 80/20, (◆) BA-a/PU 60/40, (▲) BA-a/PU 40/60 and (▼) BA-a/PU 0/100*.

* BA-a/PU 0/100 obtained by moisture cure method.

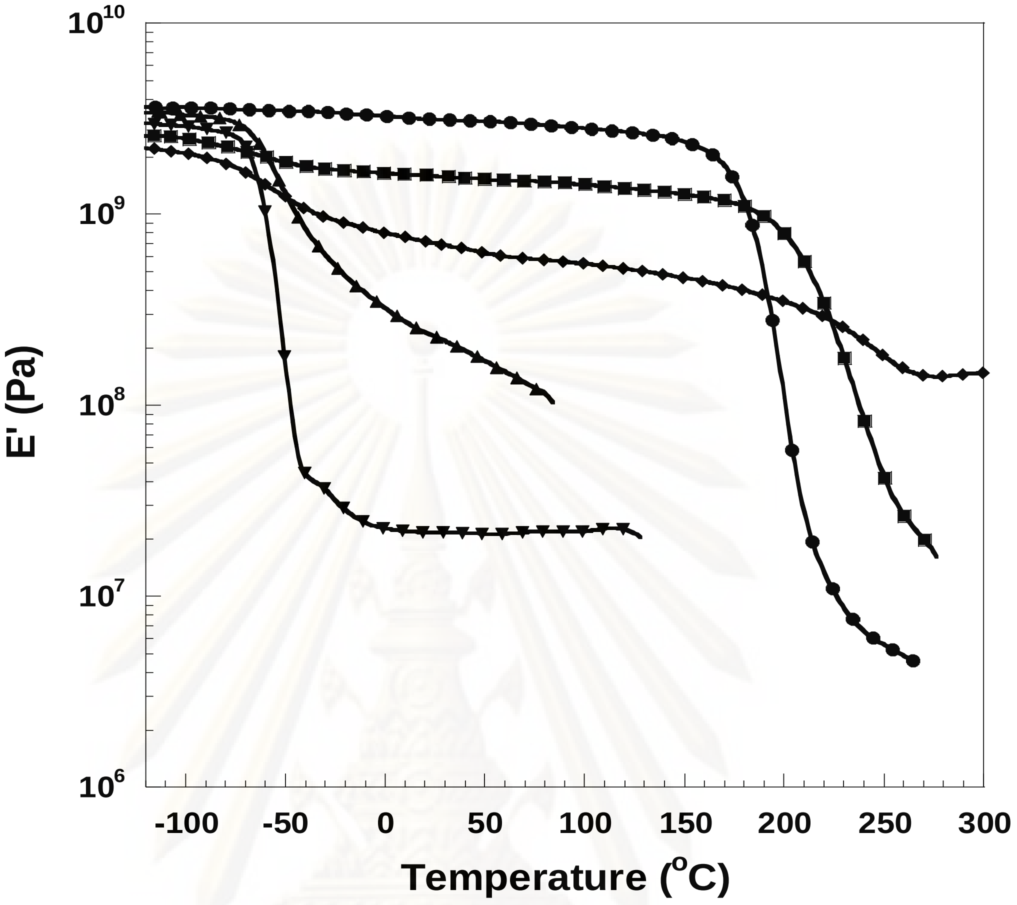


Figure 5.14. Storage modulus of BA-a/PU alloys obtained by sequential cure method at various PU compositions: (●) BA-a/PU 100/0, (■) BA-a/PU 80/20, (◆) BA-a/PU 60/40, (▲) BA-a/PU 40/60 and (▼) BA-a/PU 0/100*.

* BA-a/PU 0/100 obtained by moisture cure method.

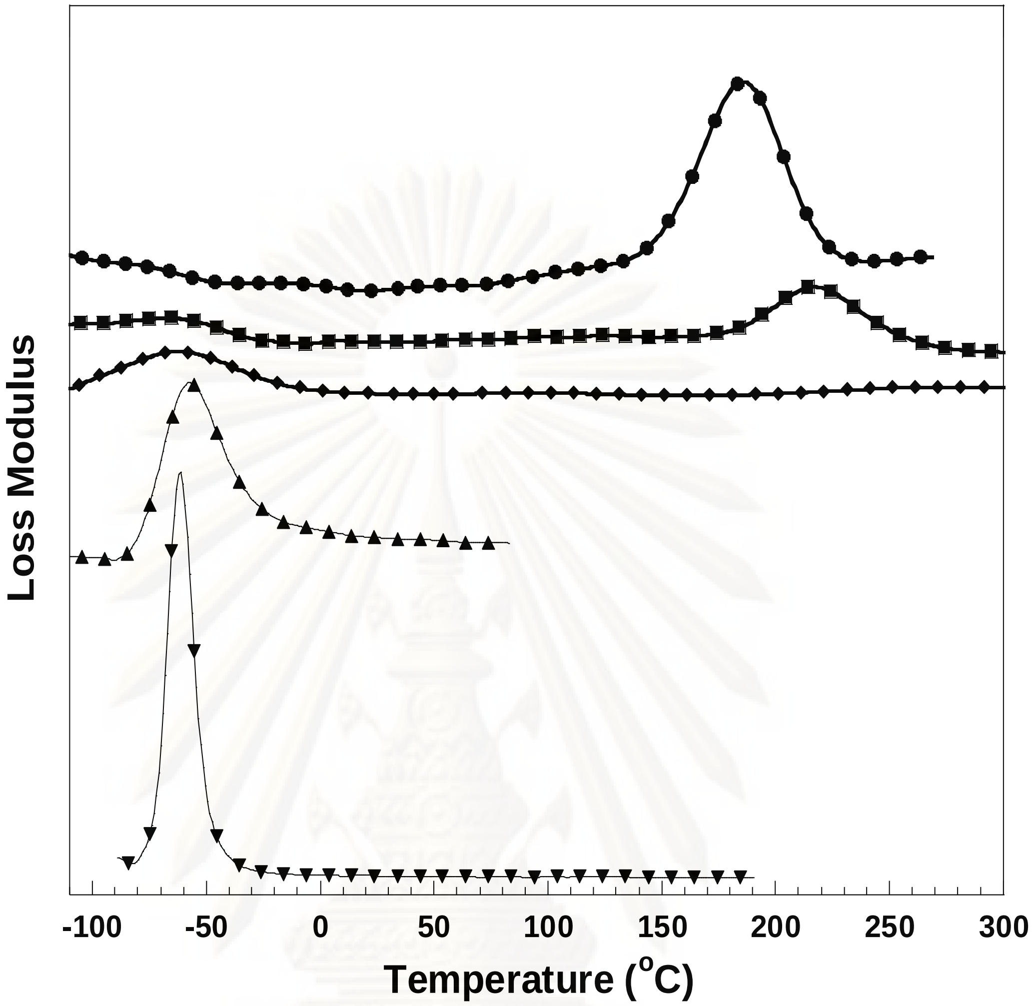


Figure 5.15. Loss modulus of BA-a/PU alloys obtained by sequential cure method at various PU compositions: (●) BA-a/PU 100/0, (■) BA-a/PU 80/20, (◆) BA-a/PU 60/40, (▲) BA-a/PU 40/60 and (▼) BA-a/PU 0/100*.

* BA-a/PU 0/100 obtained by moisture cure method.

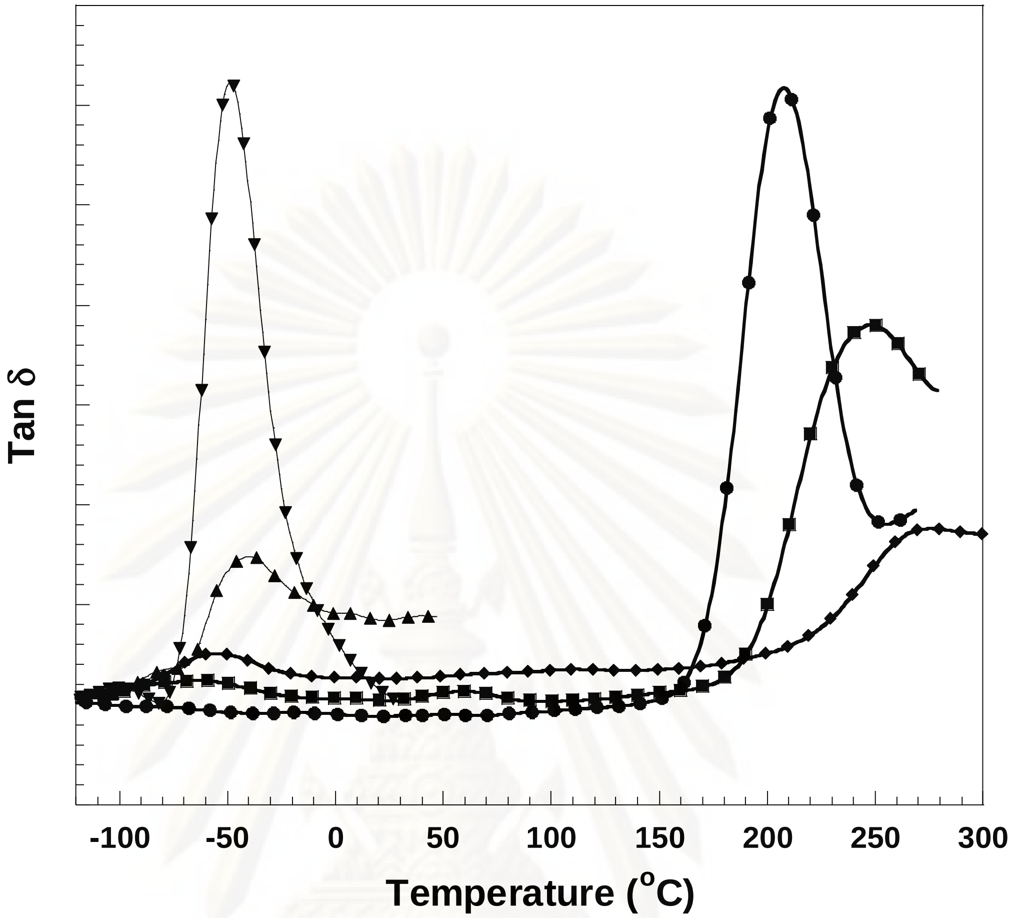


Figure 5.16. Tan δ of BA-a/PU alloys obtained by sequential cure method at various PU compositions: (●) BA-a/PU 100/0, (■) BA-a/PU 80/20, (◆) BA-a/PU 60/40, (▲) BA-a/PU 40/60 and (▼) BA-a/PU 0/100*.

* BA-a/PU 0/100 obtained by moisture cure method.

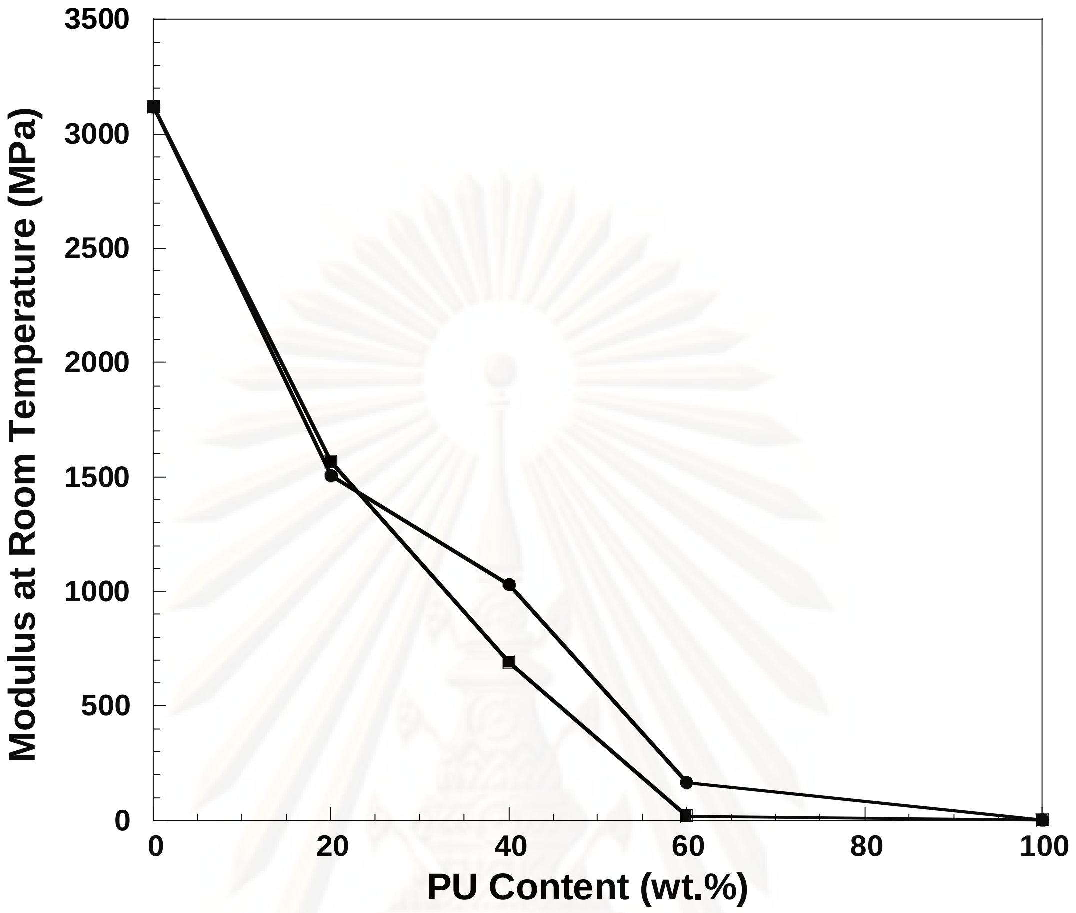


Figure 5.17. Storage modulus at room temperature of BA-a/PU alloys at various PU compositions: (●) Traditional cure method, (■) Sequential cure method.

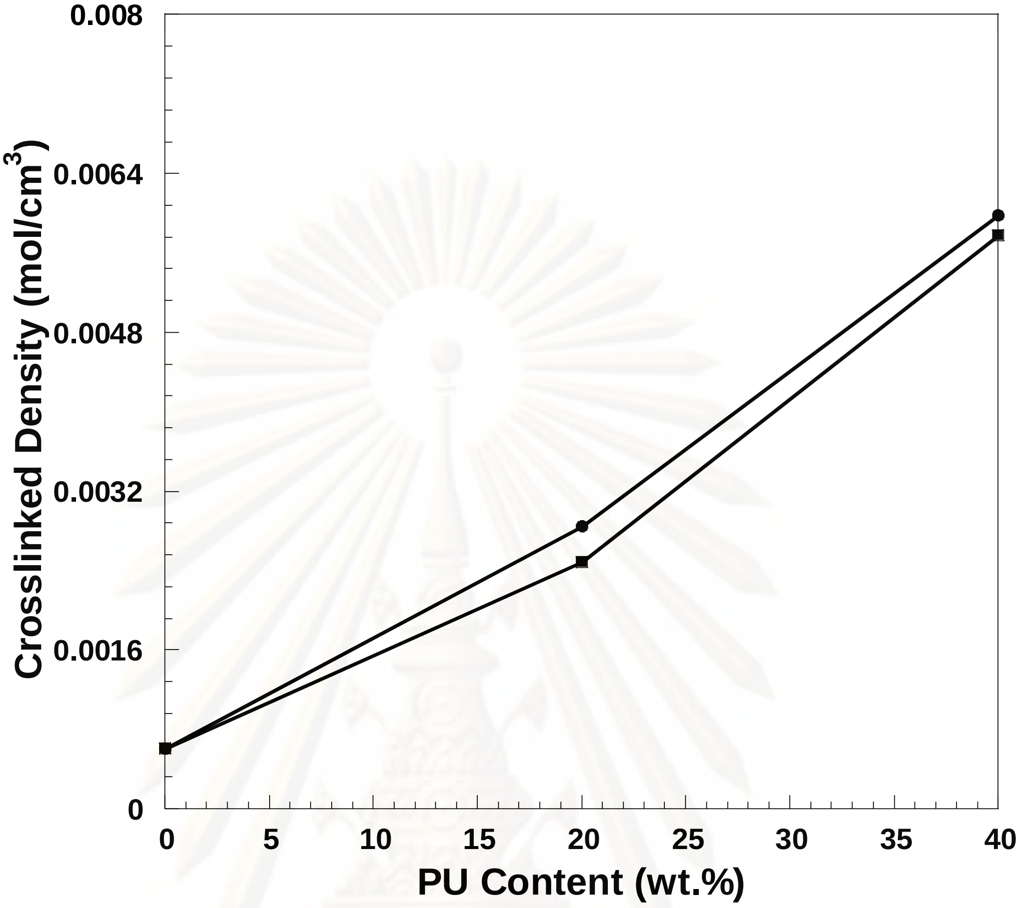


Figure 5.18. Crosslinked density of BA-a/PU alloys at various PU compositions: (●) Traditional cure method, (■) Sequential cure method.

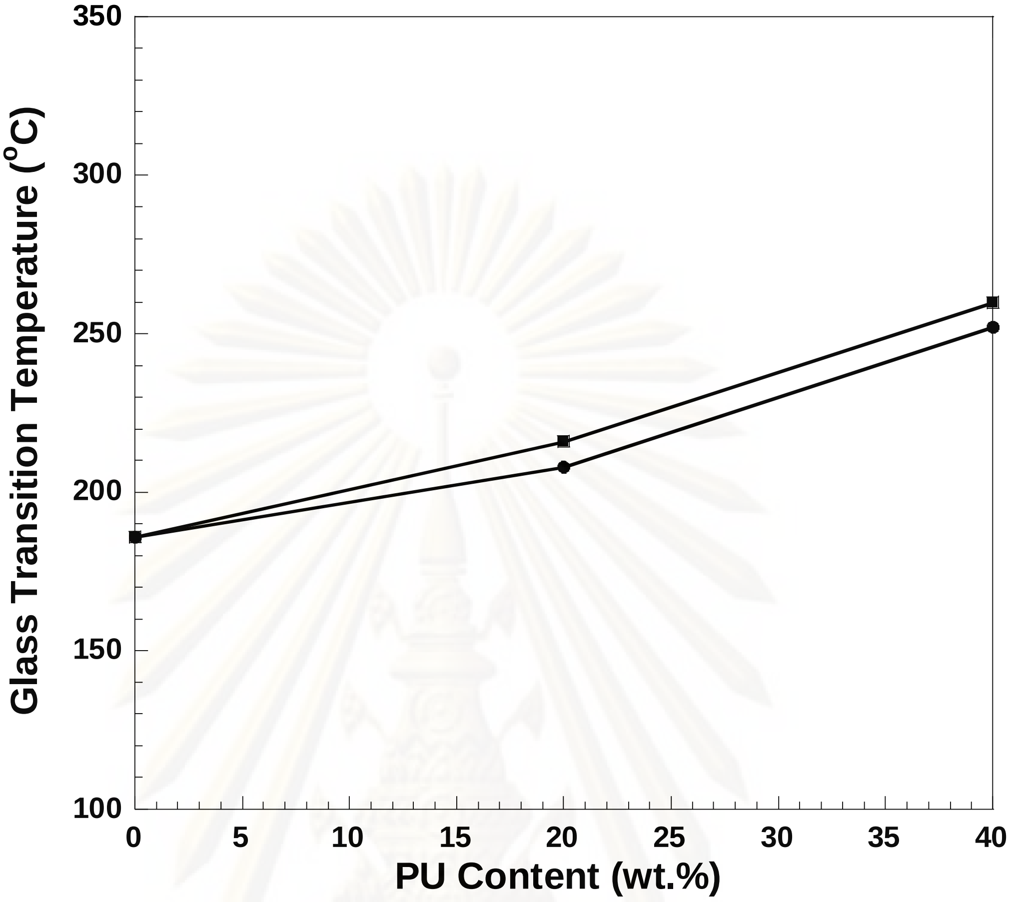


Figure 5.19. Glass transition temperature of BA-a/PU alloys at various PU compositions: (●) Traditional cure method, (■) Sequential cure method.

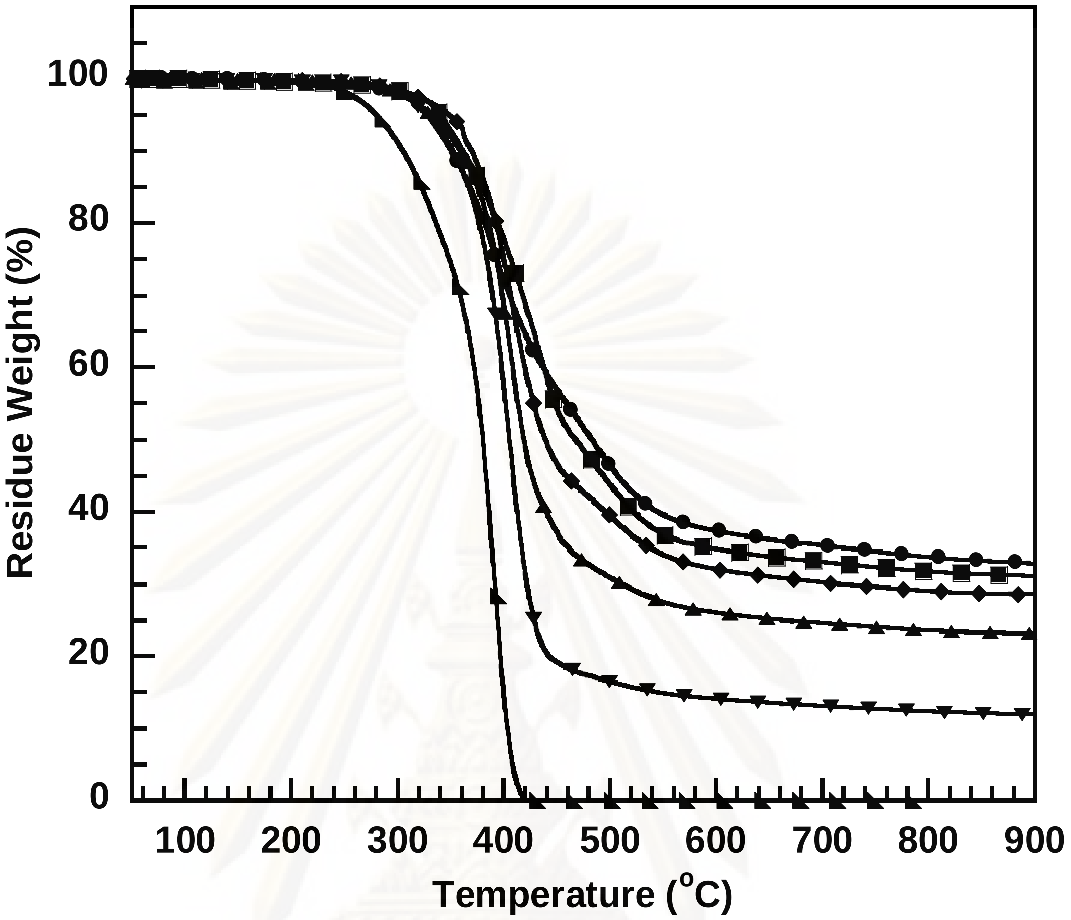


Figure 5.20. TGA thermogram of BA-a/PU alloys obtained by traditional cure method at various PU compositions: (●) BA-a/PU 100/0, (■) BA-a/PU 80/20, (◆) BA-a/PU 60/40, (▲) BA-a/PU 40/60, (▼) BA-a/PU 20/80 and (◣) BA-a/PU 0/100*.

* BA-a/PU 0/100 obtained by moisture cure method.

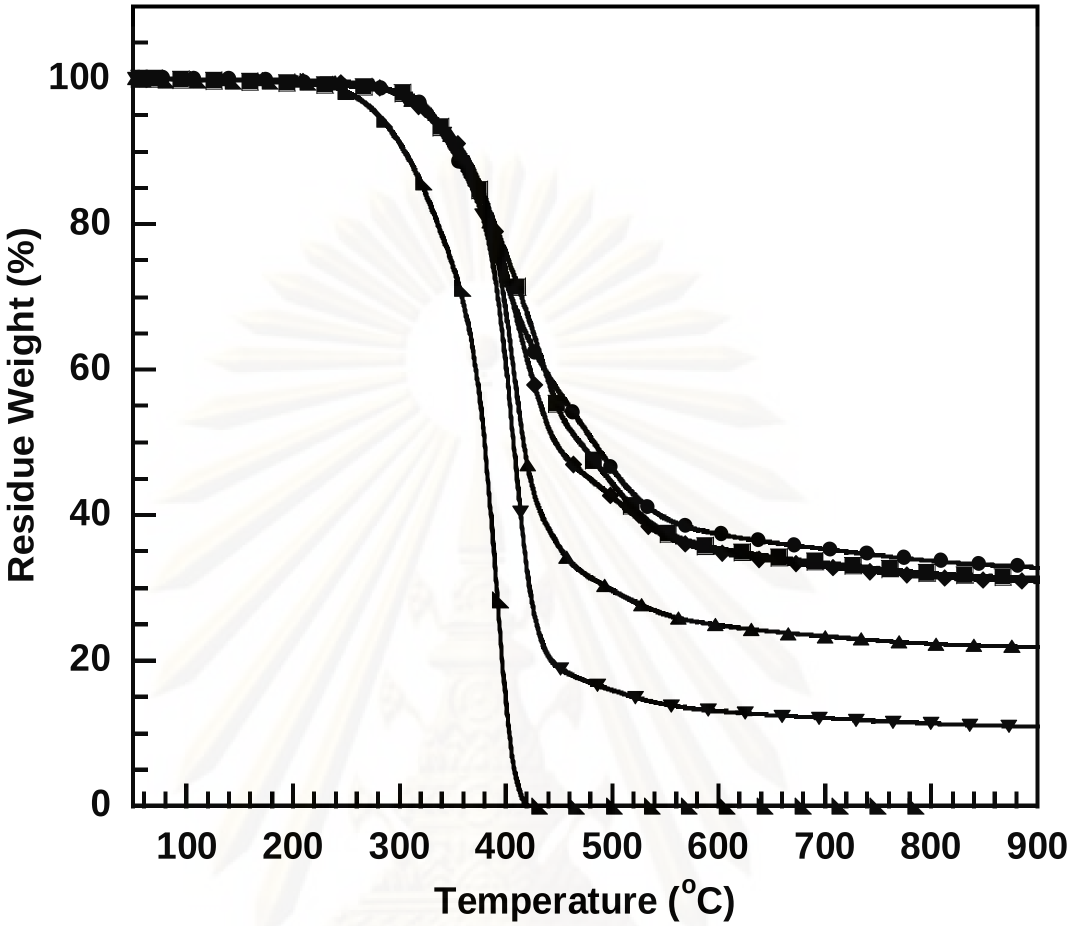


Figure 5.21. TGA thermogram of BA-a/PU alloys obtained by sequential cure method at various PU compositions: (●) BA-a/PU 100/0, (■) BA-a/PU 80/20, (◆) BA-a/PU 60/40, (▲) BA-a/PU 40/60, (▼) BA-a/PU 20/80 and (◣) BA-a/PU 0/100*.

* BA-a/PU 0/100 obtained by moisture cure method.

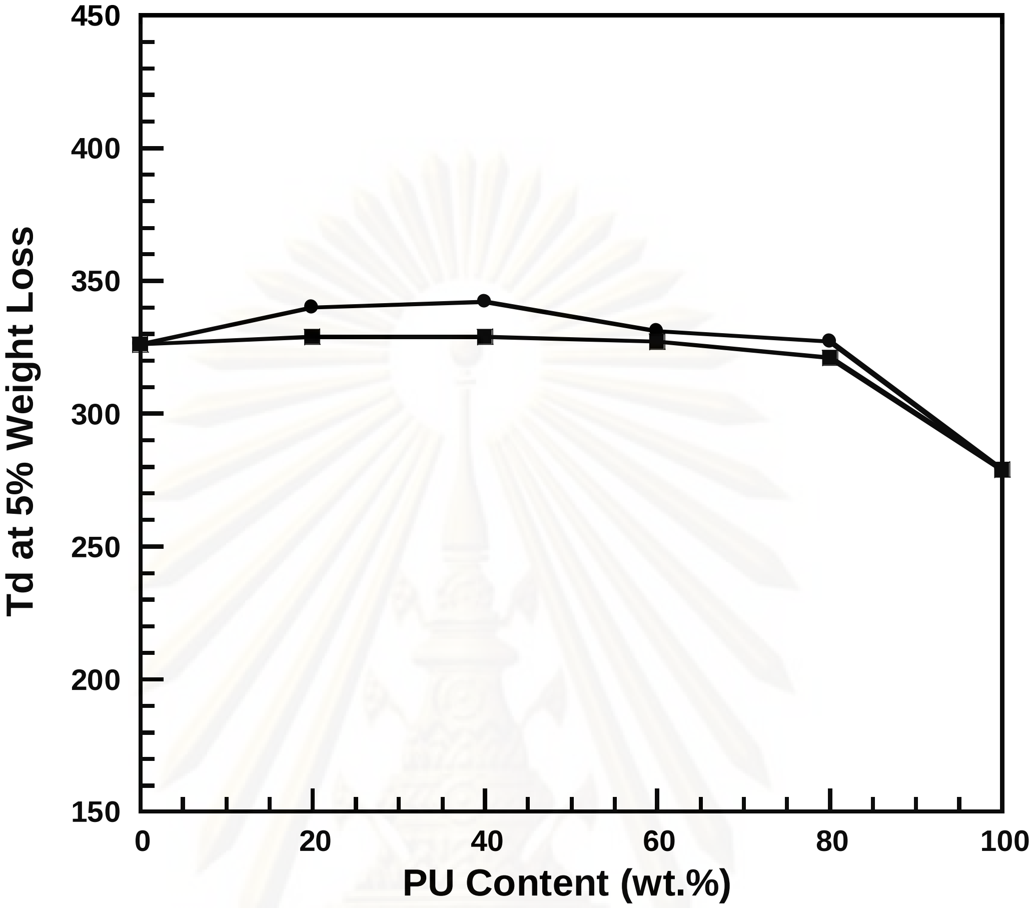


Figure 5.22. Initial degradation temperature at 5% weight loss of BA-a/PU alloys at various PU compositions: (●) Traditional cure method, (■) Sequential cure method.

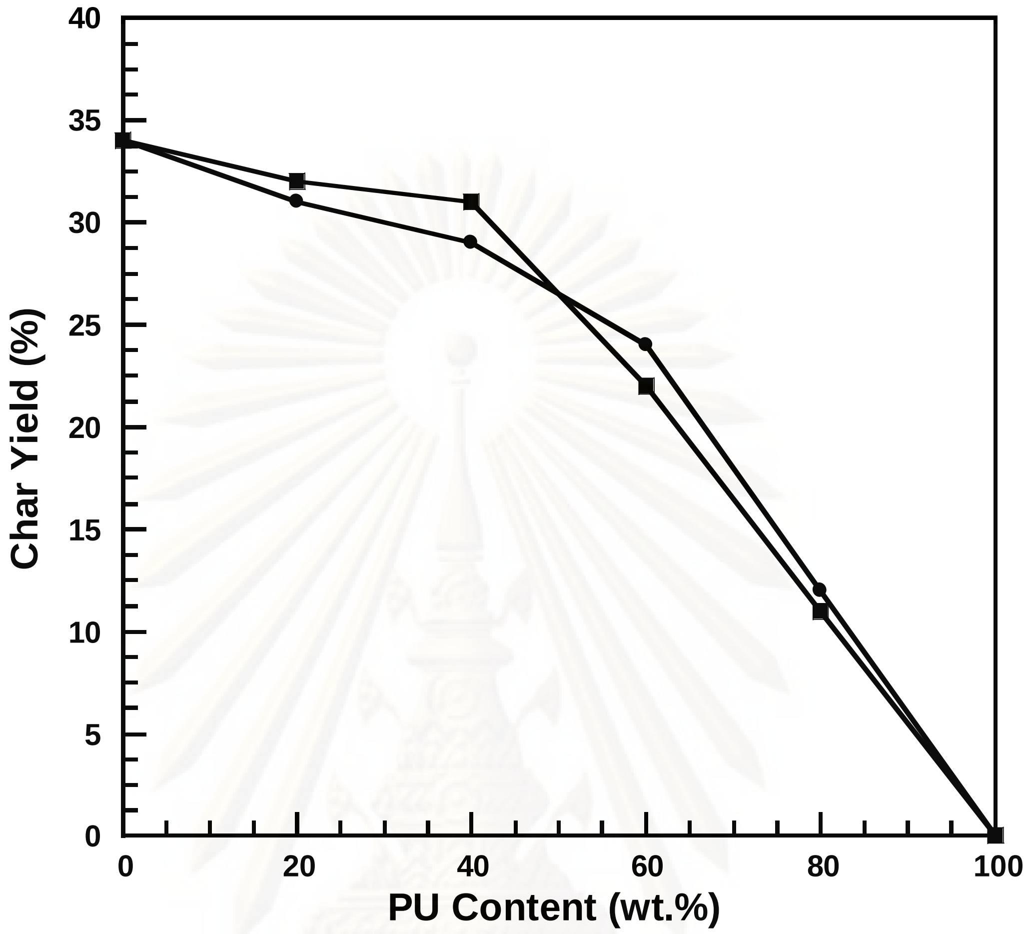


Figure 5.23. Char yield of BA-a/PU alloys at various PU compositions: (●) Traditional cure method, (■) Sequential cure method.

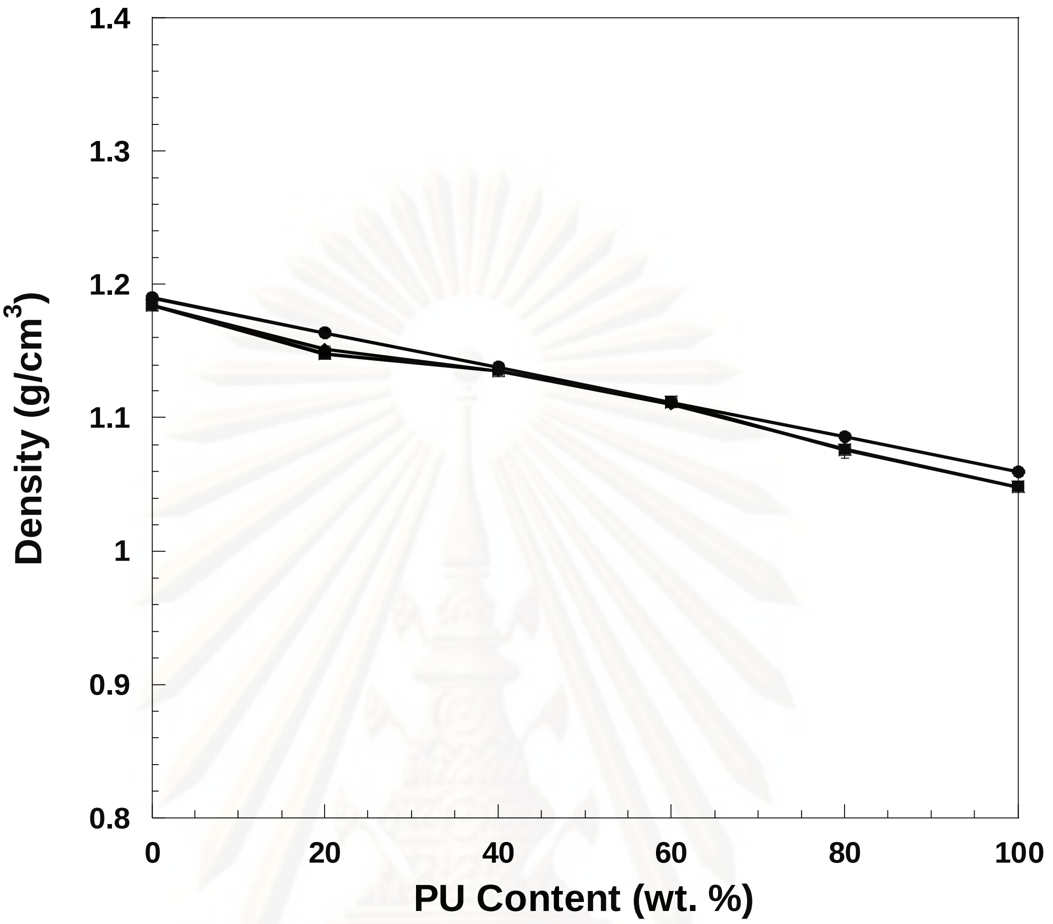


Figure 5.24. Density of BA-a/PU alloys at various PU compositions: (●) Theory density, (■) Actual density of traditional cure method (◆) Actual density of sequential cure method.

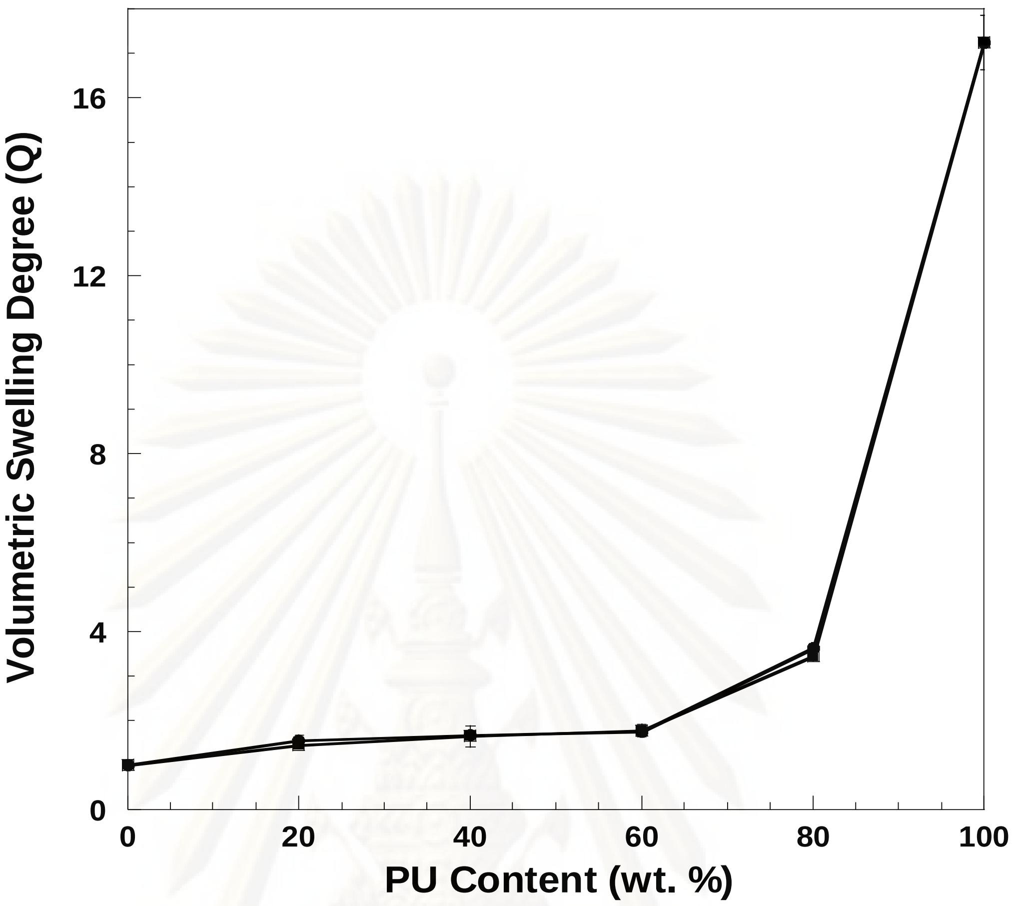


Figure 5.25. Volumetric swelling degree of BA-a/PU alloys at various PU compositions: (●) Traditional cure method, (■) Sequential cure method.

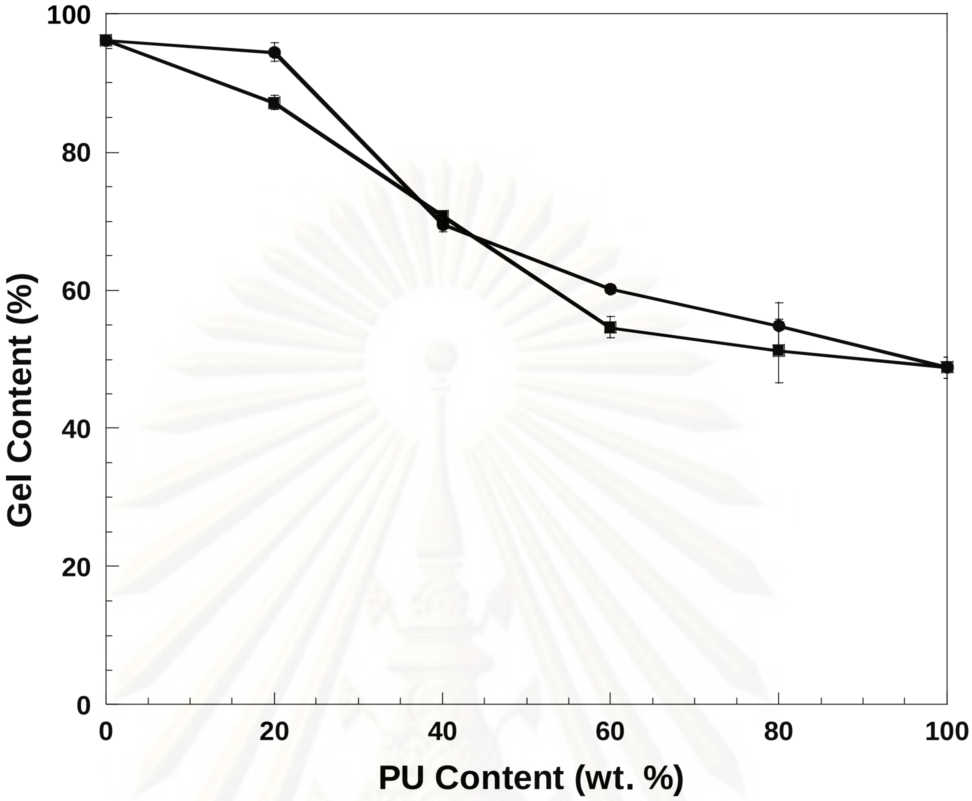


Figure 5.26. Gel content of BA-a/PU alloys at various PU compositions: (●) Traditional cure method, (■) Sequential cure method.

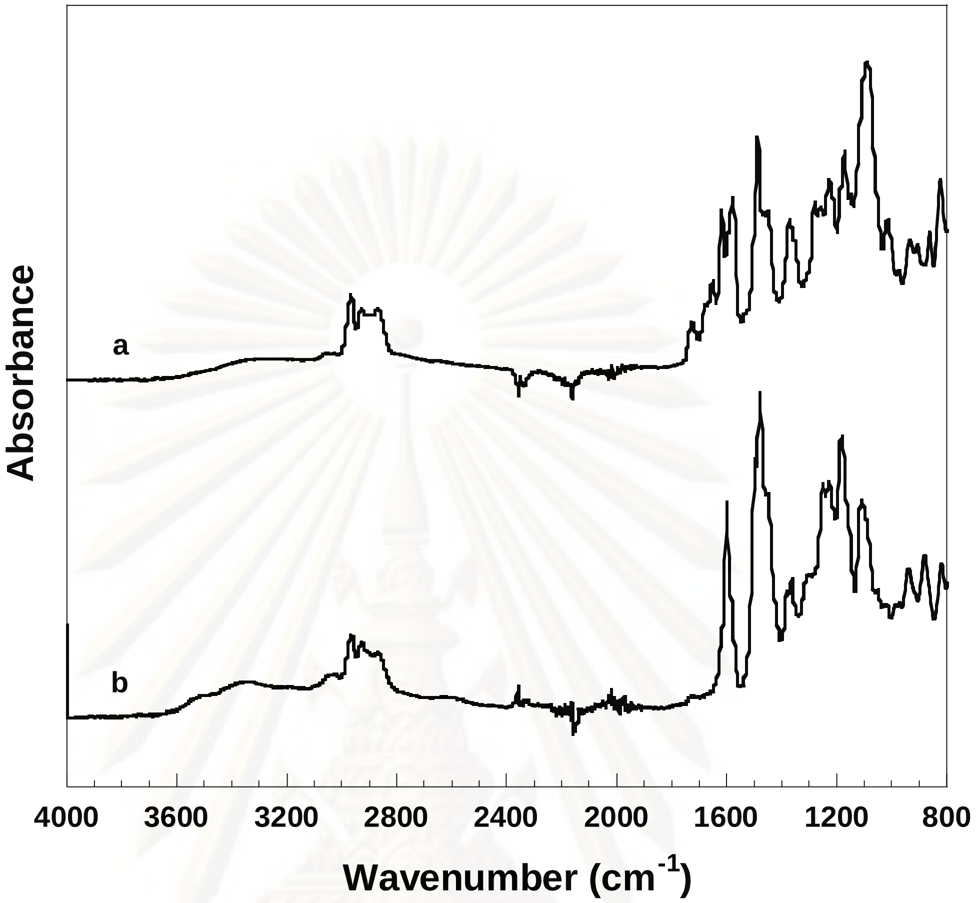


Figure 5.27. FT-IR Spectra of BA-a/PU 80/20 obtained by sequential cure method cured at 180 ^{o}C/5hr : a)Top surface; b) Bottom surface.

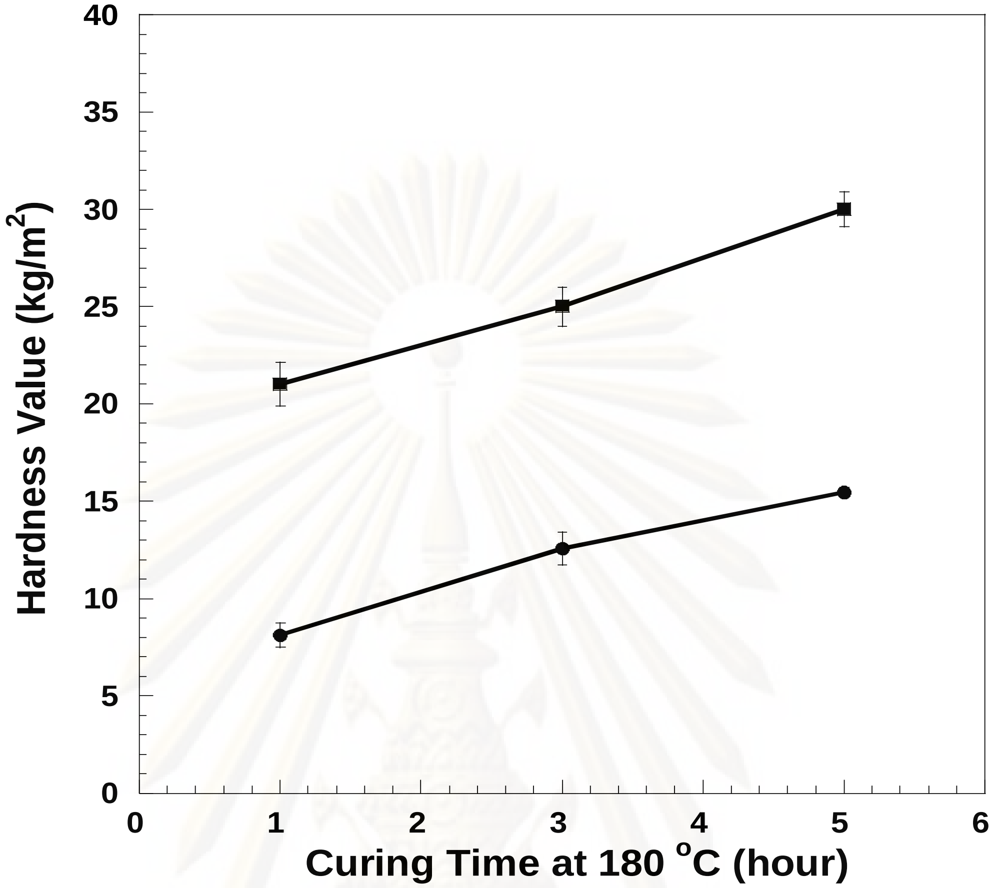


Figure 5.28. Hardness of BA-a/PU 80/20 obtained by sequential cure method at various curing times: (●) Top surface, (■) Bottom surface.

CHAPTER VI

CONCLUSIONS

Polybenzoxazine alloying with urethane elastomer was developed. The curing process can significantly affect the network formation and thus the obtained properties of the alloys. Polymer alloys of polyurethane and polybenzoxazine can process in two methods i.e. traditional cured and sequential cured method. The major characterizations in this research include processability, thermal stability, mechanical properties and physical properties of both the BA-a/PU alloy.

The processing window was widened with an addition of the urethane prepolymer that mean the lowering their liquefying temperature and increasing their gel point. Additionally, the resin mixture curing reaction was observed to occur at higher temperature from the addition of the urethane prepolymer. From FT-IR results, the alloys of polybenzoxazine and polyurethane were prepared sequentially by curing at room temperature to complete the urethane network formation followed by thermal curing to polymerize the benzoxazine resin portion. The moisture cure reaction produced a crosslink network further reacted to produce urea linkages. Whereas, the alloys of polybenzoxazine and polyurethane were prepared by tradition curing step method. Network formation was prepared immediately by thermal heating to polymerize the benzoxazine and polyurethane portion.

Synergism in glass transition temperature of both processing condition, obtained from the peak of loss modulus in the dynamic mechanical analysis, was clearly examined. Moreover, the degradation temperature was also about the same up to the PU content of 40 % by weight. Therefore, the addition of the urethane prepolymer into the polybenzoxazine was able to maintain the thermal stability of the polybenzoxazine. The char yield of the BA-a/PU alloys was found to increase with the increasing amount of the benzoxazine mass fraction. The storage modulus of a solid polymer at its glassy state tends to decrease with increasing the PU mass fraction in the polymer alloys that affected to improve flexibility. Furthermore, the volumetric swelling degree of the BA-a/PU alloys under both processing conditions increased along with polyurethane content. The gel content of both processing conditions decreased with an increase of polyurethane content.

Finally, from above results, it can be concluded that the two processing conditions had no significant effect on those major properties of the obtained alloys. The major factor that greatly influenced most properties of those BA-a/PU alloys was mainly the composition of the alloys.

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APPENDICES

APPENDIX A

Resin mixtures of BA-a/PU

Appendix A-1 Liquefying and gel temperature of BA-a/PU mixtures.

PU content (wt.%)	Liquefying temperature (^oC)	Gel temperature (^oC)
0	68	195
20	59	210
40	50	218
60	-	232
80	-	237

Appendix A-2 Curing temperature of BA-a/PU mixtures.

PU content (wt.%)	Curing temperature (^oC)
0	232
20	242
40	250
60	253
80	255

APPENDIX B

Dynamic Mechanical Properties of BA-a/PU Alloys

- Traditional cure method

Appendix B-1 Storage modulus of BA-a/PU alloys at 30^{o}C.

PU content (wt.%)	Storage modulus (GPa)
0	3.12
20	1.51
40	1.03
60	0.17
100	0.002

Appendix B-2 Glass transition temperature from DMA of BA-a/PU alloys.

PU content (wt.%)	Glass transition temperature (^{o}C)	
	Tg of PU	Tg of BA-a/PU
0	-	186
20	-69	208
40	-61	252
60	-51	-
100	-61	-

- Sequential cure method

Appendix B-3 Storage modulus of BA-a/PU alloys at 30^{o}C.

PU content (wt.%)	Storage modulus (GPa)
0	3.12
20	1.57
40	0.69
60	0.02
100	0.002

Appendix B-4 Glass transition temperature from DMA of BA-a/PU alloys.

PU content (wt.%)	Glass transition temperature (^{o}C)	
	Tg of PU	Tg of BA-a/PU
0	-	186
20	-67	216
40	-62	260
60	-57	-
100	-61	-

APPENDIX C

Thermal Properties of BA-a/PU Alloys

- Traditional cure method

Appendix C-1 Degradation temperature (Td) of BA-a/PU alloys.

PU content (wt.%)	Td of BA-a/PU alloys	
	At 5 wt% loss	At 10 wt% loss
0	326	350
20	340	361
40	348	369
60	331	359
80	327	351
100	279	304

Appendix C-2 Char yield of BA-a/PU alloys.

PU content (wt.%)	Char yield at 800^{o}C (%)
0	34
20	31
40	29
60	24
80	12
100	-

- Sequential cure method

Appendix C-3 Degradation temperature (Td) of BA-a/PU alloys.

PU content (wt.%)	Td of BA-a/PU alloys	
	At 5 wt% loss	At 10 wt% loss
0	326	350
20	329	354
40	329	359
60	327	357
80	321	352
100	279	304

Appendix C-4 Char yield of BA-a/PU alloys.

PU content (wt.%)	Char yield at 800^{o}C (%)
0	34
20	32
40	31
60	22
80	11
100	-

APPENDIX D

Physical Properties of BA-a/PU Alloys

Appendix D-1 Surface hardness of BA-a/PU alloys at ratio 80/20 various curing condition.

Curing Condition	Vicker Hardness (Kg/m^2)	
	Top surface	Bottom surface
180 ^{o}C/1 hr.	8.13	21.01
180 ^{o}C/3 hr.	12.59	25.00
180 ^{o}C/5 hr.	15.48	31.01

Appendix D-2 Density of BA-a/PU alloys obtained by traditional cure method.

PU content (wt.%)	Actual density (g/cm^3)	Theoretical density (g/cm^3)
0	1.190	1.184
20	1.164	1.152
40	1.138	1.135
60	1.112	1.110
80	1.086	1.077
100	1.060	1.049

Appendix D-3 Density of BA-a/PU alloys obtained by sequential cure method.

PU content (wt.%)	Actual density (g/cm^3)	Theoretical density (g/cm^3)
0	1.190	1.184
20	1.164	1.148
40	1.138	1.135
60	1.112	1.112
80	1.086	1.076
100	1.060	1.049

APPENDIX E

Swelling Degree and Gel Content of BA-a/PU Alloys in Chloroform

Appendix E-1 Swelling degree and gel content of BA-a/PU alloys obtained by traditional cure method.

PU content (wt.%)	Volumetric swelling degree	Gel content (%)
0	0.98984	96.161
20	1.5440	87.180
40	1.6672	70.691
60	1.7461	54.658
80	3.6278	51.236
100	17.251	48.815

Appendix E-2 Swelling degree and gel content of BA-a/PU alloys obtained by sequential cure method.

PU content (wt.%)	Volumetric swelling degree	Gel content (%)
0	0.98984	96.161
20	1.4404	94.458
40	1.6413	69.487
60	1.7761	60.164
80	3.4520	54.929
100	17.251	48.815

VITAE

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