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ของเบนซอกซาซีนและยูรีเทนพอลิเมอร์อัลลอย



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EFFECT OF TYPES OF ISOCYANATES ON MECHANICAL AND THERMAL PROPERTIES
OF BENZOXAZINE AND URETHANE POLYMER ALLOYS

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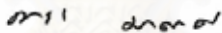
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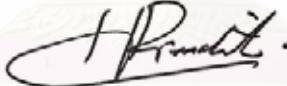
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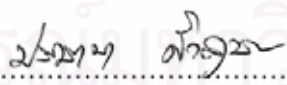

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ชาลินี เลี้ยววิชานนท์ : อิทธิพลของชนิดไอโซไซยาเนตที่มีผลต่อคุณสมบัติทางกลและทางความร้อนของเบนซอกซาซีนและยูรีเทนพอลิเมอร์อัลลอย (EFFECT OF TYPES OF ISOCYANATES ON MECHANICAL AND THERMAL PROPERTIES OF BENZOXAZINE AND URETHANE POLYMER ALLOYS อาจารย์ที่ปรึกษา: ผศ. ดร. ศราวุธ ริมดุสิต, 95 หน้า.

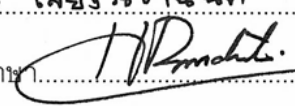
งานวิจัยนี้มีจุดมุ่งหมายเพื่อศึกษาอิทธิพลของชนิดไอโซไซยาเนตที่มีผลต่อคุณสมบัติทางกลและทางความร้อนของเบนซอกซาซีนและยูรีเทนพอลิเมอร์อัลลอย โดยพอลิเบนซอกซาซีนเป็นเทอร์โมเซตชนิดใหม่ ซึ่งมีคุณสมบัติที่ดีหลายประการ ไม่ว่าจะเป็น เสถียรภาพทางความร้อนสูง ง่ายต่อการขึ้นรูป ค่าการดูดซึมน้ำต่ำ ค่าการหดตัวเข้าใกล้ศูนย์ และมีคุณสมบัติเชิงกลที่ดี อีกทั้งพอลิเบนซอกซาซีนยังสามารถทำอัลลอยกับเรซินอื่น ๆ ได้หลายชนิด อย่างไรก็ตามข้อเสียของพอลิเบนซอกซาซีนคือ มีความแข็งเกร็งสูงทำให้ไม่เหมาะสมกับการใช้งานในบางประเภท ในงานวิจัยนี้จึงมีจุดประสงค์ที่จะปรับปรุงคุณสมบัติของพอลิเบนซอกซาซีนโดยการทำอัลลอยกับยูรีเทนอีลาสโตเมอร์ที่ใช้ชนิดของไอโซไซยาเนตแตกต่างกัน เช่น โทลูอินไดไอโซไซยาเนต ไดฟีนีลเมเทนไดไอโซไซยาเนต และไอโซพอร์โธไดไอโซไซยาเนต จากผลการทดลองพบว่า อุณหภูมิการเปลี่ยนสถานะคล้ายแก้วของอัลลอยที่ใช้ชนิดของไอโซไซยาเนตต่าง ๆ มีค่าสูงขึ้นจาก 160 องศาเซลเซียสในพอลิเบนซอกซาซีน เป็น 253 องศาเซลเซียสในอัตราส่วนของพอลิเบนซอกซาซีนกับยูรีเทนอีลาสโตเมอร์ที่ 60:40 โดยน้ำหนักและอุณหภูมิการสลายตัวทางความร้อนสูงขึ้นจาก 321 องศาเซลเซียส เป็น 330 องศาเซลเซียส เมื่อเพิ่มพอลิยูรีเทนในทุกอัตราส่วน สำหรับการทดสอบสมบัติการดัดโค้งของพอลิเมอร์อัลลอย พบว่า ค่ามอดูลัสในการดัดโค้งของพอลิเบนซอกซาซีนลดลงจาก 5.8 จิกกะปาสคาล เป็น 1.7- 2.0 จิกกะปาสคาล เมื่อทำการเติมพอลิยูรีเทนลงไป 40% โดยน้ำหนัก ในทุกพอลิเมอร์อัลลอย นอกจากนี้จากการทดสอบค่าความแข็งแรงในการดัดโค้งพบว่า เกิดสมบัติที่ช่วยเสริมกันที่อัตราส่วนของพอลิเบนซอกซาซีนกับยูรีเทนอีลาสโตเมอร์ที่ 90:10 โดยน้ำหนัก ในทุกพอลิเมอร์อัลลอยทั้ง 3 ชนิด และผลของยูรีเทนพรีพอลิเมอร์ที่ใช้โทลูอินไดไอโซไซยาเนตสามารถให้ค่าอุณหภูมิการเปลี่ยนสถานะคล้ายแก้ว ค่ามอดูลัสในการดัดโค้ง ค่าความแข็งแรงในการดัดโค้ง สูงที่สุดในพอลิเมอร์อัลลอยที่ใช้ไอโซไซยาเนตทั้ง 3 ชนิด (เมื่อเปรียบเทียบที่ปริมาณของพอลิพรีพอลิเมอร์เท่ากัน) ดังนั้นไอโซไซยาเนตที่เหมาะสมสำหรับทำคาร์บอนไฟเบอร์คอมพอสิตคือ ระบบของพอลิเบนซอกซาซีนกับยูรีเทนพรีพอลิเมอร์ที่ใช้โทลูอินไดไอโซไซยาเนต สำหรับความแข็งแรงในการดัดโค้งในระบบของพอลิเบนซอกซาซีนกับยูรีเทนพรีพอลิเมอร์ที่ใช้โทลูอินไดไอโซไซยาเนต เมื่อปริมาณเส้นใยเป็น 80%โดยน้ำหนักและทำการจัดเรียงเส้นใยแบบ cross-ply มีค่าประมาณ 490 เมกกะปาสคาล ส่วนค่ามอดูลัสในการดัดโค้งมีค่าลดลงเล็กน้อยจาก 51 จิกกะปาสคาล สำหรับพอลิเบนซอกซาซีน เป็น 48 จิกกะปาสคาล เมื่อเติมพอลิยูรีเทนลงไป 40% โดยน้ำหนักในพอลิเมอร์อัลลอย

ภาควิชา.....วิศวกรรมเคมี.....

สาขาวิชา.....วิศวกรรมเคมี.....

ปีการศึกษา.....2549.....

ลายมือชื่อนิสิต.....ชาลินี เลี้ยววิชานนท์.....

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CHALINEE LIENGVACHIRANON: EFFECT OF TYPES OF ISOCYANATES
ON MECHANICAL AND THERMAL PROPERTIES OF BENZOXAZINE
AND URETHANE POLYMER ALLOYS. THESIS ADVISOR: ASSISTANT
PROFESSOR SARAWUT RIMDUSIT, Ph.D., 95 pp.

This research aims to investigate the effect of types of isocyanates on mechanical and thermal properties of benzoxazine and urethane polymer alloys. Polybenzoxazine, a new thermoset plastics, possesses various intriguing properties including high thermal stability, easy processability, low water absorption, near zero shrinkage, excellent mechanical properties, as well as an ability to alloy with various types of resins. However, one shortcoming of this resin is its rather high rigidity making the polymer unsuitable for some applications. This work aims to develop an approach to further improve properties of polybenzoxazine by alloying with urethane elastomer based on various types of isocyanates such as toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), and isophorone diisocyanate (IPDI). The experimental results showed that glass transition temperature (T_g) of the alloys at various types of isocyanates increased from 160°C of the neat polybenzoxazine to 253°C in the 60:40 BA:PU system and the degradation temperature increased from 321°C to about 330°C with increasing the urethane content for all evaluated compositions. In addition, flexural modulus of the polybenzoxazine decreased from 5.8 to 1.7-2.0 GPa when adding 40wt% of PU for all BA:PU alloys. Furthermore, the flexural strength showed a synergistic behavior at the BA:PU ratio of 90:10 for all three types of the alloys. The effect of urethane prepolymer based on TDI provided the highest T_g , flexural modulus, and flexural strength of the alloys among the three isocyanates used (i.e. in comparison at the same urethane content). The optimum isocyanate of the binary systems for making high processable carbon fiber composites was BA:PU based on TDI. The flexural strength of the carbon fiber-reinforced BA:PU based on TDI at 80wt% of the fiber in cross-ply orientation rendered relatively high values of about 490 MPa. The flexural modulus slightly decreased from 51GPa for polybenzoxazine to 48 GPa for the alloys having 40wt% of the PU fraction.

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 จุฬาลงกรณ์มหาวิทยาลัย

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CHAPTER I

INTRODUCTION

1.1 Overview

Polybenzoxazine is a newly developed class of thermosetting resins derived from ring-opening polymerization of their precursors. The polymer possesses various good properties such as high thermal stability, easy processability, low water absorption, near zero shrinkage after processing with excellent mechanical properties (Ishida et al.,1996). The polymer can be synthesized using the patented solventless technology to yield a clean precursor without the need for solvent elimination or monomer purification (Ishida et al.,1996). It can be synthesized from inexpensive raw material and does not release by-products during polymerization, thus showing high potential in many applications (Rimdusit, 2005). However, one shortcoming of this resin is its rather high rigidity that makes it not suitable for some applications. Fortunately, benzoxazine resin is reported to be able to alloy with several other polymers. Alloying is considered to be a potentially effective measure to toughen polybenzoxazine because the polybenzoxazine has been reported to be able to undergo hybrid network formation with several other polymers or resins; therefore, rendering various useful properties. For example, epoxy and urethane elastomer were used to alloy with benzoxazine resin to improve thermal stability and mechanical properties of the polymer. The reaction of epoxide and isocyanate functional groups with benzoxazine resin can yield potentially useful alloys such as these reported in the works of Takeichi et al. and Rimdusit et al. (Takeichi, 2000 and Rimdusit, 2005). The poly(urethane-benzoxazine) films showed single T_g , implying no phase separation in the resulting alloys. The properties of the films ranged from elastomers to plastics, depending on the content of the benzoxazine fraction in the alloys (Takeichi et al, 2000)

This research aims to develop an alternative approach to improve toughness of polybenzoxazine by alloying with urethane elastomer and examined the characteristics of the obtained alloys based on different types of isocyanates in the urethane precursor. Elastomeric urethane can be produced by a reaction of a polyfunctional isocyanate, most often, with hydroxyl compounds. The polyfunctional isocyanates can be aromatics, aliphatic, cycloaliphatic, or polycyclic in structure and can be used directly as produced or modified urethane resins. This research will be carried out in order to study the effects of different types of isocyanates such as toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI) to substitute the presently used isophorone diisocyanate (IPDI) system as IPDI is less available in Thailand and has much higher cost comparing with the first two systems. The type of isocyanate in urethane resin with best alloy performance with benzoxazine resin at varied composition will be determined. And finally, this alloy mixture will be utilized as a matrix of carbon fiber. The resulting carbon fiber-reinforced BA/PU alloys will be characterized as a potential use as high performance, light weight composites.

1.2 Objectives

1. To investigate the effect of types of isocyanates in urethane prepolymers on the alloying ability with benzoxazine resin.
2. To study the suitable composition ratio of polymeric alloys between benzoxazine resin and the urethane prepolymers on their curing and processing conditions.
3. To compare the effect of types of isocyanates on mechanical and thermal properties of the resulting alloys with benzoxazine resin.

1.3 Scopes of The Study

1. Synthesis of benzoxazine resin by solventless synthesis technology.
2. Synthesis of urethane prepolymer at a fixed diol molecular weight of 2000

using different types of isocyanates i.e. isophorone diisocyanate (IPDI), toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI).

- Determining prepolymer molecular weight by GPC.
 - Finding functional groups by FT-IR.
3. Preparation of polymeric alloys between the benzoxazine resin and the three urethane prepolymers at various weight ratios of the benzoxazine resin and urethane prepolymer i.e. 100:0, 90:10, 80:20, 70:30 and 60:40.
 4. Evaluation of the curing condition or crosslinking process of the alloys.
 - Finding curing condition by DSC.
 5. Examination of mechanical properties of the alloys.
 - Dynamic mechanical analysis.
 - Flexural testing.
 6. Investigation of thermal properties of the alloys.
 - Differential scanning calorimetry (DSC).
 - Thermogravimetric analysis (TGA).
 7. Studying of mechanical and thermal properties of the carbon fiber composites based on the above alloys.
 - Dynamic mechanical analysis.
 - Flexural testing.

CHAPTER II

THEORY

2.1 Benzoxazine Resin

Benzoxazine resin is a novel kind of phenolic resin that can be synthesized from phenol, formaldehyde and amines (Nair, 2004). Solvent may be used in this synthesis depending on initiator and heating (Ning and Ishida, 1994). The resin is developed to provide optimal properties in electronics and high thermal stability applications.

Benzoxazine resin can be classified into a monofunctional and a bifunctional type depending on a type of phenol used as shown in Figures 2.1 and 2.2. An example of the monomer synthesis is

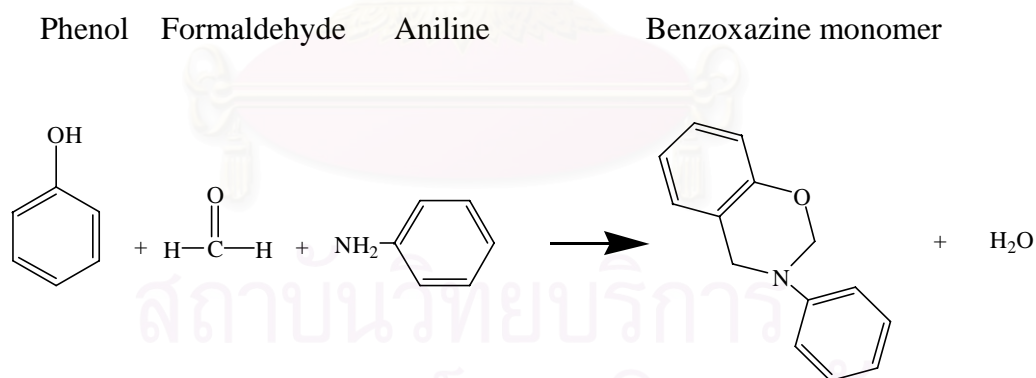


Figure 2.1 : Schematic synthesis of monofunctional benzoxazine monomer.

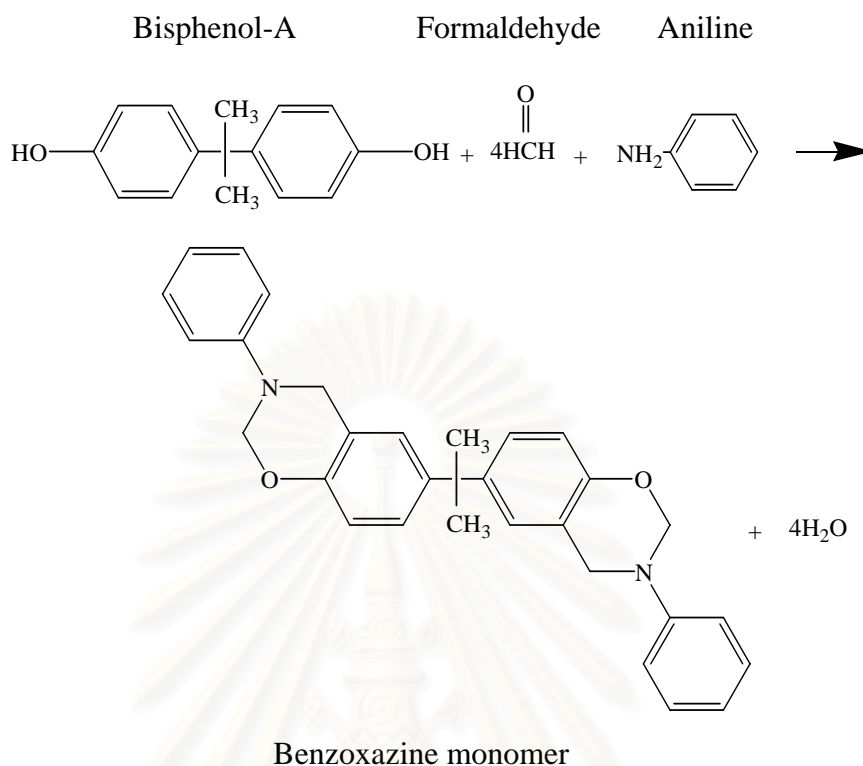


Figure 2.2 : Schematic synthesis of bifunctional benzoxazine monomer.

The interesting properties of benzoxazine resin reported in the literature include:

- Solvent-less synthesis provides almost contaminant-free monomers. Thus, we can neglect the purification process which can save a production cost and also decrease pollution from the use of solvent (Ning and Ishida, 1994).
- Self-polymerized upon heating.
- No catalyst or curing agent required.
- No by-products during cure (Riess, 1985)
- Low melt viscosity (Nair, 2004).
- Near zero mold shrinkage (Ishida and Allen, 1996).
- Low water absorption (Ishida and Allen, 1996).
- Excellent electrical properties (Ishida and Allen, 1996).
- High mechanical integrity (Nair, 2004).

Those properties particularly ease of processing, lack of volatile formation during cure, and high mechanical properties are all attractive for composite material manufacturing. Furthermore, benzoxazine resin was reported to be able to alloy with several other polymers or resins; therefore, rendering broader range of useful properties. Those alloys include the alloys of polybenzoxazine with bisphenol A-typed epoxy (Riess et al, 1985), with flexible epoxy (EPO732)(Rimdusit et al, 2005) with polyimide (Takeichi et al, 2005), with toluene diisocyanates (TDI)/polyethylene adipate polyol-typed urethane resin (Takeichi et al, 2005), with isophorone diisocyanate (IPDI)/polyether polyol-typed urethane resin) (Rimdusit et al, 2005) etc.

2.2 Polyurethane

Polyurethane is a polymer that contains urethane functional group. The urethane functional group is formed by the chemical reaction between an alcohol and an isocyanate as shown in Figure 2.3. The polymer is resulted from a reaction between alcohols having two or more reactive hydroxyl groups per molecule (diol or polyols) and isocyanates that have more than one reactive isocyanate group per molecule (a diisocyanate or polyisocyanate). This type of polymerisation is called addition polymerisation.

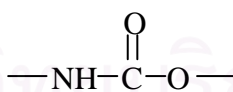
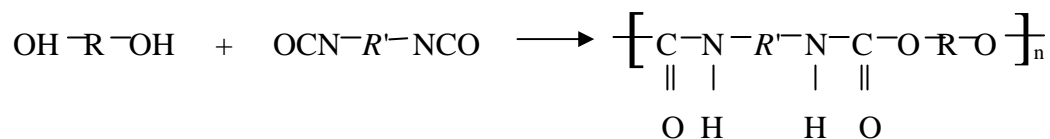


Figure 2.3 Structure of urethane linkage (Hepburn, 1992)

Polyurethane addition reaction (Wood, 1990)



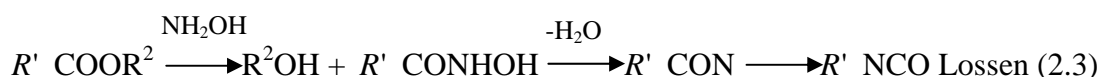


The rate of the polymerisation reaction depends upon the structure of both the isocyanate and the polyol. The functionality of the hydroxy-containing reactant or the isocyanate can be varied; a wide variety of linear, branched and crosslinked can be formed. The hydroxyl-containing components cover a wide range of molecular weights and types, including polyester and polyether polyols. Aliphatic polyols with primary hydroxyl end-groups are the most reactive. They react with isocyanates faster than similar polyols with secondary hydroxyl groups. The polyfunctional isocyanates can be aromatic, aliphatic, cycloaliphatic, or polycyclic in structure and can react with any compound containing “active” hydrogen atoms, and diisocyanates may, therefore, be used to modify many other products. This flexibility in the selection of reactants leads to the wide range properties of polyurethane.

Raw Materials

2.2.1 Isocyanates

Isocyanates can be made in many ways. The chemical reactions, the Curtius, Hoffman, and Lossen rearrangements, that may involve nitrene as an intermediate, were reported to be unsatisfactory for a large scale operation (Wood, 1990)



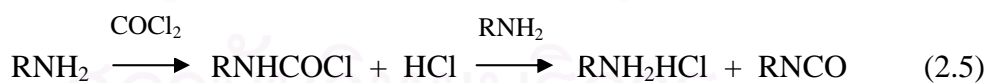
The use of azides in the Curtius reaction is hazardous. Thus, Hoffman and Lossen rearrangements are limited to preparation of aliphatic isocyanates, as aqueous media are employed (aromatic isocyanates react readily with water to form substituted ureas). Tertiary butyl hypochlorite can be used for non-aqueous Hoffman rearrangements but is somewhat costly.

In practice, only phosgenation of a primary amine is commercially important:



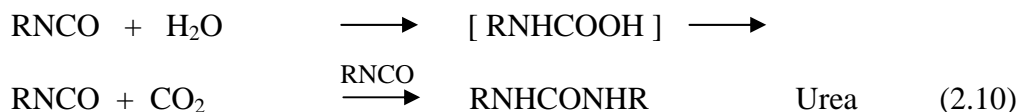
The reaction, first used by Hentschel in 1884, enables a wide range of aliphatic and aromatic isocyanates to be obtained from amines.

Isocyanates are difficult to prepare in high yield and purity with a detailed account of side reactions. All are made by phosgenation of amines or amine hydrochlorides in an inert medium (o-dichlorobenzene). The reaction is normally processed in two stages: the first at room or higher temperature to generate the carbamyl chloride and HCl; further treatment with phosgene at temperatures of the order of 150-170 °C to form the isocyanate



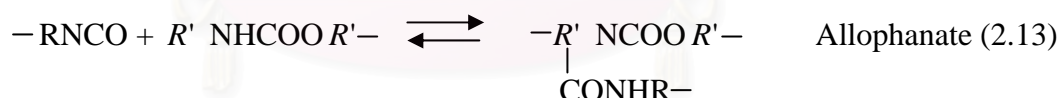
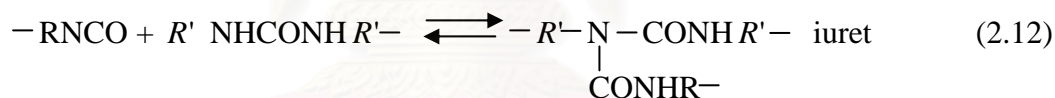
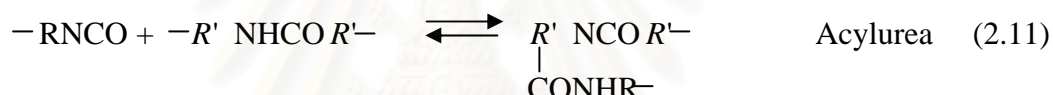
The isocyanate group can generally react with compounds containing active hydrogen atoms according to the following reactions:





From equation (2.8), being the most rapid, they were controlled by use of catalysts. Reactions (2.8) and (2.9) give rise to carbon dioxide, a feature of value when forming foamed products but introducing difficulty when bubble-free castings and continuous surface coatings are required.

The reactions of isocyanates with amide, urea linkages, and urethane due to the formation of acylurea, biuret, and allophanate links onto the main chain are shown below:



Only the diisocyanates are of interest for urethane polymer manufacture and relatively few of these are employed commercially. The most important isocyanates used in elastomer manufacture are the 2,4-toluene diisocyanate (2,4-TDI) and 2,6-toluene diisocyanate (2,6-TDI); 4,4'-diphenylmethane diisocyanate (MDI) and its aliphatic analogue isophorone diisocyanate (IPDI); 4,4'-dicyclohexylmethane diisocyanate (H₁₂MDI); 1,5 naphthalene diisocyanate (NDI); 1,6-hexamethylenediisocyanate (HDI); xylylene diisocyanate (XDI); and 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (TMDI).

In this work, we will prepare urethane prepolymer in our laboratory. The raw materials consist of a diol and diisocyanates of three types of isocyanates including toluene diisocyanate (TDI), and 4,4'-diphenylmethane diisocyanate (MDI), to substitute the currently used isophorone diisocyanate (IPDI) system.

2.2.1.1 Isophorone Diisocyanate (IPDI)

The structure formulae of isophorone diisocyanate (IPDI) as shown in Figure 2.4.

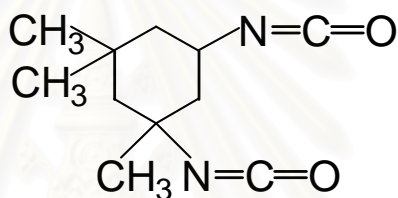


Figure 2.4 Isophorone diisocyanate, IPDI (Hepburn, 1992)

Isophorone diisocyanate (IPDI) is prepared by the phosgenation of isophorone diamine. IPDI is a cycloaliphatic diisocyanate and is a preferred raw material for the synthesis of light-stable and weather-resistant polyurethanes. It is a low viscous liquid with a weak but specific odour. The specifications of isophorone diisocyanate are shown in Table 2.1

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Table 2.1: General specification of isophorone diisocyanate (Wood, 1987 and Randall, 2002)

Properties	Value
Molecular weight	222.3
NCO content (% by weight)	37.5-37.8
Purity (% by weight)	>99.5
Melting point (°C)	-60
Boiling point (°C)	158
Flash point (°C)	100
Density (g/cm ³)	1.062 at 20°C
Viscosity (mPa.s)	15 at 20°C
Vapor pressure (Pa)	0.04 at 20°C
Reactivity	Much less reactive than MDI or TDI

2.2.1.2 Toluene Diisocyanates (TDI)

Most of TDI used is a mixture of the 2,4- and 2,6-isomer. TDI is an aromatic diisocyanate. The structure formulae of toluene diisocyanate (TDI) are shown in Figure 2.5

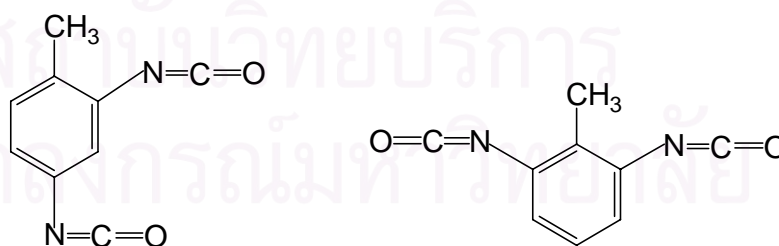


Figure 2.5 2,4 Toluene diisocyanate and 2,6 Toluene diisocyanate, TDI (Hepburn, 1992)

Toluene diisocyanate are prepared by direct nitration of toluene to give an 80:20 mixture of the 2,4- and 2,6-dinitro derivatives, followed by hydrogenation to the corresponding diaminotoluenes. Though toluene diisocyanate (TDI) is stable with a relatively high-flash point, it is reacted by water, acid, base, organic, and inorganic compounds. The 80:20 mixture of 2,4-TDI and 2,6-TDI is today the most important commercial product. The specifications of toluene diisocyanate are shown in Table 2.2

Table 2.2 General specification of toluene diisocyanate (Wood,1990)

Properties	Value
Molecular weight	174.16
NCO content (% by weight)	48.3
Purity (% by weight)	99.5
Melting point (°C)	19-22
Boiling point (°C)	251
Flash point (°C)	135
Density (g/cm ³)	1.22 at 20 °C
Viscosity (mPa.s)	3.2 at 20 °C
Vapor pressure (Pa)	3.3 at 25 °C

2.2.1.3 Diphenylmethane Diisocyanates (MDI)

MDI is an aromatic diisocyanate. The structure formula of diphenylmethane diisocyanate (MDI) is shown in Figure 2.6.

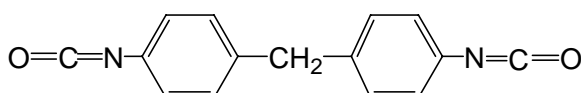


Figure 2.6 : 4,4'-Diphenylmethane diisocyanates, MDI (Hepburn, 1992)

Diphenylmethane diisocyanate (MDI) based on diaminodiphenylmethane is considerable safer to use, having a much lower volatility. MDI is often used in the crude (undistilled) form. This type of isocyanate is derived from phosgenation of the diamino diphenylmethanes formed by condensation of aniline with formaldehyde. Its preparation is depicted in Figure 2.7.

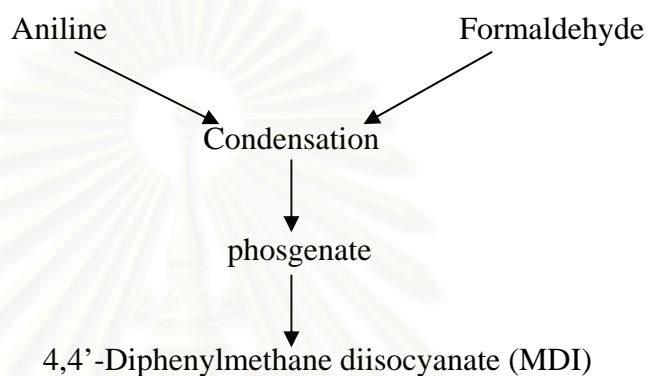


Figure 2.7: Diphenylmethane diisocyanate preparation scheme (Hepburn, 1979).

The specifications of diphenylmethane diisocyanate is listed in Table 2.3

Table 2.3: General specification of diphenylmethane diisocyanate (Wood, 1990)

Properties	Value
Molecular weight	250.26
NCO content (% by weight)	33.6
Melting point (°C)	38-43
Boiling point (°C)	314
Flash point (°C)	212-214
Density (g/cm ³)	1.19 at 20°C
Vapor pressure (Pa)	0.0006 at 25 °C

2.2.2 Polyol

The polyols that are used to make polyurethanes have been developed to have 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 a large part 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 controlling properties of the obtained urethane resin.

2.2.2.1 Polyether Polyols

About 90 percent of polyols used in making polyurethanes are polyethers with terminal hydroxyl groups. The first report of experiments with polyethers as intermediates for polyurethanes utilized polyethers derived from ethylene oxide or propylene oxide. The first polyether designed specifically for use in preparing polyurethanes was a poly(oxytetra methylene) glycol derived from tetrahydrofuran. These are made by the addition of alkylene oxides usually propylene oxide, onto alcohols or amines which are usually called starter or 'initiators'. The addition polymerization of propylene oxide occurs with either anionic (basic) or cationic (acidic) catalysis although commercial polyol product is usually based on base catalysis. The epoxide ring of propylene oxide may theoretically open at either of two positions on the ring but, in practice, the ring opens preferentially at the less sterically-hindered position with base catalysis. Polyethers based on propylene oxide thus contain predominantly secondary hydroxyl end-group. Secondary hydroxyl end-groups are several times less reactive with isocyanates than primary hydroxyl groups and for some applications polyether polyols based only on propylene oxide may possess inconveniently low reactivity.

The manufacture of polyether polyols is usually carried out in stainless steel or glass-lined reactors by essentially batch processes. The catalyst is usually sodium or potassium hydroxide in aqueous solution although sodium methoxide, potassium carbonate and sodium acetate are also utilized. A polymerization initiator is employed to control the type of polyether produced. Ethylene glycol, propylene glycol, diethylene glycol and dipropylene glycol can be used as initiator in the manufacture of difunctional polyethers, whereas glycerol is a general-purpose initiator for trifunctional polyethers as depicted in Figure 2.8.

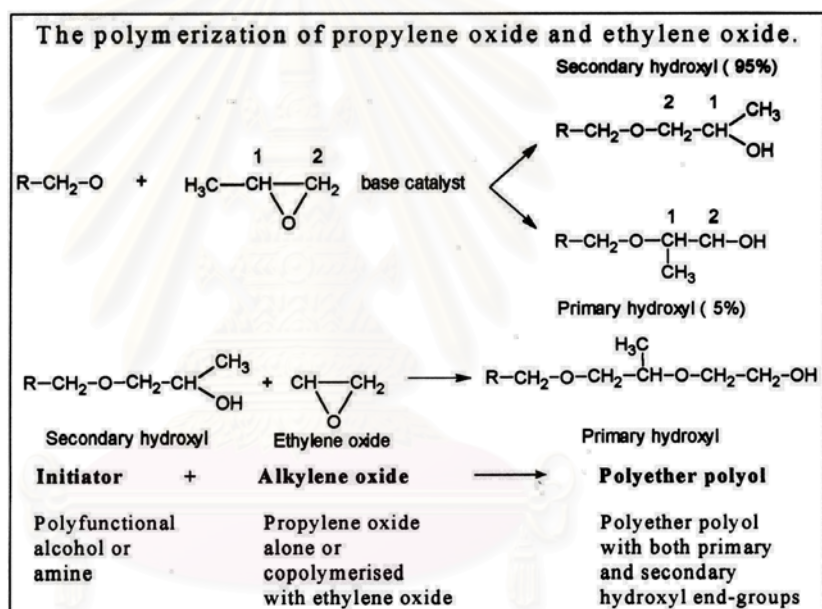


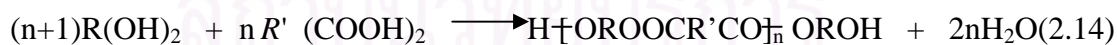
Figure 2.8 : Manufacture of polyether polyols (Wood, 1990)

The polyethers used in polyurethane applications are nonvolatile and viscous liquids. Most of the polyethers are soluble in the common organic solvents such as alcohols, ketones, esters, hydrocarbons, and halogenated solvent.

2.2.2.2 Polyester Polyols

Polyester polyols tend to be more expensive than polyether polyols and they are usually more viscous and, therefore, more difficult to handle. They also provide polyurethane polymers which are more readily hydrolyzed, consequently they are only used to make polyurethanes for demanding applications where the particular physical properties attainable from polyesters are important. Polyester-based polyurethane elastomers combine high levels of tensile properties with resistance to flexure and abrasion. They also have good resistance to many type of oil. Polyesters are also more difficult to be oxidized and resist higher temperatures than polyethers.

The polyesters are typically made by a condensation reaction of dibasic acids (usually adipic but other components such as sebacic or phthalic acid may be present) with diol such as ethylene glycol, 1,2-propylene glycol, and diethylene glycol where linear polymer segments are required. For preparation of the polyesters, conventional methods of polyesterification, i.e. reaction between acid and diol or polyol, are used. The water of condensation is removed by distillation and the reaction is assisted, if necessary, by use of vacuum or an azeotrope. Branching can be introduced by adding of small amount of a triol to the reaction mixture. As the esterification proceeds the water produced is removed from the reaction to drive the reaction forward: (Hepburn, 1992)



The manufacture is usually carried out as a batch process in glass-lined or stainless steel reactors as a condensation polymerization.

This esterification dose not require a use of catalysts, though catalysts based on the organic-metallics of titanium or zirconium, e.g. tetrabutyl titanate, are often used to reduce reaction times.

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

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

aliphatic NH_2 > aromatic NH_2 > primary OH > water >
 secondary OH > tertiary OH > phenolic OH > COOH

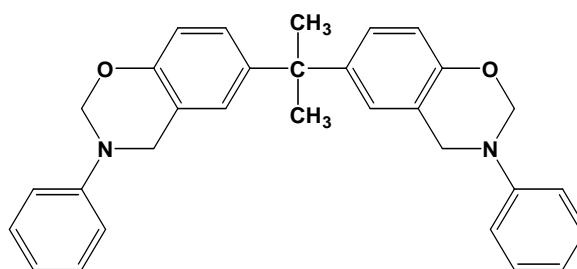
and

RNHCONHR > RCONHR > RNHCOOR

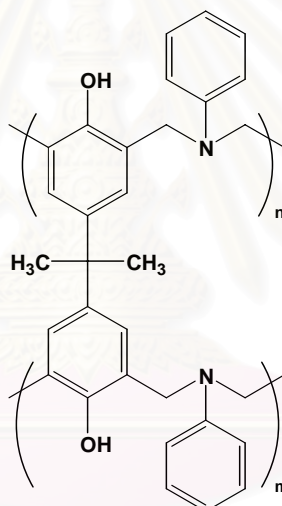
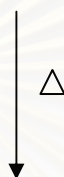
The excellent application properties of polyurethane account for the facts that their use is economically feasible and that their range of applications is constantly increasing. In some instance, they are even irreplaceable. Among these properties are unique combination of a high elastic modulus, good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

2.3 Interaction between Benzoxazine and Urethane Resins to Form Polymeric Alloys.

The bifunctional benzoxazine monomers thermally polymerized through their ring-opening reaction to give polybenzoxazine as shown in Figure 2.9.



Benzoxazine resin



Polybenzoxazine

Figure 2.9 Ring-opening polymerization of BA-a (Takeichi et al.2000)

The alloy forming reaction was also confirmed by Fourier-transform infrared (FT-IR) spectra in the case of benzoxazine resin and urethane prepolymer at a fixed mass ratio of 70/30. In Figure 2.10 (a) (Rimduisit et al,2005), the characteristic infrared absorption peaks of benzoxazine resin were found at 942 and 1232 cm^{-1} , which were assigned to the benzene mode of the benzene ring that is adjacent to the oxazine ring and the trisubstituted benzene of the oxazine ring, respectively. As the curing process proceeded, a nearly infinite three-dimensional network was formed.

According to the polymerization mechanism reported by Dunkers and Ishida (Dunkers and Ishida,1999), the oxazine ring is opened by the breakage of a C-O bond in it. Thereby the benzoxazine molecule was transformed from a ring structure to a network structure. During this process, the trisubstituted benzene ring, the backbone of the benzoxazine ring, became tetrasubstituted; therefore, leading to the formation of a phenolic Mannich base polybenzoxazine structure.

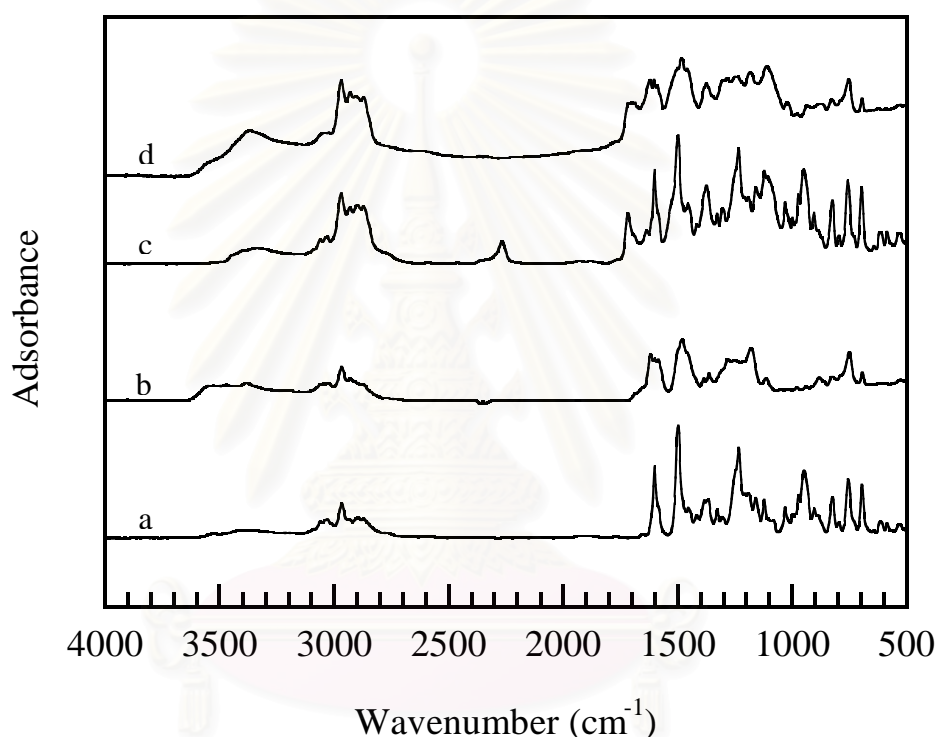


Figure 2.10 FT-IR Spectra of compounds: (a) BA-a, (b) PBA, (c) BA-a/PU (Diol1000)-70/30 uncured, (d) BA-a /PU (Diol 1000)-70/30 fully cured.

The urethane prepolymers containing isocyanate groups react with each other by the inter- or intramolecular reaction between the isocyanate and urethane groups. Thermal treatment of the urethane prepolymer itself was examined by FT-IR as depicted in Figure. 2.11 (Takeichi, 2000). It was found that the absorbance of the isocyanate group located at 2275 cm^{-1} almost disappeared after $180\text{ }^{\circ}\text{C}$ for 1 h

treatment. On the other hand, the absorbance bands centered at 1620 and at 1536 cm^{-1} assigned to the secondary amide in the urethane groups became smaller and remained as a shoulder instead of disappearing. Because the molar ratio of the isocyanate group and the urethane group in the urethane prepolymer is equal, the disappearance of the isocyanate absorbance means that the corresponding amount of the urethane was reacted by inter- or intramolecular reaction. The reaction was proposed to form an allophanate linkage that contains secondary amide groups. The good solubility of the thermally treated urethane prepolymer suggested low crosslink density from the thermal curing of the neat urethane prepolymer.



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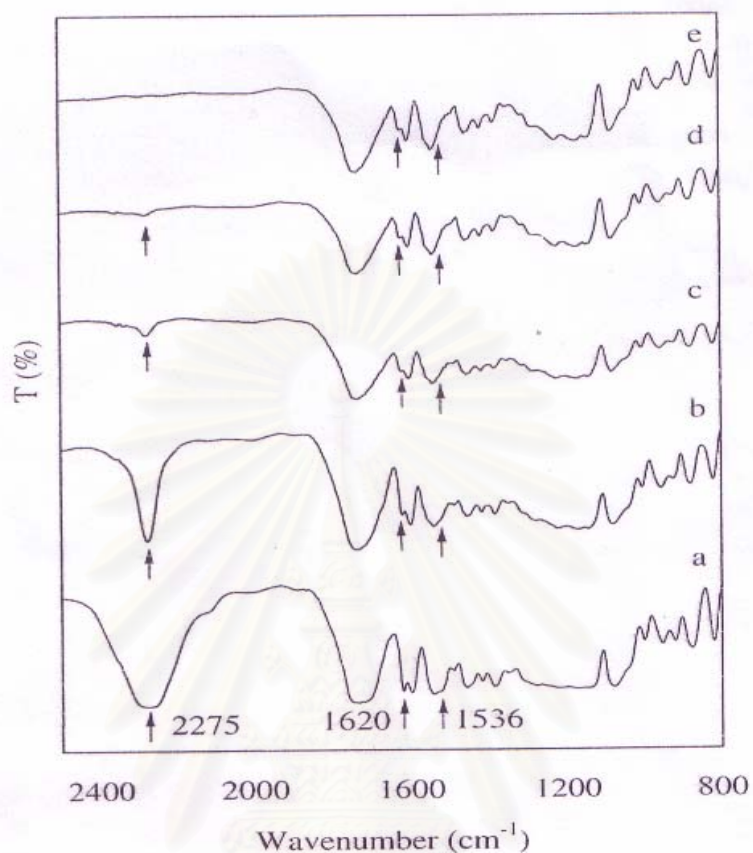


Figure 2.11 FT-IR Spectra of thermally treating program of polyurethane prepolymer: (a) before treatment, (b) at 150 °C/1 h, (c) at 170 °C/1 h, (d) at 180 °C/1 h, and (e) at 190 °C/1 h.

The isocyanate groups of the urethane prepolymer can react with both phenolic hydroxyl groups of polybenzoxazine and the urethane groups of the urethane prepolymer to yield affording urethane and allophanate linkage, respectively. The authors also observed that both of the above two products dissociated at high temperature. It has been reported that urethane linkage from isocyanate and phenolic OH dissociates at 150 °C, and allophanate linkage from isocyanate and urethane can also dissociate above 150 °C. Therefore, the reaction of the urethane prepolymer and benzoxazine is actually highly complicated. Almost all the linkages, once formed, dissociate at high temperature and then combine with each other by cooling down the reaction mixture, probably giving both of the above linkages (Takeichi et al, 2000)

Polybenzoxazines obtained by thermal ring-opening polymerization of their precursors have phenolic hydroxyl group. This phenolic hydroxyl group has a strong potential for reacting with isocyanate group in urethane prepolymer. The reaction between the isocyanate group of the urethane prepolymer and the phenolic hydroxyl group of polybenzoxazine resulted in a crosslinked structure as shown in Figure 2.12. This reaction also suggested that the benzoxazine ring thermally opened, followed by the reaction between the hydroxyl group and isocyanate group to form a polymer network structure.

The detailed mechanism of benzoxazine-urethane alloy formation was reported and illustrated in Figure 2.12 (T.Takeichi et al, 2000)

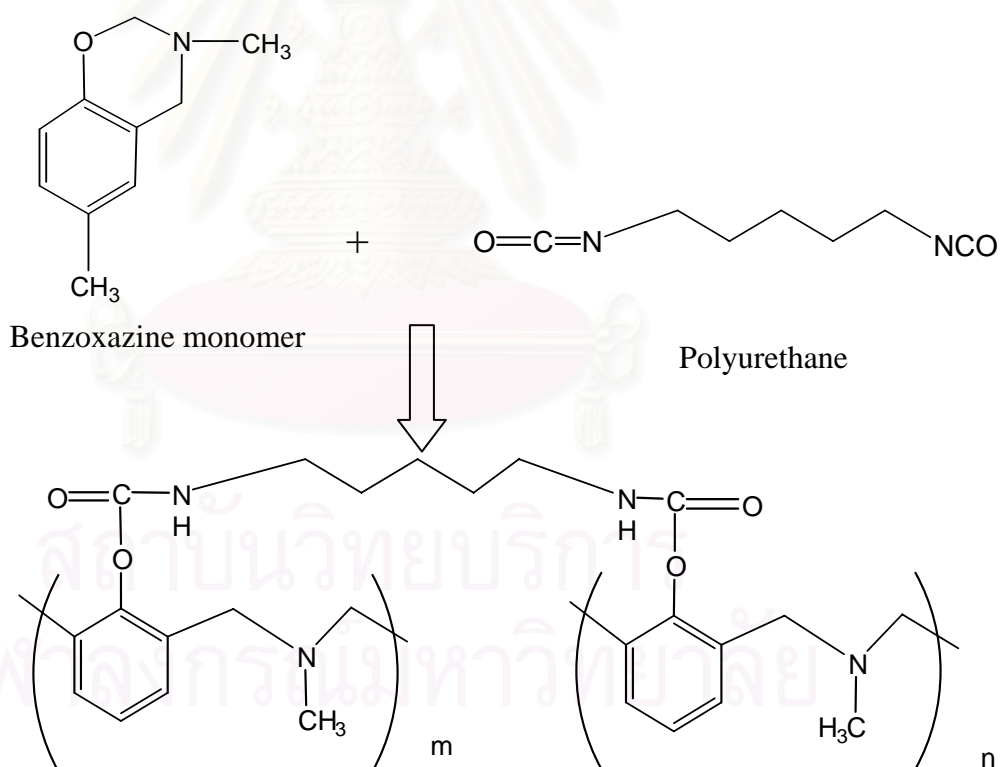


Figure 2.12: Benzoxazine-urethane crosslinked

2.4 Advanced Composites Materials

Composite materials have been used extensively in many engineering fields. Most composite materials consist of a selected filler or reinforcing material and a compatible resin binder to obtain specific characteristics and properties desired (Smith and Hashemi, 2006). Depending on type of matrix used, composites may be classified as polymer matrix composites (PMC), ceramic matrix composites (CMC), metal matrix composites (MMC), carbon – carbon composites, intermetallic composites or hybrid composites (Schwartz, 1997). In addition, based on the form of the dispersed phase, composite materials can also be classified into three commonly accepted types, fibrous composites, laminated composites, and particulate composites (Jones, 1975). Fiber-reinforced composites consist of continuous or discontinuous fibers in a matrix, while laminated composites consist of layers of various materials whereas particulate composites compose of particles dispersed within a matrix.

Modern structural composites frequently referred to as advanced composites. The term ‘advanced’ means the composite materials based on polymer materials with oriented, high-modulus carbon, aramid, glass or ceramic fiber (High performance composites, 1999). Composite materials may be defined as two or more materials that are combined on a microscopic scale to form a useful material. A resinous binder or matrix will hold the fiber in place, distribute or transfer load, protect the dispersed either in the structure or before fabrication and control chemical and electrical properties. The fiber is strong and stiff relative to the matrix especially the fiber with a length-to-diameter ratio of over 100. The strength and stiffness of the fiber are generally much greater or multiples of those of the matrix material. The useful application of advanced composite materials is aerospace application (60% capacity) (High performance composites, 1999). High-strength fibers used in advanced composites can be the same material or mixed (hybrid combination). The available fibers are not only carbon, glass and aramid, but also high-modulus polyethylene (PE), boron, quartz, ceramic, and newer fiber such as poly p-phenylene-2,6-benzobisoxazole (PBO) (www.compositesworld.com). These fibers can be grouped

into three broad categories: carbon, organic resin, and inorganic compound. Within each group, several classes of high performance fiber materials have been developed that satisfy the basic criteria of low density, high strength and high stiffness to varying degrees. The mechanical properties of typical fiber reinforcement are shown in Table 2.4. Due to its outstanding specific properties, particularly the specific modulus, carbon fiber was selected as a reinforcing agent for our BA:PU alloys. The composite mechanical and physical properties are also investigated for their potential use as high performance materials.

Table 2.4 Properties of fiber reinforcement (Encyclopedia of Polymer Science, 1985)

Reinforcement	Specific gravity	Tensile strength GPa	Specific strength 10^4 m	Tensile modulus GPa	Specific modulus 10^6 m
Glass					
E glass	2.54	3.4	13.8	72.4	2.9
S glass	2.48	4.6	18.7	85.5	3.5
Boron on tungsten substrate	2.63	3.1	12.0	400.0	15.5
Carbon or Graphite					
High strength	1.80	2.7	15.6	262.0	14.8
High modulus	1.94	2.0	10.9	380.0	19.9
Intermediate	1.74	2.5	14.5	186.0	10.9
Organic fiber					
aramid	1.44	2.7	19.5	124.0	8.8

2.5 Carbon Fiber

Carbon fiber is a generic name representing a family of fibers. Over the years, it has become one of the most important reinforcement fibers in many different types of composites, especially in polymer matrix composites (Chawla, 1998). Carbon and its graphite derivatives have emerged prominently in twentieth century technology. Carbon fibers are fine filament composed largely of carbon with structures and properties varying from those of amorphous carbon to those of well-developed crystalline graphite. Carbon in the graphitic form has hexagonal structure and is highly anisotropic. The fibers have the widest variety of strengths and moduli. Carbon fibers are divided into high-strength and high modulus according to their mechanical properties. Possible strength of carbon fiber is estimated to be about 100 GPa. Though the theoretical tensile strength of single crystal of graphite is 150 GPa, highest of all the materials known. The commercial high-strength carbon fibers have a reported maximum strength of 7 GPa (Chand, 2000). The ratio of stiffness to density is very high for most carbon fiber because the density of carbon is low. For this reason, they are the most widely used and are notably effective as reinforcing elements in advanced composite materials.

Physico-chemical properties of carbon fibers depend on the type of the precursor, manufacture conditions, the subsequent processing methods and other factors. Carbon fibers are a monocomponent system but they can be imparted with various properties often changeable in a wide range depending on the purposes and fields of application. The structure and properties of carbon fiber significantly depend on the raw material used, generally a polymer fiber. Numerous precursors have been used to produce carbon fiber. However three precursors which are being used for large-scale production of carbon fiber are PAN, rayon, and pitch. The first high-stiffness carbon fibers were produced from rayon. However, rayon-based carbon fiber did not compete with the PAN-based carbon fiber that became commercially available by the late sixties due to higher carbon yields which is 50% against 30% of rayon.

The carbon fibers produced from PAN have good-to-excellent strength up to 6895 MPa and high stiffness. Later carbon fibers were also prepared from pitch, an available by-product of the coal gasification and petrochemical industries. The properties of pitch carbon fibers are generally inferior to PAN carbon fiber. The properties of typical carbon fiber from these three precursors are shown in Table 2.5

Table 2.5 Axial tensile properties of carbon fiber (Smith, 1987)

Precursor	Tensile strength (GPa)	Tensile modulus (GPa)	Elongation at break (%)
PAN	2.5-7.0	250-400	0.6-2.5
Pitch	1.5-3.5	200-800	0.3-0.9
Rayon	~1.0	~50	~2.5

Processing of Carbon Fiber

Carbon fibers are fabricated by controlled pyrolysis of an organic fiber precursor i.e. pyrolytic degradation of a fibrous organic precursor (Chawla, 1998). By heating an organic polymeric fiber under tension to high temperatures in an inert atmosphere, the volatile constituents are driven off. The residual carbon atom tends to orient themselves along the fiber axis into graphitic crystallites and thus form a high strength, high modulus fiber. The properties of this fiber product are a function of the composition of the precursor and of the time-temperature profile of the pyrolytic process. The greater maximum processing temperature, the higher the extent of crystallite orientation parallel to the fiber axis, and thus the higher modulus of the fiber.

There are certain essential steps common to all processes of carbon fiber manufacture (Chawla, 1998). These are:

(a) Fiberization

This involves converting the precursor material into a fibrous form, i.e. extrusion of a polymer melt or solution into a precursor fiber.

(b) Stabilization

This treatment renders the precursor material infusible during the subsequent high temperature processing. This involves preoxidation or cross-linking of the polymer by thermosetting and is done at relatively low temperatures (200-450 °C), usually in air.

(c) Carbonization

This step involves conversion of the stabilized precursor fiber into a carbon fiber. This is carried out in an inert atmosphere (pure N₂ generally) at a temperature between 1,000 and 2,000 °C. At the end of this step the fiber has approximately 85-95% carbon content.

(d) Graphitization

This is an optional treatment. It is done in Ar or N₂ at a temperature between 2400 and 3000 °C. This step increases the carbon content to more than 99% and imparts a very high degree of preferred orientation to the fiber, thus, the strength of the fiber.

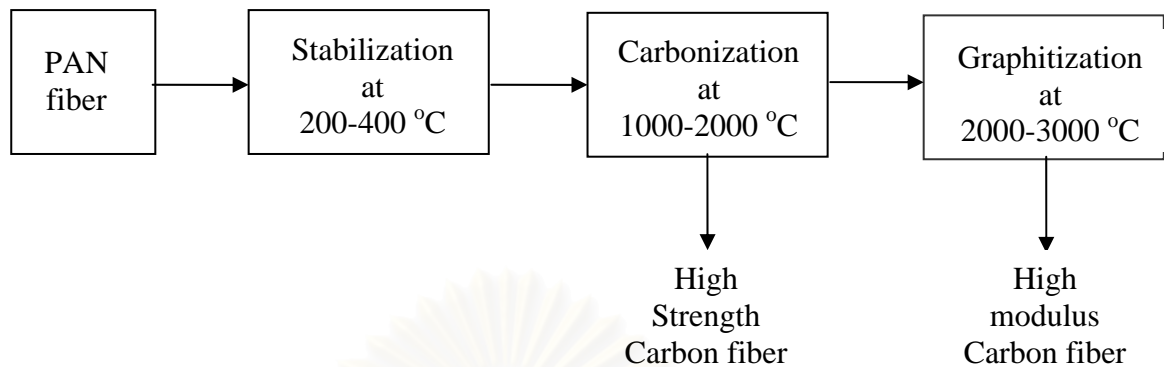


Figure 2.13 Flow diagram of the fabrication of PAN-based carbon fiber.

In addition, surface and sizing treatment are usually necessary to realize higher compressive strengths in carbon fiber composites. Carbon fibers when used without surface treatment produce composites with low interlaminar shear strength. Surface treatments increase the surface area and surface acidic functional groups and improve bonding between fiber and matrix resin. In addition, to achieve desirable properties in composite components, adhesion between fiber and matrix must be optimized. Adhesion requires sufficient saturation with resin (wet-out) at the fiber-matrix interface. To ensure good adhesion, attention must be given to fiber surface finish or coupling agent, often termed sizing. Sizing not only enhances the fiber/matrix bond, but also eases processing and protects the fibers from breakage during processing.

Applications of Carbon Fiber

Large weight savings are possible when carbon fiber composites are used to replace more conventional materials. They are frequently applied in areas where weight reductions are valuable. Especially, they are used in variety of aerospace components. Typical aerospace-grade tow size range from 1K to 12K PAN- and pitch-based 12K carbon fibers are available with a moderate (228 to 276 GPa), intermediate (276 to 345 GPa), high (345 to 483 GPa), and ultrahigh (483 to 925 GPa) modulus. (Tow is an untwisted bundle of continuous untwisted filaments. A term

commy used in referring to carbon or graphite fibers). Heavy tow carbon fibers with filament counts from 48K up to 320K are also available at a lower cost than aerospace-grade fibers. They typically have a modulus values ranging from 228 to 241 GPa and tensile strength up to 3.8 GPa and are used when fast part build-up is required, most commonly in recreational, industrial, construction and automotive markets. Carbon fibers and their composites exhibit many characteristics apart from their basic mechanical properties and weight saving. Electrical conductivity is coupled with excellent mechanical properties in thermoplastics molding compounds for structures in electronic equipment. Corrosion resistance is useful for making pipes, reactors or containers for chemical plants or in marine environment. Example of sports equipments that contain carbon fiber reinforcement include skis and ski poles, golf clubs, tennis racquets, fishing rods, and racing cycles.



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CHAPTER III

LITERATURE REVIEWS

In this work, a new thermoset resin namely benzoxazine resin is selected to be examined. The polymer possesses various reported outstanding properties. For examples, it can be synthesized from inexpensive raw materials and the polymerization reaction of benzoxazine monomer is initiated by heat, without using a curing agent, thereby, it is a good candidate for a wide variety of applications.

X. Ning and H. Ishida studied the synthesis and characterization of bifunctional benzoxazine precursors. These polyfunctional benzoxazines were found to exhibit excellent mechanical and thermal properties with good handling capability for material processing and composite manufacturing, e.g., the glass transition temperature of 190°C, tensile modulus of 3.2 GPa, and tensile strength of 58 MPa. In addition, they offered greater flexibility than conventional phenolic resins in terms of molecular design. They do not release by-product during curing reactions and there is no solvent other than for the solvency which the reactants may have for each other. One shortcoming of this resin is its rather high rigidity, therefore not suitable for some applications. (X. Ning and H. Ishida, 1994)

However, the above shortcoming can also be solved effectively due to an ability of the resin to be alloyed with several other polymers. For example, H. Ishida and D.J. Allen investigated benzoxazine resin combined with epoxy based on DGEBA. The benzoxazine was copolymerized with epoxy resin in order to modify their performance. The addition of epoxy to the polybenzoxazine network greatly increases the crosslink density of the thermosetting matrix and strongly influences its mechanical properties. Copolymerization leads to significant increase in the glass transition temperature, flexural strength, and flexural strain at break over those of the polybenzoxazine homopolymer, with only a minimal loss of stiffness. By

understanding the structural changes induced by variation of epoxy content and their effect on material properties, the network can be tailored to specific performance requirements. (H. Ishida and D.J. Allen, 1996)

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

S. Rimdusit and H. Ishida observed the synergism in the glass-transition temperature (T_g) of ternary systems based on benzoxazine, epoxy, and phenolic resins. The systems showed the maximum T_g up to about 180°C in benzoxazine / epoxy / phenolic at 5 / 4 / 1 mass ratio. Adding a small fraction of phenolic resin enhanced the crosslink density and, therefore, the T_g in the copolymers of benzoxazine and epoxy resins. To obtain the ultimate T_g in ternary system, 6-10 wt% phenolic resin was needed. The molecular rigidity from benzoxazine and the improved crosslink density from epoxy contribute to the observed synergistic behavior. The mechanical relaxation spectra of the fully cured ternary systems in a temperature range of -140 to 350°C showed four types of relaxation transitions : gamma transition at -80 to -60°C, beta transition at 60-80°C, α_1 transition at 135-190°C, and α_2 at 290-300°C. The partially cured specimens showed an additional loss peak that was frequency-independent as a result of the further curing process of the materials (Rimdusit and Ishida, 2000).

T. Takeichi et al. improved the performance of polybenzoxazine by alloying with polyimide. Polymer alloys of polyimide and polybenzoxazine were prepared from the combination of bifunctional benzoxazine monomer, 6,6'-(1-

methylethylidene)bis(3,4-dihydro-3,2H-1,3-benzoxazine) (B-a) and a soluble polyimide (PI) or its precursor, poly(amide acid) (PAA), that was synthesized from oxydianiline (ODA) and bisphenol A di(phthalic anhydride) ether (BPADA). It was observed from DSC that the onset temperature for the curing exotherm of B-a in the blend with PAA was remarkably lowered compared with that of the pristine B-a, while the curing temperature of B-a in the blend with PI was almost the same as that of pristine B-a. The cast films of PI/B-a or PAA/B-a were thermally treated at 150, 200 and 240°C for 2 h each, affording deep wine, transparent films. The PI component in the polymer alloy films from PI/B-a dissolved thoroughly. On the other hand, the polymer alloy films from PAA/B-a were not soluble in NMP. The polymer alloy films from both PI/B-a and PAA/B-a showed only one glass transition temperature (T_g) from their viscoelastic analyses. The T_g values remarkably increased as the content of PI increased. Thermal stabilities of both films from PI/B-a and PAA/B-a increased as the PI component increased in the similar manner (Takeichi et al., 2005).

T. Takeichi et al. prepared poly(urethane-benzoxazine) films as novel polyurethane/phenolic resin composites from blending benzoxazine monomers and urethane prepolymer, that was synthesized from 2,4-tolylene diisocyanate (TDI) and polyethylene adipate polyol (MW ca. 1000) in 2:1 molar ratio. DSC of the polymer blend showed an exotherm with maximum at about 246°C due to the ring-opening polymerization of the benzoxazine resin, giving phenolic OH functionalities that react with isocyanate groups in the urethane prepolymer. The poly(urethane-benzoxazine) films obtained by thermal curing were transparent with color ranging from yellow to pale red by increasing the benzoxazine content. All the films exhibited one glass transition temperature (T_g) from viscoelastic measurements, indicating no phase separation in poly(urethane-benzoxazine) due to the in-situ polymerization. The T_g was also found to increase with an increase of the benzoxazine content. The films containing 10 and 15% of benzoxazine had characteristics of an elastomer, with elongation at break of 244 and 182%, respectively. Whereas the films containing more than 20% of benzoxazine had characteristics of plastics. The poly(urethane-benzoxazine) films showed excellent resistance to the solvents such as

tetrahydrofuran, N,N-dimethyl formamide, and N-methyl-2-pyrrolidinone that easily dissolved the urethane prepolymer. Thermal stability of the urethane prepolymer was greatly enhanced even with the incorporation of a small amount of the benzoxazine resin. (Takeichi et al., 2000).

S. Rimdusit et al. improved the toughness of polybenzoxazine by alloying with urethane prepolymer (PU) using isophorone diisocyanate (IPDI)-polyether polyol system and a flexible epoxy (EPO732) system. The experimental results, i.e., flexural testing and dynamic mechanical analysis, revealed that toughness of the alloys of the rigid polybenzoxazine and the PU or the EPO732 systematically increased with the amount of either toughener, due to an addition of the more flexible molecular segments in the polymer hybrids. Curing temperature of the benzoxazine resin (bisphenol A-aniline type BA) at about 225°C shifted to a higher value when the fraction of BA in either alloy decreased. Interestingly, the enhancement in the glass transition temperature (T_g) of BA/PU alloys was clearly observed, i.e., T_g s of the BA/PU alloys are significantly higher (T_g beyond 200°C) than those of the parent resins, i.e., 165°C for BA and -70°C for PU. However, this characteristic was not observed in the BA/EPO732 alloy systems. The enhanced T_g of the BA/PU alloy at a 70/30 mass ratio was found to be 220°C, while that of BA/EPO732 at the same mass ratio was observed to be only 95°C, which further decreased as the content of epoxy fraction increased. Furthermore, the degradation temperature based on 5% weight loss in the thermogravimetric analyzer (TGA) thermograms of the BA/PU alloys was found to improve with the presence of the PU, though the opposite trend was observed in the BA/EPO732 systems. The char yield of both alloy systems was steadily enhanced with the increased benzoxazine content because the char yield of the polybenzoxazine was inherently higher than that of the two tougheners. Therefore, the polybenzoxazine alloys with the IPDI-based urethane prepolymer, e.g., the 70/30 BA/PU, were a promising system for a tough, high thermal stability polymeric network, suitable for both bulk and composite matrix applications. (S. Rimdusit et al., 2005)

Carbon fiber-reinforced composite materials have been used extensively in many engineering fields, especially in civilian and military aircraft, on account of their high specific strength and specific modulus. The composites used for structural applications require excellent mechanical properties.

Jang and Yang reported the flexural strength of polybenzoxazine reinforced by the untreated carbon fiber plain fabric to be about 365 MPa and the value can be enhanced to about 880 MPa or 240 % improvement using carbon fiber with nitric acid treatment. However, the authors did not mention on thermal stability of the obtained carbon fiber-reinforced polybenzoxazine. (Jang et al., 2000)

Jang and Yang also investigated the effect of rubber modification on carbon fiber/polybenzoxazine composites. The flexural strength of these composites with varied rubber content from 0 to 20 phr was found to show a relatively constant value of about 390 MPa using ATBN rubber system but exhibited a substantial decrease in the flexural strength using CTBN system i.e. 140 MPa with CTBN content of 20 phr. No study on thermal stability of the composites was reported. (Jang et al., 2000)

For high performance composites, Ishida and Chaisuwan improved the mechanical properties of carbon fiber-reinforced polybenzoxazine composites by rubber interlayering. The resin used is based on bisphenol A and xylylene because it shows the highest thermal stability achieved from the neat benzoxazine based on bisphenol-A and unfunctionalized aniline derivatives ($T_g = 236\text{ }^\circ\text{C}$ of BA-35X and $T_g = 170\text{ }^\circ\text{C}$ of BA). Carbon fiber woven fabric (T300) was used either as-received or desized condition. The fiber content of the composite is about 60% by volume. They reported the optimizing concentration of ATBN rubber provided the mechanical properties comparable or superior to those of the modified epoxy and phenolic matrices i.e. flexural strength: ≈ 718 MPa of rubber interlayered BA-35X, 780 of modified epoxy, and 650 of modified phenolic; flexural modulus: 58 GPa of rubber interlayered BA-35X, 58 GPa of modified epoxy, and 56 GPa of modified phenolic. Though substantial improvement in carbon fiber composite strength from using the neat polybenzoxazine matrix and the rubber interlayered system (i.e. 618 MPa and

718 MPa using desized carbon fiber) was observed, relatively narrow range of rubber interlayer thickness was needed to be determined. The optimal thickness of the rubber interlayer was approximately 15.7-19.6 nm. Too thick or too thin rubber interlayer was found to result in a significant decrease of the composite flexural strength. The same phenomenon was also observed in the composite flexural modulus. Moreover, glass transition temperature of these composite systems was observed to slightly decrease with an addition of the rubber interlayer due to the low T_g of the ATBN modifier.(Ishida and Chaisuwan, 2003).



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CHAPTER IV

EXPERIMENTAL

4.1. Materials

The materials used in this research are benzoxazine resin and urethane prepolymer. Benzoxazine resin is based on bisphenol-A, aniline and formaldehyde. The bisphenol-A (Commercial grade) was supported by Thai Polycarbonate Co.,Ltd. (TPCC). Para-formaldehyde (AR grade) was purchased from Merck Company and aniline (AR grade) was purchased from Panreac Quimica S.A. Company. Urethane prepolymer was prepared using polyether polyol at a molecular weight of 2000 with different types of diisocyanates i.e. toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), and isophorone diisocyanate (IPDI). Isophorone diisocyanate (IPDI) was obtained from Degussa-Huls AG. Toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI) were obtained from South City Group whereas the polyether polyol at a molecular weight of 2000 was kindly supplied by TPI Polyol Co., Ltd. Carbon fiber is Beslon HTA-N-6000 kindly from Toho Beslon Co., Ltd., Japan.

4.2 Matrix Resin Preparation

4.2.1 Benzoxazine Resin Preparation

Benzoxazine monomer (BA) was synthesized from bisphenol A, aniline, and paraformaldehyde at a 1:2:4 molar ratio. The mixture was constantly stirred at 110 °C using the patented solventless technology (Ishida, H. 1996). The benzoxazine monomer is solid powder at room temperature with yellow color. The powder was ground into fine powder and was kept in a refrigerator for future use.

4.2.2 Urethane Resin Preparation

The urethane prepolymer was prepared using polyether polyol at a molecular weight of 2000 with different types of diisocyanates i.e. toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), and isophorone diisocyanate (IPDI). The two reactants for urethane resin preparation were mixed in a four-necked round bottomed flask and the mixture was stirred under a nitrogen stream at 90 °C for 2 hours for isophorone diisocyanate (IPDI), at 70 °C for 1 hour for toluene diisocyanate (TDI), and at 45 °C for 1 hour for diphenylmethane diisocyanate (MDI) at a 2:1 molar ratio. 0.4 g of Dibutyltin dilaurate was used as a catalyst. After the completion of the reaction, the obtained clear and viscous urethane prepolymers were cooled to room temperature and kept in a refrigerator to prolong their shelf-lives.

4.3 Benzoxazine/Urethane Polymer Alloys Preparation

The benzoxazine monomer (BA) was blended with different types of the urethane prepolymers (PU) to provide BA:PU mixtures. Preparation of the benzoxazine resin and the three urethane prepolymers (i.e. having different types of isocyanates) was made at various weight ratios of the benzoxazine resin and urethane prepolymers i.e. 100:0, 90:10, 80:20, 70:30 and 60:40. The mixture was typically heated to about 80 °C in aluminum pan and mixed by hand until a homogeneous mixture was obtained. The molten mixture was poured into an aluminum mold and step-cured in an air-circulated oven at 150, 170, 190 °C for 1 hour each and 200 °C for 2 hours. The specimen was finally left to cool down to room temperature and then was ready for further characterizations.

4.4 Composite Manufacturing

Unidirectional carbon fiber and BA:PU prepregs were prepared by brushing the binary mixture matrix resin onto an unidirectional carbon fiber tape. Twenty plies of the prepregs were laminated in a (0°/90°) arrangement and were cured at 150, 170, 190 °C for 1 hour at each temperature by hot pressing in a hydraulic press at a pressure of 14 MPa and at 200°C for 2 hours in an air-circulating oven.

4.5 Characterization Methods

4.5.1 Gel Permeation Chromatography (GPC)

The molecular weight of the polyether polyol (Diol) at a molecular weight of 2000 for urethane resin preparation was confirmed by gel permeation chromatography. The analysis was performed at 40 °C on a Waters 600 GPC apparatus using three Waters Styragel® HT columns (Styragel® HT 0.5, Styragel® HT 1, and Styragel® HT 4). The detector was Waters 2414 refractive index (RID) analyzer. The calibration curve of the GPC column was obtained using polystyrene standards. Polyether polyol (Diol) was prepared at a concentration of 0.25 % (w/v) by dissolving the polyol (Diol) in tetrahydrofuran (THF) at room temperature. The sample solution of 100 µl was injected in the chromatogram and the elution time of the specimen was obtained.

4.5.2 Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier transform infrared spectra of the samples undergoing various curing conditions were acquired by a Perkin Elmer's Spectrum GX FT-IR spectrometer equipped with a KBr beam splitter and a deuterated triglycine sulfate (DTGS) detector. All spectra were taken as a function of time with 32 scans at a resolution of 4 cm⁻¹ and a spectral range of 4000-400 cm⁻¹. For urethane prepolymer before and after synthesis, a small amount of a viscous liquid sample was casted as thin film on a

potassium bromide (KBr) window at room temperature. For solid polymer alloy samples, a small amount of solid sample, preferably 0.5-1.0 mg., was ground and mixed with potassium bromide (KBr) powder and was pressed into a disk shape. All samples used were sufficiently thin with optical thickness small enough to conform to Beer-Lambert's law.

4.5.3 Differential Scanning Calorimetry (DSC)

The curing behavior and glass transition temperature of the benzoxazine resin with urethane prepolymer (different types of isocyanates) at various weight ratios are examined using a differential scanning calorimeter (DSC) model 2910 from TA Instruments. The thermogram was obtained using a heating rate of 10°C/min from room temperature to 300°C under nitrogen atmosphere. The purge nitrogen gas flow rate was maintained to be constant at 50 ml/min. The sample mass was measured to be approximately 5-10 mg. All samples were placed in a non-hermetic aluminum pan with aluminum lid. The glass transition temperature is obtained from the temperature at half extrapolated tangents of the step transition midpoint.

4.5.4 Thermogravimetric Analysis (TGA)

The degradation temperature (T_d) and char yield of the benzoxazine alloys at various mass fractions of urethane prepolymers (different types of isocyanates) as well as carbon fiber composites were studied using a Perkin Elmer Instrument Technology SII Diamond TG/DTA thermogravimetric analyzer. A heating rate of 20°C/min from room temperature to 900°C under nitrogen atmosphere was used to acquire the thermograms. The purge nitrogen gas flow rate was 100 ml/min. The sample was measured to be approximately 8-12 mg. Weight loss of the samples was measured as a function of temperature. The degradation temperature (T_d) of the BA:PU alloys were reported at 5 and 10 % weight loss. Char yield of the above alloys were also reported at 900 °C.

4.5.5 Density Measurement

The densities of benzoxazine resin alloyed with urethane prepolymer and of their carbon fiber composites were determined by water displacement method according to the ASTM D 792-91 (Method A). The dimension of specimens is in rectangular shape $50 \times 25 \times 1 \text{ mm}^3$

The density is calculated by a following equation:

$$\rho = \left(\frac{A}{A - B} \right) \times \rho_o \quad (4.1)$$

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

The average value from three specimens was calculated.

4.5.6 Fiber Volume Fraction Determination

All tested specimens were evaluated for fiber volume fraction by measuring the density of the composites (water displacement method). The fiber volume fraction was then calculated using the rule of mixtures

$$v = (\rho_c - \rho_{\text{resin}}) / (\rho_{\text{fiber}} - \rho_{\text{resin}}) \quad (4.2)$$

where v = Fiber volume fraction

ρ_{fiber} = Density of the carbon fiber = 1.76 g/cc

ρ_{resin} = Cured resin density of each composition

ρ_c = Composite density

4.5.7 Flexural Property Measurement

The flexural modulus and strength of the polymer alloy specimens and the carbon fiber composites were determined using a universal testing machine (model 5567) from Instron Co., Ltd. The test method used was a three-point loading with the supporting span of 48 mm and tested at a crosshead speed 1.2 mm/min. The dimension of the specimens is $25 \times 60 \times 3 \text{ mm}^3$. The flexural properties were determined based on ASTM D790M-93. The flexural modulus and strength were calculated by the following equations:

$$E_B = \frac{L^3 m}{4bd^3} \quad (4.3)$$

$$S = \frac{3PL}{2bd^2} \quad (4.4)$$

where E_B = Flexural modulus, GPa

S = Flexural strength, MPa

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

L = Support span, mm

b = Width of beam tested, mm

d = Depth of beam tested, mm

m = Slope of the tangent to the initial straight-line portion of the load-deflection curve, N/mm

4.5.8 Dynamic Mechanical Analysis (DMA)

The dynamic mechanical analyzer (DMA) model DMA242 from NETZSCH is used to investigate the dynamic mechanical properties and relaxation behaviors of the polymer alloys and the carbon fiber composites. The dimension of specimens is $10 \times 50 \times 2 \text{ mm}^3$. The tested was performed in a bending mode. In a temperature sweep experiment, a frequency of 1 Hz and a strain value of 0.1% were applied. The temperature was scanned from 30°C to 300°C with a heating rate of $2^\circ\text{C}/\text{min}$ under nitrogen atmosphere. The storage modulus (G'), loss modulus (G''), and loss tangent or damping curve ($\tan \delta$) were then obtained. The glass transition temperature (T_g) was taken as the maximum point on the loss modulus curve in the DMA thermogram.



CHAPTER V

RESULTS AND DISCUSSION

5.1 Polyurethane Characterization

5.1.1 Gel Permeation Chromatography (GPC)

Table 5.1 shows the molecular weight of polyether polyols used for urethane prepolymer synthesis. The chromatogram results provide M_n and M_w values of the polyols are compared with the molecular weight values informed by the supplier (TPI Polyol Co., Ltd.). The results exhibited that molecular weights of the polyols measured by Gel Permeation Chromatography (GPC) was in relatively good agreement with the molecular weights derived from the monomer/initiator ratio obtained from the supplier. Moreover, the polydispersity index (PDI) values of the polyols was close to unity, i.e. 1.06, implying a relatively narrow molecular weight distribution of the polyol used.

5.1.2 Fourier Transform Infrared Spectroscopy (FT-IR)

Polyurethane is sometimes considered as a macromolecule with alternating soft and hard segments. Soft segments generally derive from a polyether or polyester polyol, whereas the diisocyanates in conversion to urethane linkages form hard segment (Sebenik. et al.,2006). FT-IR spectroscopic technique is generally used to indicate the completion of the reaction between an isocyanate group and the polyol's hydroxyl group. In this study, urethane (PU) prepolymer was prepared by reacting polyether polyol at a fixed molecular weight of 2000 with different types of isocyanates i.e. isophorone diisocyanate (IPDI), toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI). The important functional groups of urethane prepolymer are $N=C=O$, $C=O$, CH_2 and CH_3 which were used to characterize the

presence of the urethane prepolymer in the polymerization reaction. In general, the absorption band around $2280\text{-}2240\text{ cm}^{-1}$ is assigned to the $\text{N}=\text{C}=\text{O}$ stretching of isocyanate structure. The carbonyl absorption ($\text{C}=\text{O}$) implies the reaction of the isocyanate group with the hydroxyl group of the polyol to form a urethane prepolymer. The carbonyl signal of urethane is usually located between $1730\text{-}1700\text{ cm}^{-1}$ while several C-H stretching bands are located between $3000\text{-}2800\text{ cm}^{-1}$. Figures 5.1(a), 5.1(b) and 5.1(c) show the FT-IR spectra of three mixtures of polyether polyol with isophorone diisocyanate (IPDI), toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI) before and after their formation reactions, respectively. From Figures 5.1(a), 5.1(b) and 5.1(c), spectra (b) indicated absorption bands at $1740\text{-}1700\text{ cm}^{-1}$ for the $\text{C}=\text{O}$ stretching to increase but the absorption band at 2242 cm^{-1} of the $\text{N}=\text{C}=\text{O}$ stretching decreased with the progress of the reaction to form the urethane prepolymer. The reaction was confirmed to be completed under a nitrogen stream at 90°C for 2 hours for isophorone diisocyanate (IPDI), at 70°C for 1 hour for toluene diisocyanate (TDI), and at 45°C for 1 hour for diphenylmethane diisocyanate (MDI). The synthesis conditions above were also in good agreement with those used by Rimdusit et al., Ghosh et al., and Bai et al., respectively. (Rimdusit et al., 2005, Ghosh et al. 2001, and Bai et al., 1997)

5.2 Thermal and Mechanical Properties of BA:PU Alloys

5.2.1 Differential Scanning Calorimetry (DSC) of BA:PU Alloys.

The curing exotherms of the neat benzoxazine resin and the urethane prepolymer at various types of isocyanates, i.e. isophorone diisocyanate (IPDI), toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI) were exhibited in Figures 5.2(a), 5.2(b) and 5.2(c), respectively. The investigated compositions of the BA:PU mixtures of all three isocyanates were 60:40, 70:30, 80:20, 90:10 and 100:0 mass ratios. From these graphs, the exothermic peak of the neat benzoxazine resin was located at 227°C . The curing peak maximum was observed to shift to a higher temperature when the urethane prepolymer fraction in the alloys increased. In Figure

5.2(a), the positions of the exothermic peaks of BA:PU mixtures using isophorone diisocyanate (IPDI) at 90:10, 80:20, 70:30 and 60:40 mass ratios are 234, 236, 243 and 247 °C, respectively. Whereas Figure 5.2(b) reveals the positions of the exothermic peaks of BA:PU using toluene diisocyanate (TDI) at the same mass ratios to be 234, 238, 243, and 247°C respectively. Finally, Figure 5.2(c) shows the position of those curing peaks of BA:PU using diphenylmethane diisocyanate (MDI) at 90:10, 80:20, 70:30 and 60:40 mass ratios to be 232, 236, 237 and 240°C, respectively. In principle, the reactions between BA:PU were expected to comprise of at least two reactions; the first reaction is the exothermic curing peak among the benzoxazine monomers, while the second one should be the reaction between the isocyanate group on the polybenzoxazine (Takeichi et al., 2000 and Rimdusit et al., 2005). The reaction between the isocyanate group with phenolic hydroxyl group on polybenzoxazine was expected to proceed after phenolic hydroxyl group from ring opening of the benzoxazine monomer was produced. Furthermore, as the urethane prepolymer could not directly react to form a homopolymer by itself, its presence with an increasing amount might cause a dilution effect on the resulting mixture. As a consequence, the curing retardation was observed and was more pronounced with the increasing amount of the PU in the binary mixtures. The thermograms also suggested the decrease of the area under the curing peaks of the binary mixtures when the amount of all urethane prepolymers based on IPDI, TDI, or MDI increased. The phenomenon is attributed to the change from the BA:BA interaction to a more BA:PU interaction with increasing the PU fraction in the alloys. The systematic decrease of the exotherms with the PU implied the BA:PU interaction possessed a lower heat of reaction per mole of the reactants. Excessive amount of the PU in the binary mixtures might also lead to the presence of the unreacted PU in the fully cured alloys, thus the further reduction of the heat of reaction.

An effect of types of isocyanates in PU on the curing behaviors of the BA:PU alloys is shown in Figure 5.3. The figure illustrates the curing behaviours of the neat benzoxazine resin (BA) compared with those three binary mixtures (BA:PU) at a fixed mass ratio of 60:40. From this graph, the addition of the urethane prepolymer based on different types of isocyanates in benzoxazine resin resulted in a similar shift

of the curing peak maximum of the neat benzoxazine resin at 227°C to a higher temperature. The curing peak maximum of BA:PU based on IPDI and TDI were found to be about 248°C and 244°C, respectively whereas that of BA:PU based on MDI was about 240°C. In other words, the reaction between BA:PU based on MDI requires lower curing temperature than those of BA:PU based on TDI and IPDI. Lapprand et al. (2005) studied reactivity of different isocyanates with urethane group in the allophanate formation reaction. They reported that the reaction between urethane moieties and IPDI (cycloaliphatic isocyanates) was less reactive than that between urethane moieties and MDI (aromatic isocyanates). The results suggested that aromatic isocyanates are more reactive than aliphatic or cycloaliphatic isocyanates. Finally, the area under the exothermic peak of BA:PU based on MDI was found to be 157.0 J/g while those of BA:PU based on TDI and IPDI were 155.5 J/g and 153.0 J/g, respectively close to each other within an experimental error.

Figure 5.4 indicates the DSC thermograms of the BA:PU mixtures based on TDI at a mass ratio of 60:40 at various curing conditions. The heat of reaction determined from the area under the exothermic peak was 155.5 J/g (0% conversion) for the uncured mixture. The reaction reduced to 111.0 J/g (29% conversion) after curing at 150°C for 1 hour, and decreased to 107.1 J/g (60% conversion) after further curing at 170°C for 1 hour and decreased to 97.9 J/g (97% conversion) for further curing at 190°C for 1 hour. After post curing at 200°C for another 2 hours, the exothermic heat of reaction disappeared corresponding to the fully cured stage of the alloy. The degree of conversion of the sample was determined according to the following relationship.

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

where H_{rxn} is the heat of reaction of the partially cured specimens.
 H_o is the heat of reaction of the uncured resin.

Both H_{rxn} and H_o values can be obtained from DSC experiments. The calculated conversion suggested that the curing reaction of BA:PU polymer alloys could rapidly occur at high temperature. As a consequence, the curing temperature at 150°C for 1 hour, 170°C for 1 hour, 190°C for 1 hour and 200°C for 2 hours was chosen as an optimum curing condition of all BA:PU polymer alloys.

Figures 5.5(a), 5.5(b) and 5.5(c) show the DSC thermograms and the glass transition temperature (T_g) of the fully cured BA:PU alloys based on IPDI, TDI and MDI respectively. All polymer alloys exhibited only single T_g , which implied the miscibility of two polymers. The T_g 's of the polymer alloys between BA:PU were found to increase with the mass fraction of urethane prepolymer. The T_g 's of the fully cured BA:PU alloys based on IPDI were observed to be ranging from 169°C in 90:10 BA:PU up to 243°C in 60:40 BA:PU system. Similar trends were also observed in the BA:PU alloys with the PU based on TDI and MDI as clearly compared in Figure 5.6.

The effect of the urethane mass fraction on the glass transition temperature of the BA:PU alloys was previously reported by Rimdusit et al. (2005) using DMA. In their case, T_g of the polymer alloys at each composition was defined using the maximum of the loss modulus. In these alloy systems, their T_g 's showed a synergistic behavior with the mass fraction of urethane prepolymer. The T_g 's of the BA:PU alloys in our case also increased with the mass fraction of urethane prepolymers confirming the previous report (Rimdusit et al., 2005). The T_g 's of urethane elastomer based on IPDI and polybenzoxazine were reported to be about -70°C and 165°C, respectively. In this case, T_g 's of the alloys were also found to increase with the mass fraction of urethane prepolymer at least up to 40wt% of the urethane fraction. The observed increase in the crosslink density of the binary systems with urethane prepolymer in the DMA investigation is one possible reason for the enhancement in the T_g of the resulting alloys though urethane prepolymer is a softer molecular species having much lower T_g and was expected to lower the T_g of the binary alloys. The additional crosslinking was proposed to be caused by the reaction between isocyanate group on the urethane monomer with hydroxyl group on polybenzoxazine after the phenolic

hydroxyl group from ring opening polymerization of benzoxazine monomer was produced (Takeichi et al., 2000).

In Figure 5.6, the T_g 's of these BA:PU based on TDI at various compositions rendered the highest value among the three isocyanate systems. Ghosh et al. reported the properties of polyurethane based on polyethylene glycol at a molecular weight of 200 using different diisocyanates (HDI, IPDI and TDI). The T_g values estimated from the maximum peak of $\tan \delta$ were 10°C, 13.7°C and 50°C for polyurethane based on HDI, IPDI and TDI, respectively. Since TDI, IPDI and HDI contain a rigid aromatic ring, alicyclic ring and flexible aliphatic chain, respectively. The above results point toward the effect of structural features of diisocyanates on their T_g 's that the more rigid isocyanate gives higher T_g value in the polyurethane. Their results explained the trend to provide maximum T_g in the TDI based system of the three evaluated alloys.

5.2.2 Thermal Degradation of BA:PU Alloys

The TGA thermograms of the neat BA and BA:PU based on IPDI, TDI and MDI at various compositions are shown in Figure 5.7(a), 5.7(b) and 5.7(c). In general, degradation temperature (T_d) at 5 % weight loss is one of the key parameters that is needed to be considered for high temperature applications. From these results, the decomposition temperature of the neat BA at 5 % weight loss was determined to be 321°C. The T_d 's of our BA:PU with 0-40 wt% PU fraction were found to be about the same with slightly higher than that of the neat BA i.e. about 330°C for all tested alloy compositions. Therefore, the benefit of mixing the urethane prepolymer into benzoxazine resin was to improve the thermal stability of the polybenzoxazine. These results might be due to the reaction of the isocyanate in urethane prepolymer and the hydroxyl of the polybenzoxazine to increase a crosslink density of polymer alloys as explained before. However, the residual weights at 800°C of all three binary systems were found to decrease with increasing the PU mass fraction in the polymer alloys. The char yield at 800°C of the polybenzoxazine was determined to be about 32wt% which was also consistent with the value reported previously by Rimdusit et al., 2005. The TDI-poly(ethylene adipate) based polyurethane possessed a smaller value of char

yield of only 8wt% at 800°C (Takeichi et al., 2001). In our case, the addition of the PU in the polybenzoxazine expectedly decreased the char yield of the polymer alloys in all three types of the isocyanates as shown in 5.7(a), 5.7(b) and 5.7(c). Furthermore, the chemical structure of the polyurethane prepolymer composed of a less thermally stable aliphatic structure of the polyol compared to the predominant aromatic ring in the structure of polybenzoxazine. Therefore, the increase of the PU mass fraction resulted in the lowering of the char yield in the polymer alloys.

Figure 5.8 describes the TGA thermograms of BA:PU alloys at a fixed mass ratio of 60:40 based on different types of isocyanates. The degradation temperatures at 5 % weight loss of all alloys were found to be higher than the neat polybenzoxazine as explained before. Furthermore, different types of isocyanates revealed almost the same effect on the degradation temperature but resulted in the slightly difference in char formation of the polymer alloys. Char yield of the polymer alloys changed with the types of the isocyanates as follow: MDI > TDI > IPDI. This can be explained as chemical structure of IPDI in urethane prepolymer composed of a less thermally stable cycloaliphatic structure compared to the aromatic ring of TDI and MDI in urethane prepolymer.

5.2.3 Density Determination of BA:PU Alloys.

In this work, the density measurements of all specimens were used to examine the presence of voids in the polymeric alloy specimens. The actual densities and the theoretical densities of BA:PU at various compositions using IPDI, TDI and MDI were compared in Table 5.2. Adding the urethane prepolymer, which is a higher viscosity resin, slightly affected the densities of polymer alloys as seen in the table. From the results, the density of the polymer alloys trended to gradually decrease with increasing the mass fraction of PU. Because of the high viscosity of urethane prepolymer, adding more ratio of urethane prepolymer directly affected on the mixing behaviour and the obtained densities were slightly lower than the theoretical values. The phenomenon is likely to be caused by of the presence of voids in the specimens

as a result of mixing difficulty of the urethane prepolymer into benzoxazine resin with increasing the more viscous PU fraction.

5.2.4 Flexural Properties of BA:PU Alloys

Flexural properties of BA:PU alloys are described in Figures 5.9 and 5.10. Figure 5.9 illustrates the flexural strength of BA:PU alloys at different types of isocyanates and various mass fractions of PU. The flexural strength of the neat polybenzoxazine was determined to be 133 MPa. The strength values of the BA:PU alloys with three isocyanates were observed to exhibit a synergistic behavior with the maximum value at the BA:PU ratio of 90:10 in all three systems. Those ultimate strength values are 155 MPa in TDI system, 146 MPa in IPDI system, and 137 MPa in MDI system. This synergistic phenomenon was consistent with that reported by Rimdusit et al. (2005). In addition, the further increase of the PU fraction (i.e. 20wt%, 30wt% and 40wt%) for the three isocyanate types systematically decreased the flexural strength of the polymer alloys. At the BA:PU ratio of 60:40, the flexural strengths reduced to 70 MPa in TDI system, 57 MPa in IPDI system, and 39 MPa in MDI system. In principle, the addition of the softer PU fraction in the alloys should result in the decrease of their strength as observed in the 20-40 wt% region. However, we also knew that the addition of PU helped improving the crosslink density and also the strength of the alloys. This implies that the effect of crosslink density on the alloy's strength dominates the effect of the lower stiffness of the PU if the PU mass fraction is below 10wt%. This is possibly the reason why the synergistic behavior is observed in these polymer alloys.

Figure 5.10 exhibits the flexural modulus of BA:PU alloys at different isocyanate types and various urethane mass fractions. The maximum modulus value of 5.8 GPa belongs to neat polybenzoxazine. The flexural modulus were also found to linearly decrease with increasing the amount of PU fraction for all the alloys. The flexural modulus values of BA:PU using TDI were to be 5.3 GPa, 3.8 GPa, 3.3 GPa and 2.0 GPa for BA:PU of 90:10, 80:20, 70:30, and 60:40 mass ratios, respectively. The flexural modulus values of BA:PU using IPDI were determined to be 4.9 GPa,

3.7 GPa, 3.0 GPa and 1.8 GPa for BA:PU of 90:10, 80:20, 70:30, and 60:40 mass ratios, respectively. Finally, the flexural modulus values of BA:PU using MDI were ranging from 4.8 GPa to 1.7 GPa for BA:PU of 90:10 to 60:40 mass ratios. This phenomenon was due to the fact that the addition of the softer urethane resin into the benzoxazine resin was expected to lower the stiffness of the polybenzoxazine alloys as a result of an elastomeric nature of the PU used. Moreover, the urethane prepolymer based on TDI also exhibited the highest flexural strength and flexural modulus compared among three types of isocyanates used. Ghosh et al. reported the tensile strength of films of polyurethane containing polyol (polyethylene glycol molecular weight of 200) with different diisocyanates (HDI, IPDI and TDI). The tensile strength values were found to be ranging as follow: TDI > IPDI > HDI. The results were due to TDI, having aromatic structure, imparts least flexibility, and HDI, being aliphatic, imparts highest flexibility. Furthermore, the films prepared using IPDI showed less flexibility than those prepared with HDI, due to its alicyclic nature (Ghosh et al., 2001).

5.2.5 Dynamic Mechanical Properties of BA:PU Alloys

Due to the ultimate properties in T_g and flexural properties of TDI systems, these alloys were further evaluated as a potential use for matrices of carbon fiber composites. Figure 5.11 shows the dynamic mechanical properties of BA:PU alloys by using TDI at various compositions. The storage modulus in the glassy state of the polymer alloys was observed to systematically decrease with increasing PU mass fraction as a result of the more flexible characteristics of elastomeric PU as discussed previously. At room temperature, the storage modulus reduced from 5.4 GPa to 1.7 GPa after an incorporation of PU from 0 to 40wt%. These values showed similar trends as in our previous work (Rimduisit et al., 2005) Additionally, as the mass fraction of the PU in the alloys increased, the alloy modulus-temperature curve showed the increase of the slope. This characteristic implies the more thermal stability of the polybenzoxazine comparing with the polyurethane. The rubbery plateau modulus of BA:PU trended to increase with the PU mass fraction because the addition

of PU in polymer alloys was able to enhance the crosslink density of fully cured specimens as discussed earlier.

The glass transition temperature (T_g) of BA:PU alloys based on using TDI can also be determined using DMA. In this case, T_g of the polymer alloys at each composition was defined using the maximum of loss modulus (E''). From Figure 5.12, adding PU into polybenzoxazine was clearly found to increase the T_g of polymer alloys. This result was consistent with the observation in the DSC thermograms. The ability of the urethane prepolymer to enhance the cross-linked density of polybenzoxazine was attributed to the observed phenomenon as explained earlier.

Figure 5.13 shows $\tan \delta$ of the BA:PU based on TDI at various BA:PU compositions. As mass fraction of PU increased, the peak height of $\tan \delta$ trended to decrease, and the peak position shifted to a higher temperature. Since $\tan \delta$ is defined as the ratio of viscous to elastic components of dynamic modulus of material, it suggested the reduction in the segment mobility of chain due to increasing crosslink density with the increase of PU mass fraction in the alloys. Moreover, the broadening of the $\tan \delta$ peak of BA:PU alloys in comparison with the neat polybenzoxazine suggested the broader distribution of polymer network structure in the BA:PU alloys.

5.3 Thermal and Mechanical Properties of Carbon Fiber Composites of BA:PU Alloys Based on TDI

From the literature, Ishida and Chaisuwan (2003) studied the use of ATBN as a rubber interlayer to improve mechanical properties of carbon fiber and benzoxazine based on bisphenol-A, formaldehyde and 3,5-xylidine (BA-35X) composites. Good mechanical properties were reported, and the flexural strength from optimizing the concentration of ATBN rubber showed superior strength to the modified epoxy, modified phenolic resin, and modified BA-a composites. These results affirmed the

usefulness of a flexible elastomer, such as ATBN rubber or polyurethane, to enhance mechanical properties of carbon fiber-reinforced polybenzoxazine.

5.3.1 Flexural Properties of Carbon Fiber Composites Based on BA:PU Alloys

Flexural properties of carbon fiber reinforced BA:PU composites were illustrated in Figures 5.14 and 5.15. Figure 5.14 depicts flexural strengths of carbon fiber reinforced BA:PU composites at various mass fractions of the PU in comparison with that of BA:PU matrix. The fiber content determined from TGA was approximately 80wt% in all composites. The flexural strengths of carbon fiber reinforced BA:PU composites based on TDI at various mass fractions of PU were found to be more than 3 times of the matrix alloys for all compositions. The flexural strengths of the carbon fiber reinforced polybenzoxazine was reported to be equal to 370 MPa (Jang et al., 2000). In this work, the flexural strength of carbon fiber-reinforced polybenzoxazine was measured to be 397 MPa. The increase of the PU fraction in the matrix increased the flexural strength to 490 MPa for 60:40 BA:PU. The enhancement in the composite strength with PU was possibly due to the improved interfacial adhesion between the carbon fiber and matrix resin with increasing mass fraction of the PU. Jang et al. (2000) studied the flexural properties of the ATBN rubber, polybenzoxazine (BA), and carbon fiber composites. They reported that ATBN rubber did not decrease the flexural strengths of the composites, even though ATBN rubber was flexible. The possible reason for the observed behavior is that these ATBN modified composites had strong interface. On the other hand, the carbon fibers without ATBN rubber exhibited the adhesive failure. The failure occurred at the carbon fiber/polybenzoxazine interface as a result of poor adhesion (Ishida et al., 2003). In our case, the interfacial strength between carbon fiber and BA:PU matrix could be explained by the mechanisms of mechanical interlocking and fiber wetting. The addition of softer PU into a more rigid polybenzoxazine possibly rendered the increase interaction between the non-polar polyol of PU and the non-polar carbon fiber. That led to 25% increase of the flexural strength of the composites.

Furthermore, flexural modulus of carbon fiber reinforced BA:PU composites at various urethane mass fractions in comparison with BA:PU matrix based on TDI were depicted in Figure 5.15. The flexural modulus of carbon fiber reinforced BA:PU composites at various urethane mass fractions were found to be significantly higher than that of BA:PU matrix alloys for all BA:PU compositions. The maximum modulus value of 51 GPa belongs to the carbon fiber/polybenzoxazine system. The flexural modulus were found to slightly decrease to e.g. 48 GPa with increasing the amount of PU fraction to 40wt%. The phenomenon was due to the fact that the addition of the urethane resin into the carbon fiber composites as a result of an elastomeric nature of the PU used. Furthermore, the flexural modulus value of carbon fiber reinforced BA:PU composites is ranging from 43 GPa to 48 GPa when adding PU from 10wt% to 40wt%. The effect of PU fraction on the modulus of the BA:PU composite was thus marginal comparing with the effect of the carbon fiber reinforcement.

5.3.2 Dynamic Mechanical Properties of Carbon Fiber Composite of BA:PU Alloys Based on TDI

Figure 5.16 shows the dynamic mechanical properties of carbon fiber reinforced BA:PU composites at various BA:PU compositions. The storage modulus in the glassy state of the carbon fiber reinforced BA:PU composites expectedly decreased with increasing mass fraction of the PU as result of the more flexible characteristics of elastomeric PU used. At the room temperature, the storage modulus slightly reduced from 49 GPa to 48 GPa with an incorporation of PU from 0 to 40wt%. These values were much higher than the storage modulus of the carbon fiber-reinforced polybenzoxazine without ATBN interlayer, which was equal to 8.5 GPa (Ishida et al., 2003). Additionally, as the mass fraction of the PU in the matrix increased from 10wt% to 40wt%, the storage modulus systematically increased. The improved interface between the carbon fiber and the BA:PU matrix was attributed to this observed phenomenon.

The loss modulus (E'') from DMA of the carbon fiber reinforced BA:PU composites at various BA:PU contents is presented in Figure 5.17. T_g of carbon fiber reinforced BA:PU composites at each composition was defined using the maximum of the loss modulus. It can be seen that the addition of the PU into carbon fiber reinforced BA:PU composites was found to increase the T_g of carbon fiber reinforced BA:PU composites. The result is consistent with the trend observed in DSC and DMA thermograms of matrix alloys. The T_g values of the carbon fiber composites tended to be the same as those of the matrix alloys. The behavior suggested that the strong bonding between the carbon fibers and BA:PU matrices to be unlikely as very high stiffness of the carbon fiber can not effectively restrict the molecular mobility of the matrix and thus caused only marginal change of the T_g 's of the composites.

Table 5.1: The molecular weight of polyether polyols at molecular weight 2000 from GPC.

Sample	Supplier Values	Determined Values		
	Mn (g/mol)	Mn (g/mol)	Mw (g/mol)	PDI
Diol at MW2000	2000	2022	2137	1.06

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Table 5.2 : Density of BA/PU alloys for different types of isocyanates.

PU Content (wt%)	Density of BA:PU based on IPDI (g/cm ³)		Density of BA:PU based on TDI (g/cm ³)		Density of BA:PU based on MDI (g/cm ³)	
	Theoretical density	Actual density	Theoretical density	Actual density	Theoretical density	Actual density
0	1.190	1.190	1.190	1.190	1.190	1.190
10	1.168	1.166	1.174	1.172	1.178	1.177
20	1.146	1.144	1.159	1.157	1.166	1.164
30	1.126	1.124	1.144	1.141	1.155	1.153
40	1.106	1.104	1.130	1.127	1.143	1.142



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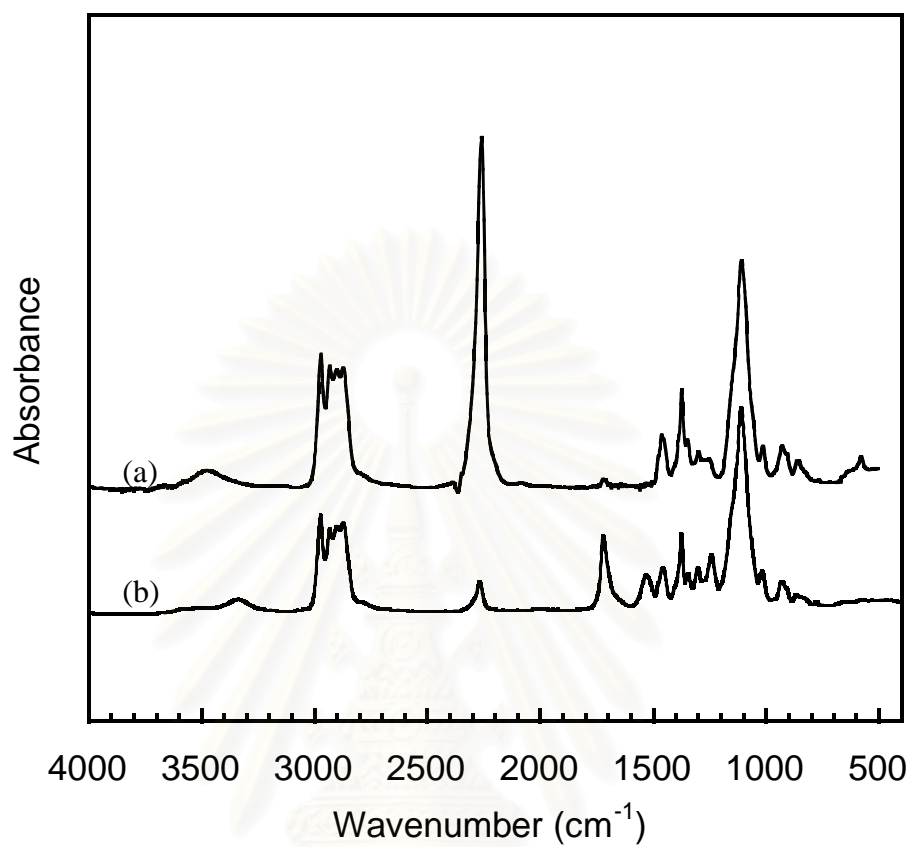


Figure 5.1(a): FT-IR spectra of a mixture of polyether polyols and isophorone diisocyanate (IPDI) before (a) and after their formation reactions (b).

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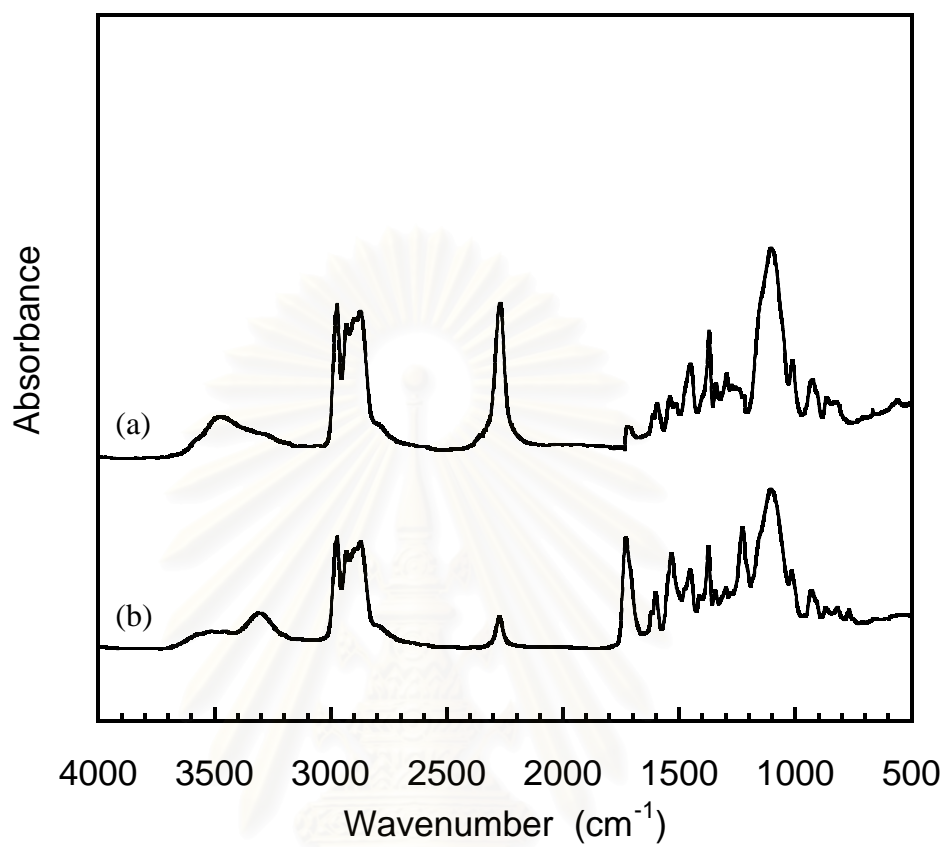


Figure 5.1(b): FT-IR spectra of a mixture of polyether polyols and toluene diisocyanate (TDI) before (a) and after their formation reactions (b).

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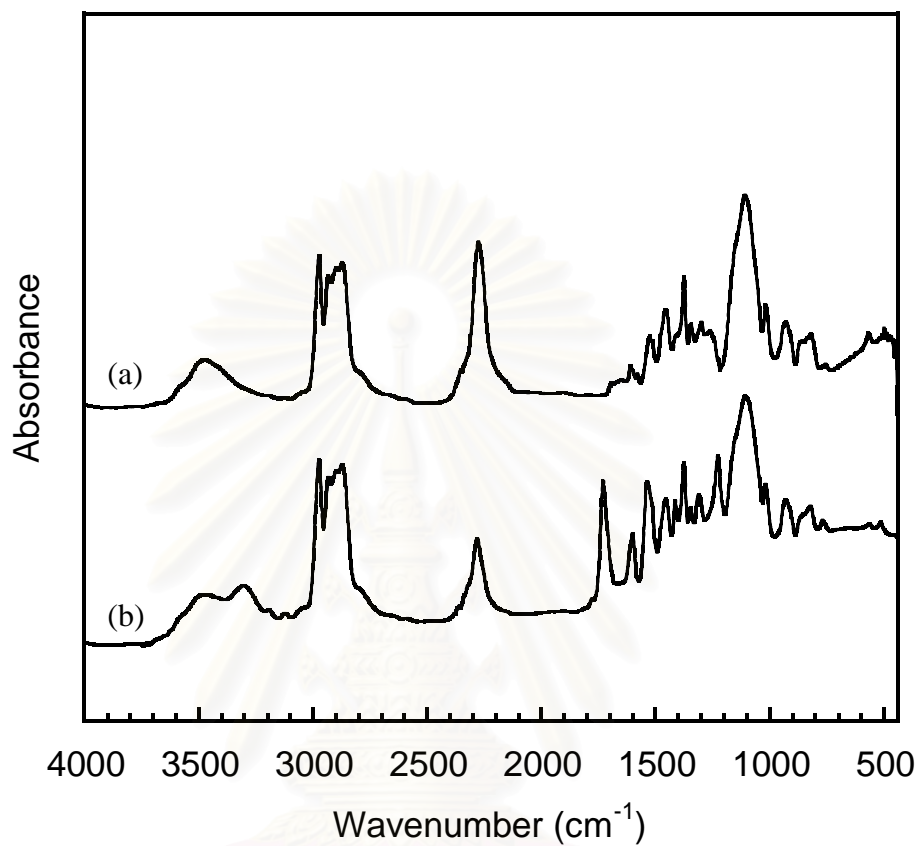


Figure 5.1(c): FT-IR spectra of a mixture of polyether polyols and diphenylmethane diisocyanate (MDI) before (a) and after their formation reactions (b).

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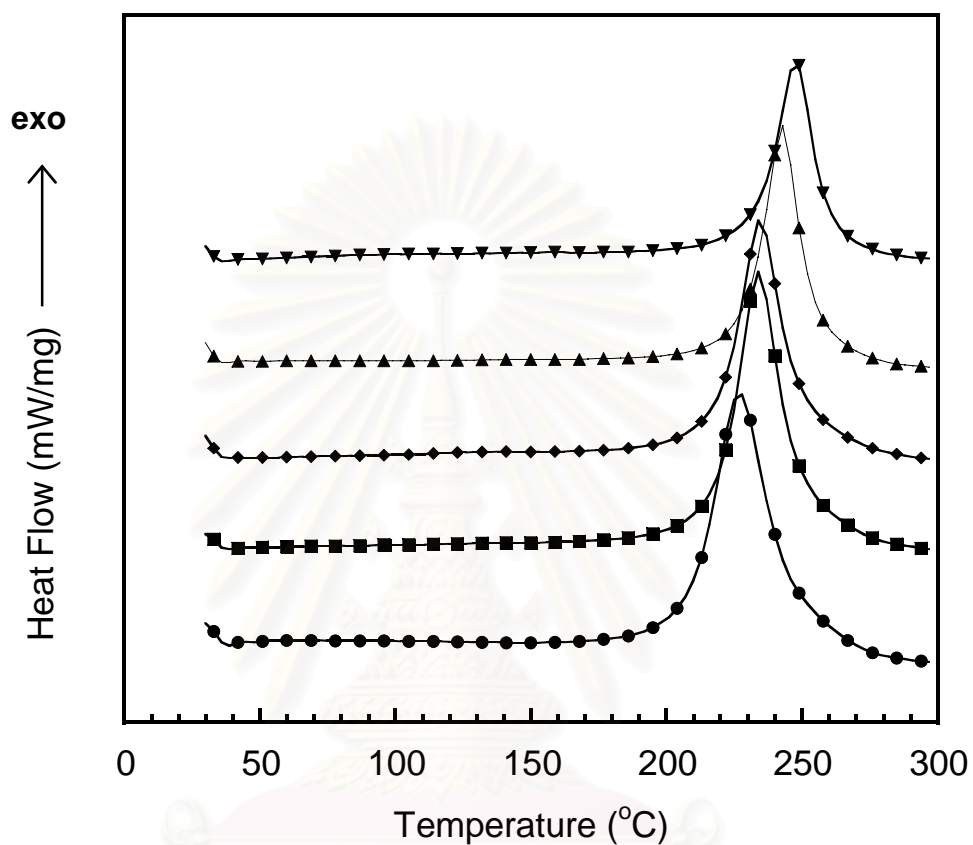


Figure 5.2(a): DSC thermograms of BA:PU using isophorone diisocyanate (IPDI) at various compositions: (●) BA, (■) 90:10 BA:PU, (◆) 80:20 BA:PU, (▲) 70:30 BA:PU, (▼) 60:40 BA:PU.

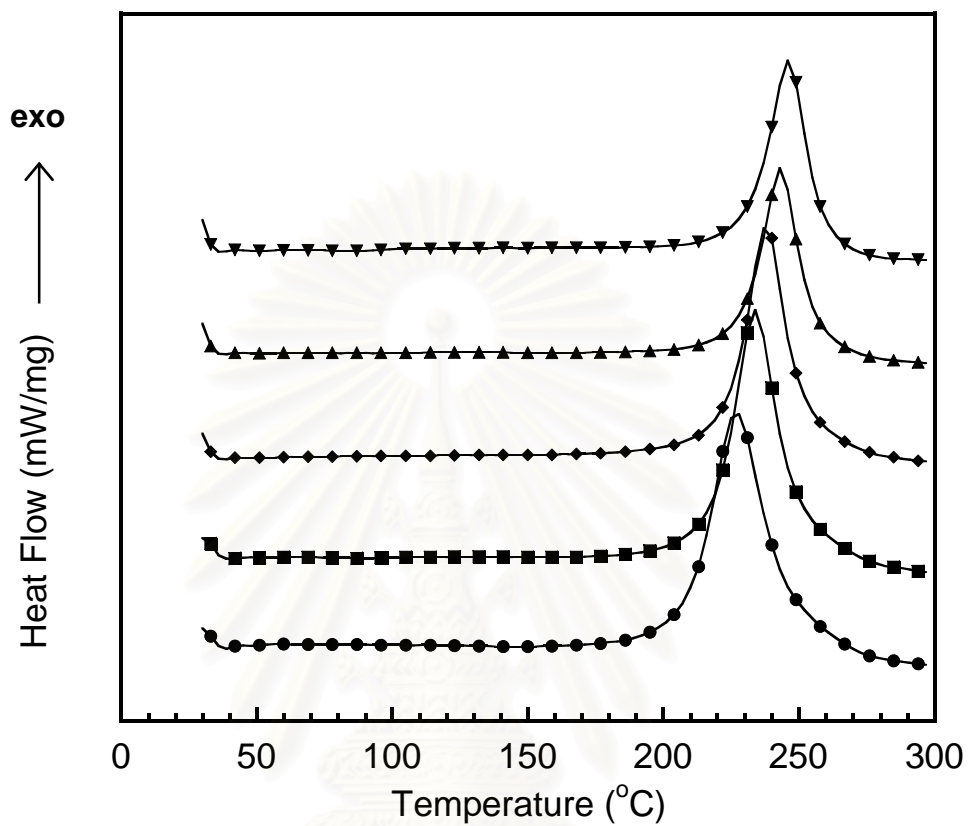


Figure 5.2(b): DSC thermograms of BA:PU using toluene diisocyanate (TDI) at various compositions:

(●) BA, (■) 90:10 BA:PU, (◆) 80:20 BA:PU,
(▲) 70:30 BA:PU, (▼) 60:40 BA:PU.

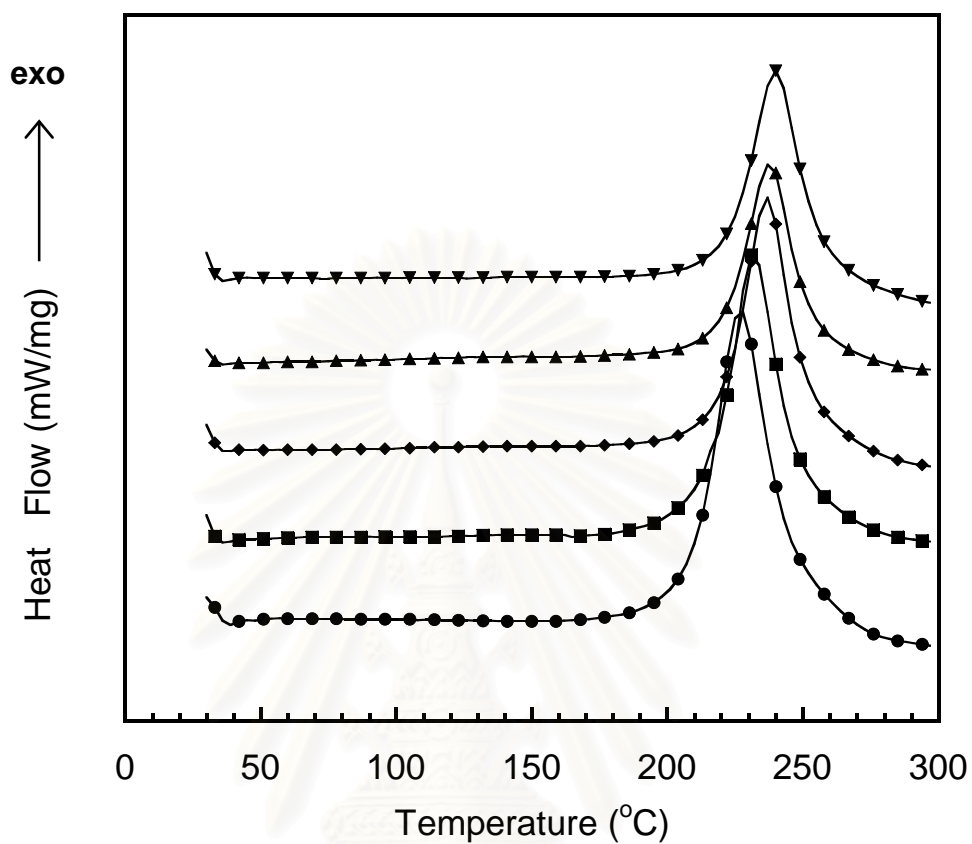


Figure 5.2(c): DSC thermograms of BA:PU using diphenylmethane diisocyanate (MDI) at various compositions: (●) BA, (■) 90:10 BA:PU, (◆) 80:20 BA:PU, (▲) 70:30 BA:PU, (▼) 60:40 BA:PU.

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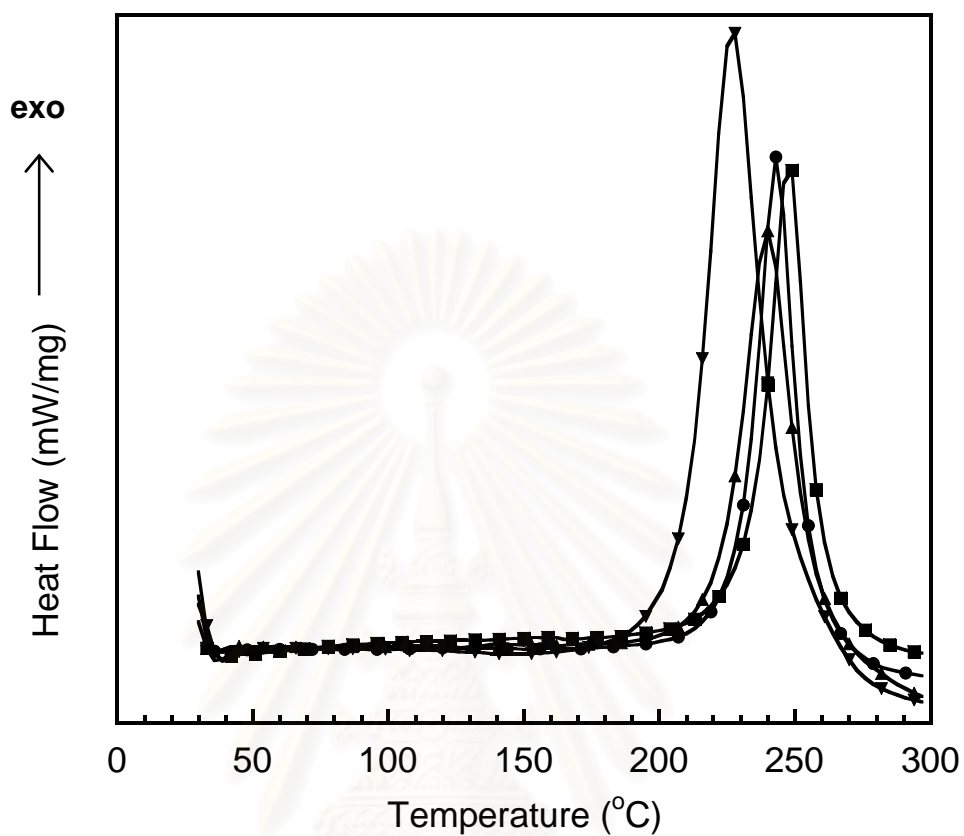


Figure 5.3: DSC thermograms and the curing behaviours of BA and BA:PU at fixed mass ratios of 60:40 for different types of isocyanates: (▼) BA, (▲) BA:PU using MDI, (●) BA:PU using TDI, (■) BA:PU using IPDI.

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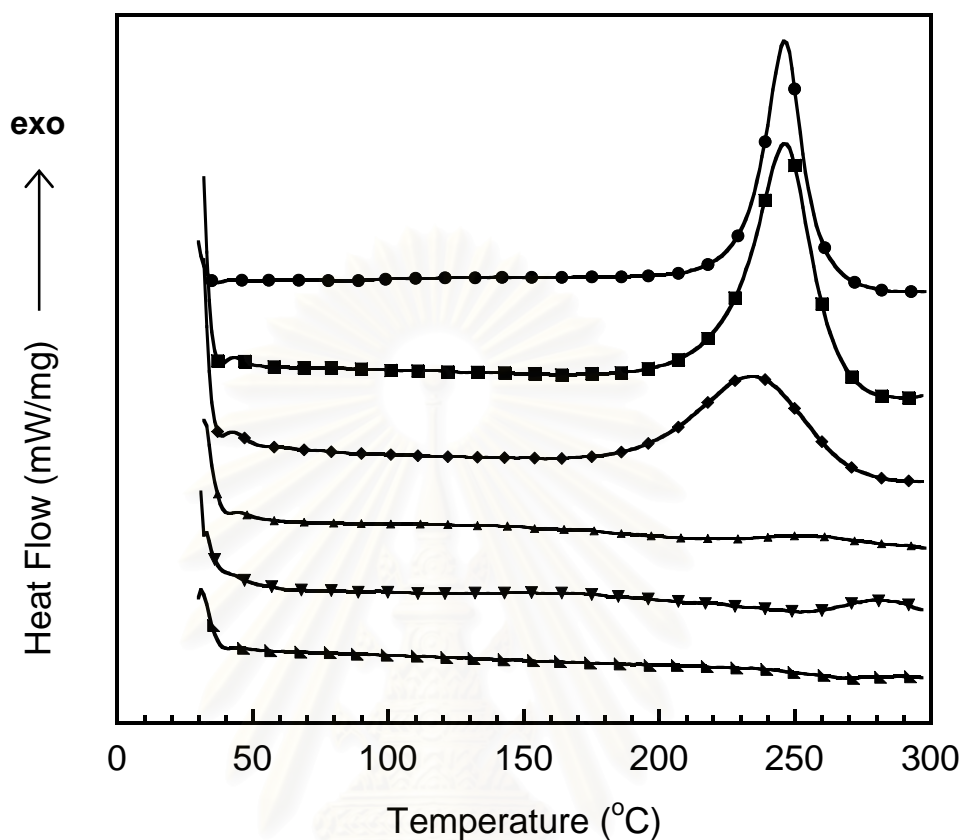


Figure 5.4: Curing condition of BA and BA:PU using TDI at fixed mass ratios of 60:40:

- (●) uncured,
- (■) 150 °C/1 hr.,
- (◆) 150 °C/1 hr.,170 °C/1 hr.,
- (▲)150 °C/1 hr.,170 °C/1 hr.,190 °C/1 hr.
- (▼) 150 °C/1 hr.,170 °C/1 hr.,190 °C/1 hr.,200 °C/1 hr.
- (▲) 150 °C/1 hr.,170 °C/1 hr.,190 °C/1 hr.,200 °C/2 hr.

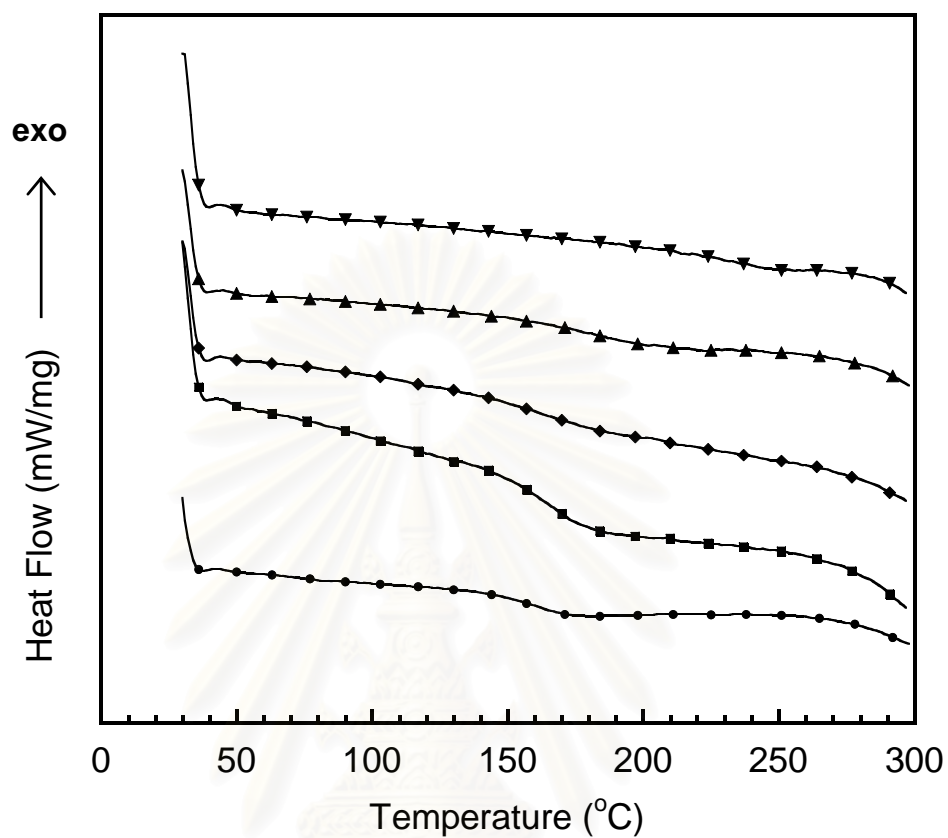


Figure 5.5(a): DSC thermograms showing glass-transition temperature of BA:PU alloys using IPDI at various compositions:
(●) BA, (■) 90:10 BA:PU, (◆) 80:20 BA:PU,
(▲) 70:30 BA:PU, (▼) 60:40 BA:PU.

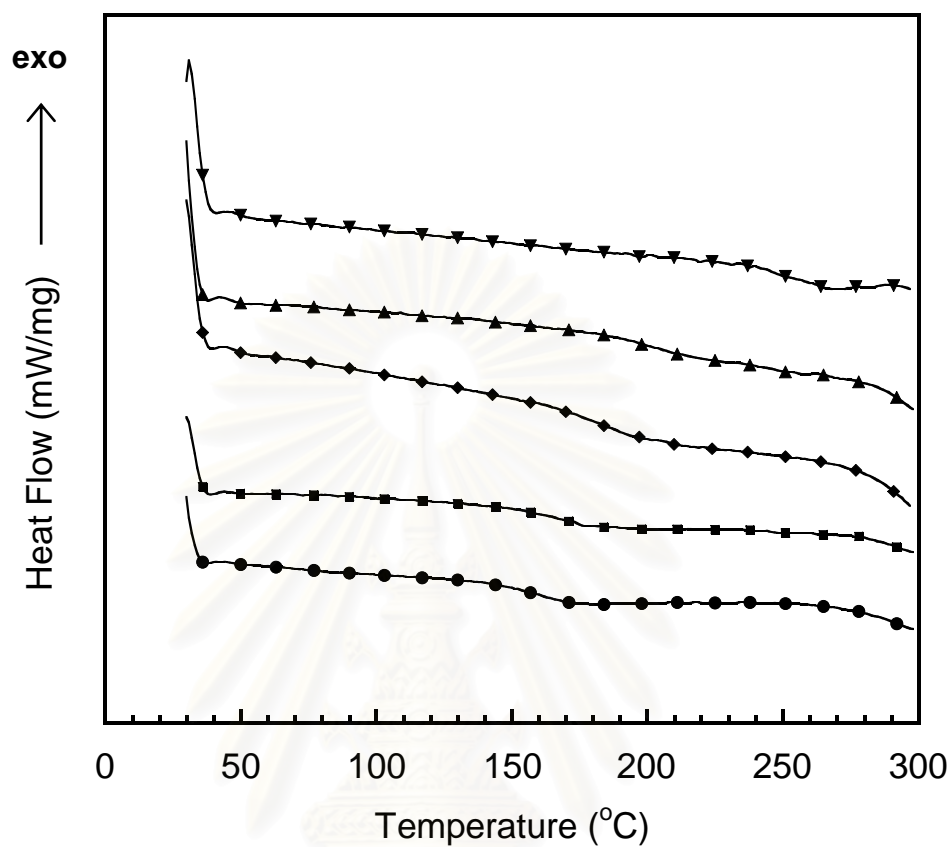


Figure 5.5(b): DSC thermograms showing glass-transition temperature of BA:PU alloys using TDI at various compositions:
(●) BA, (■) 90:10 BA:PU, (◆) 80:20 BA:PU,
(▲) 70:30 BA:PU, (▼) 60:40 BA:PU.

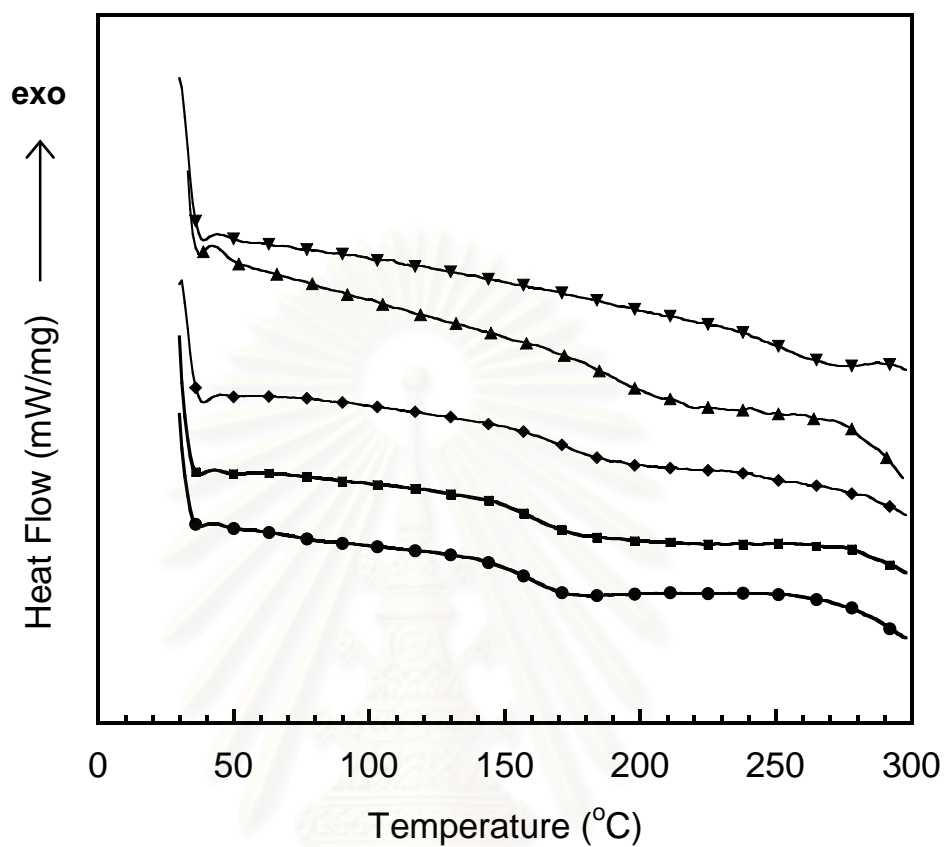


Figure 5.5(c): DSC thermograms showing glass-transition temperature of BA:PU alloys using MDI at various compositions: (●) BA, (■) 90:10 BA:PU, (◆) 80:20 BA:PU, (▲) 70:30 BA:PU, (▼) 60:40 BA:PU.

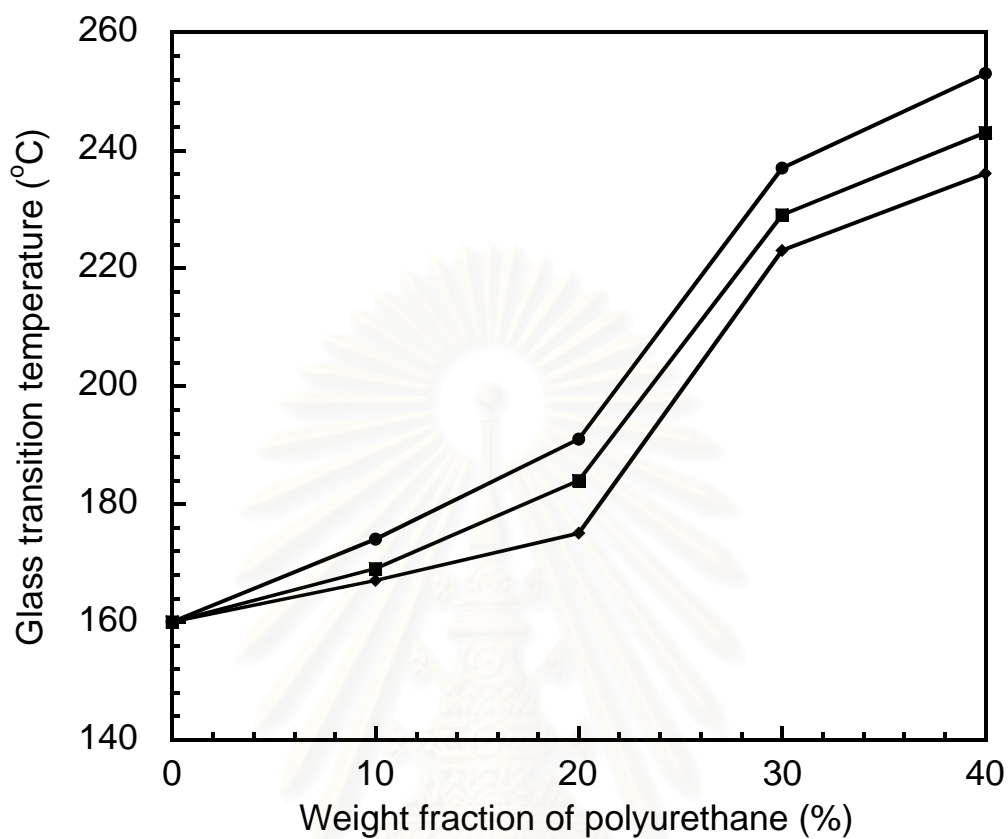
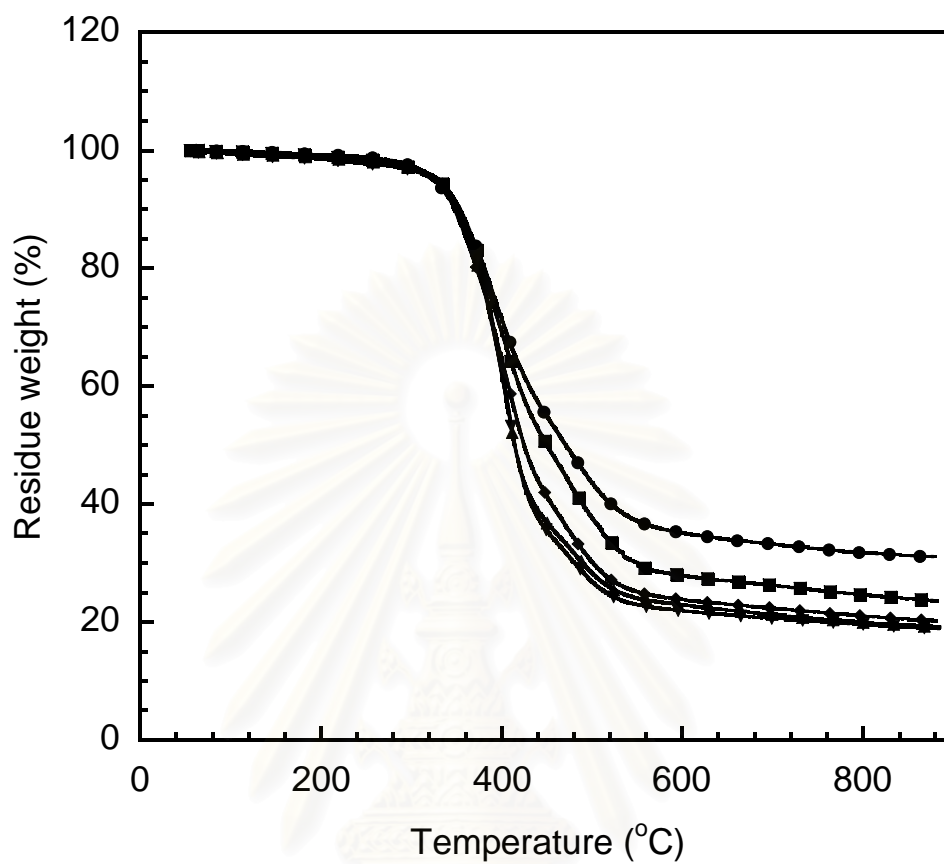


Figure 5.6: Glass-transition temperature of BA:PU alloys for different types of isocyanates at various compositions: (●) BA:PU based on TDI, (■) BA:PU based on IPDI, (◆) BA:PU based on MDI.



\ **Figure 5.7(a):** TGA thermograms of BA:PU alloys using IPDI at various compositions: (●) BA, (■) 90:10 BA:PU, (◆) 80:20 BA:PU, (▲) 70:30 BA:PU, (▼) 60:40 BA:PU.

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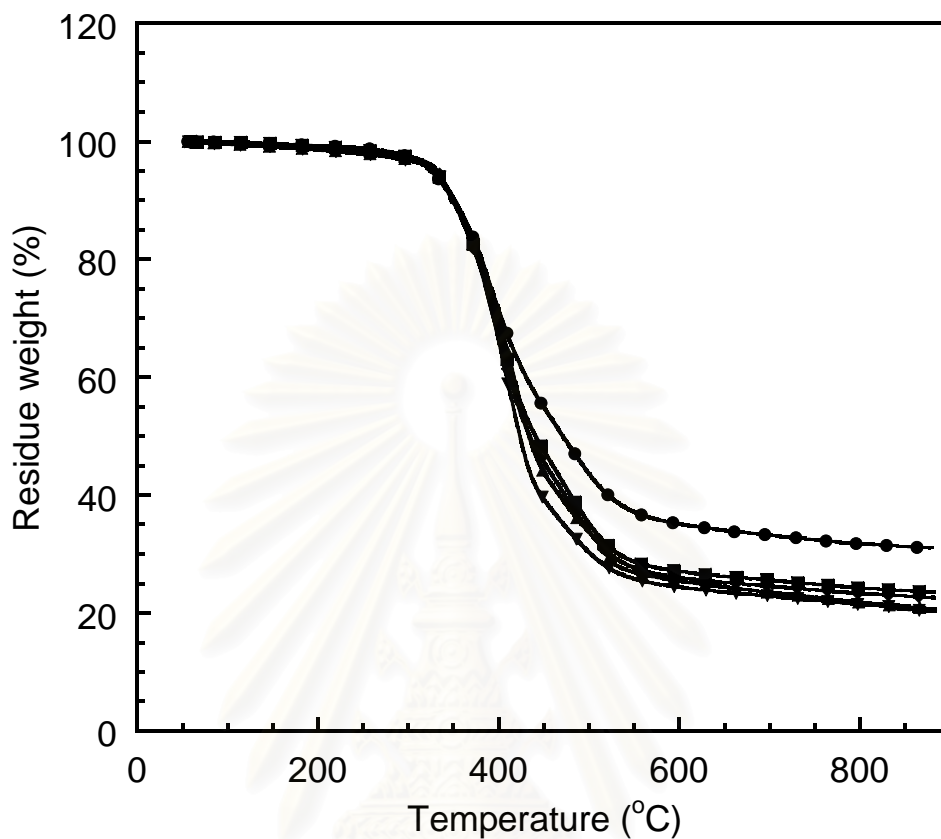


Figure 5.7(b): TGA thermograms of BA:PU alloys using TDI at various compositions: (●) BA, (■) 90:10 BA:PU, (◆) 80:20 BA:PU, (▲) 70:30 BA:PU, (▼) 60:40 BA:PU.

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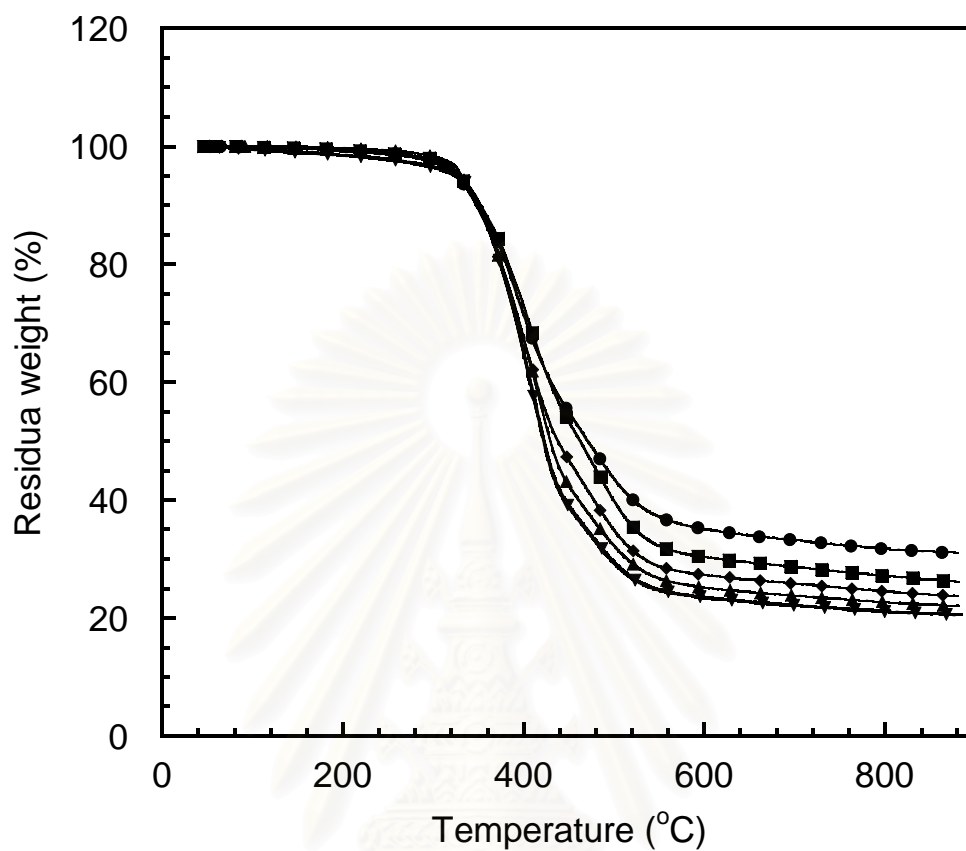


Figure 5.7(c): TGA thermograms of BA:PU alloys using MDI at various compositions: (●) BA, (■) 90:10 BA:PU, (◆) 80:20 BA:PU, (▲) 70:30 BA:PU, (▼) 60:40 BA:PU.

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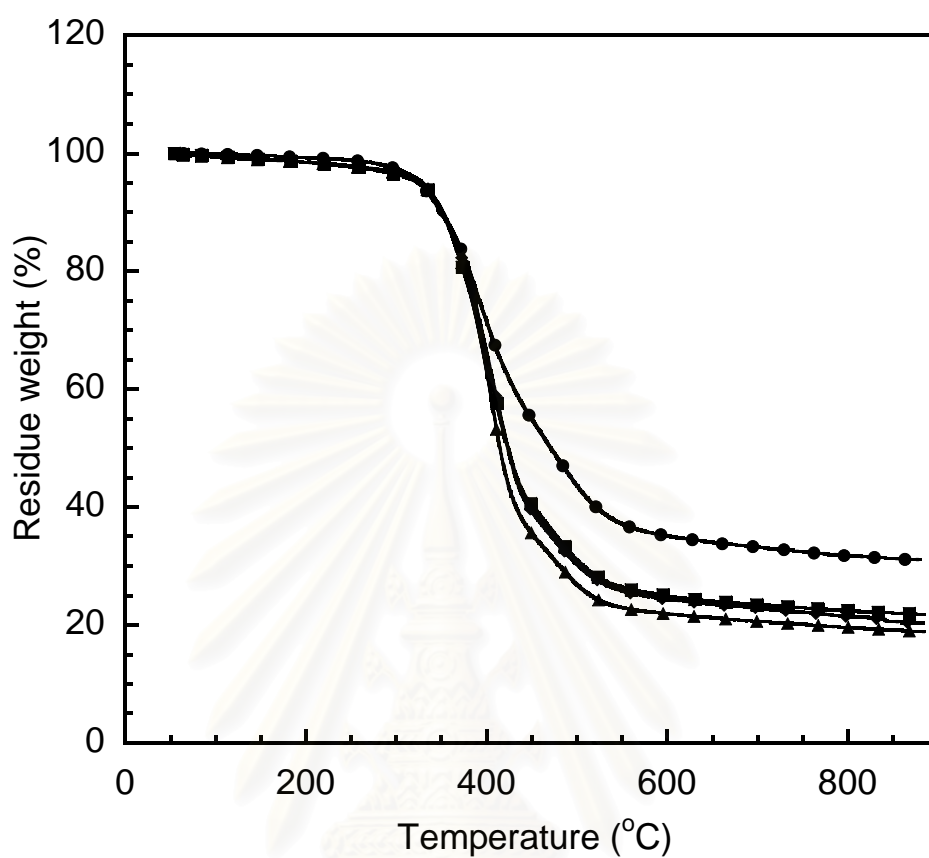


Figure 5.8: TGA thermograms of BA:PU alloys on different types of isocyanates at fixed mass ratios of 60:40: (●) BA, (■) BA:PU using MDI, (◆) BA:PU using TDI, (▲) BA:PU using IPDI.

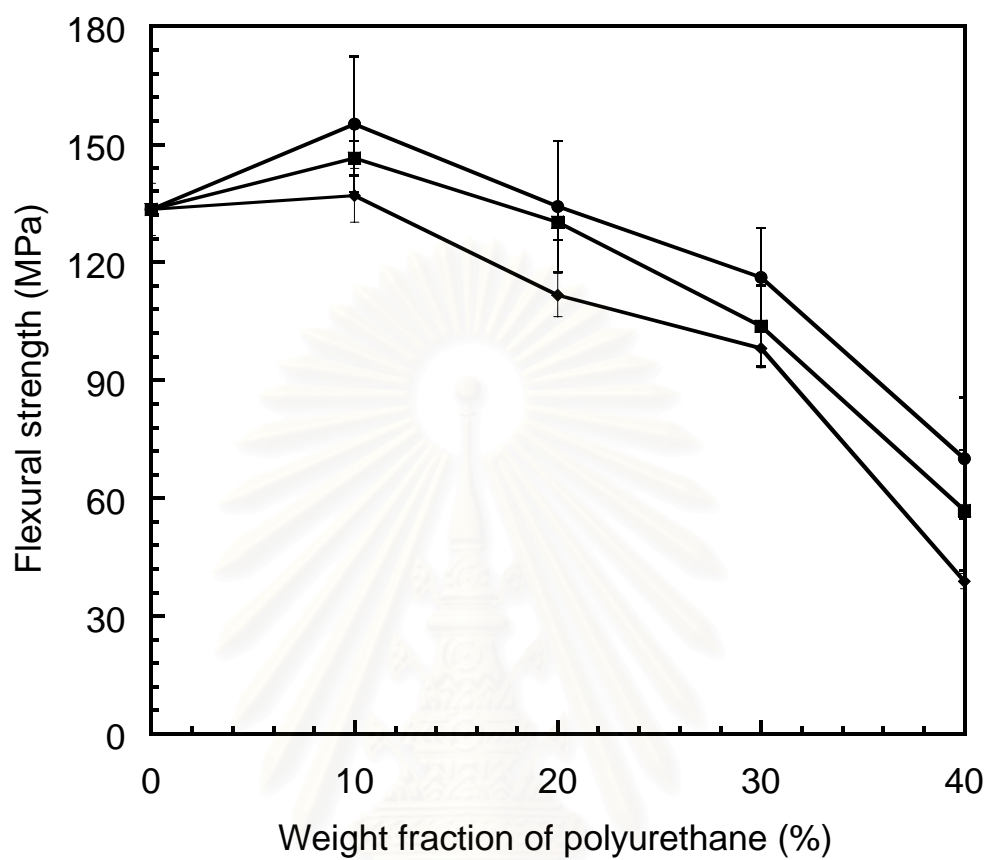


Figure 5.9 : Flexural strength of BA:PU alloys on different types of isocyanates at various compositions:

(●) BA:PU using TDI, (■) BA:PU using IPDI,

(◆) BA:PU using MDI.

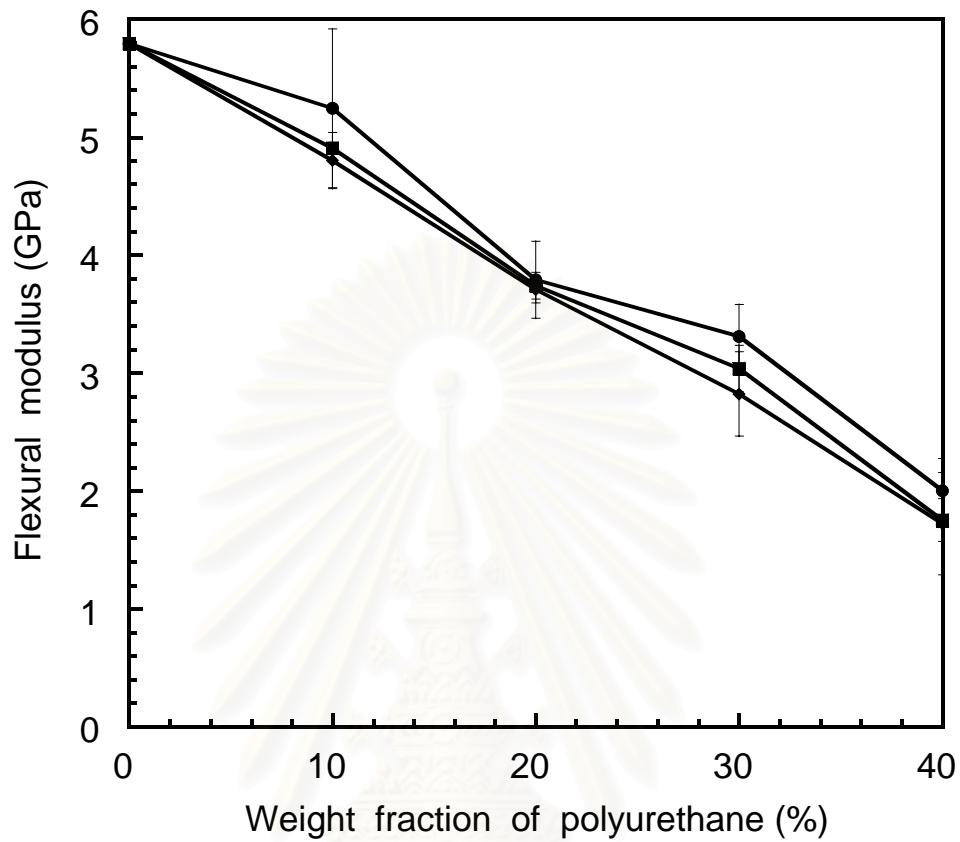


Figure 5.10: Flexural modulus of BA:PU alloys on different types of isocyanates at various compositions:

(●) BA:PU using TDI, (■) BA:PU using IPDI,

(◆) BA:PU using MDI.

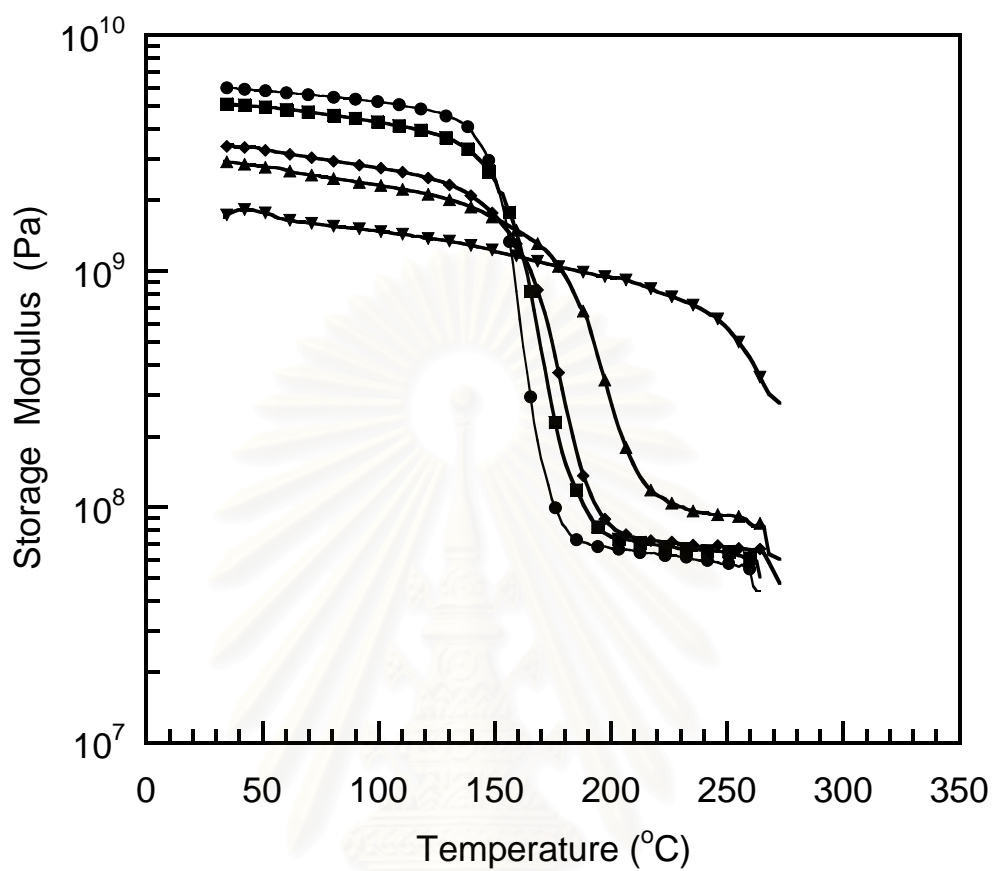


Figure 5.11: Storage modulus of BA:PU alloys using TDI at various compositions: (●) BA, (■) 90:10 BA:PU, (◆) 80:20 BA:PU, (▲) 70:30 BA:PU, (▼) 60:40 BA:PU.

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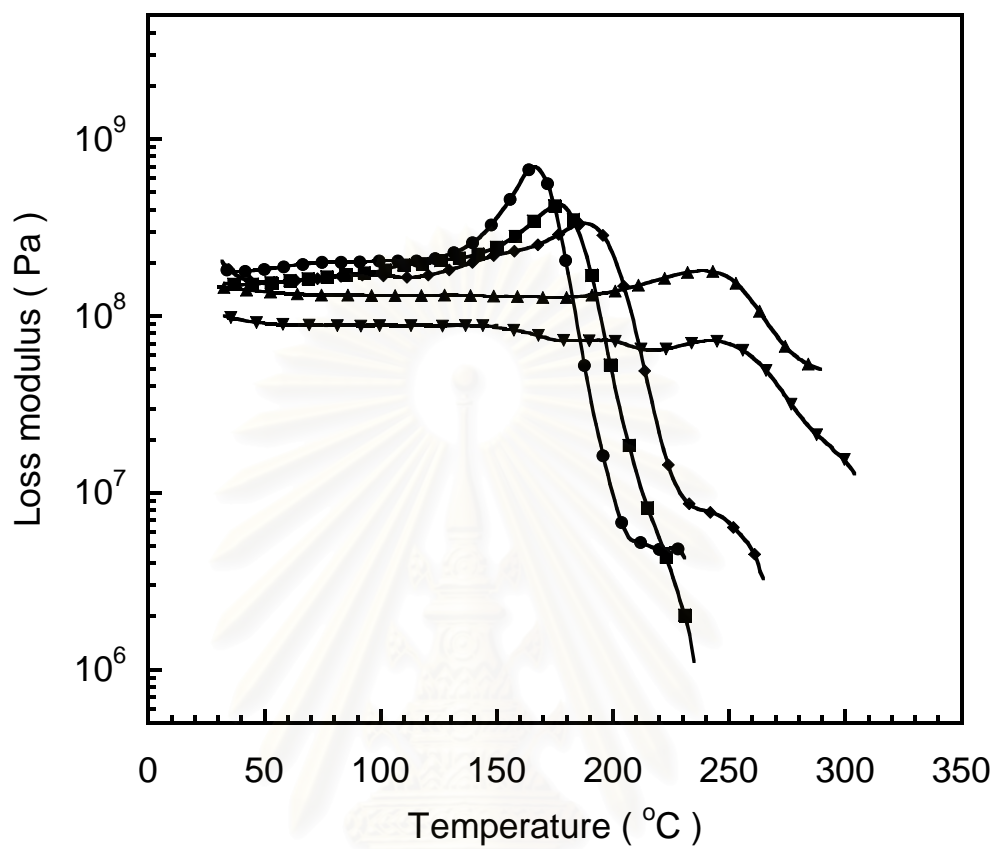


Figure 5.12: Loss modulus of BA:PU alloys using TDI at various compositions: (●) BA, (■) 90:10 BA:PU, (◆) 80:20 BA:PU, (▲) 70:30 BA:PU, (▼) 60:40 BA:PU.

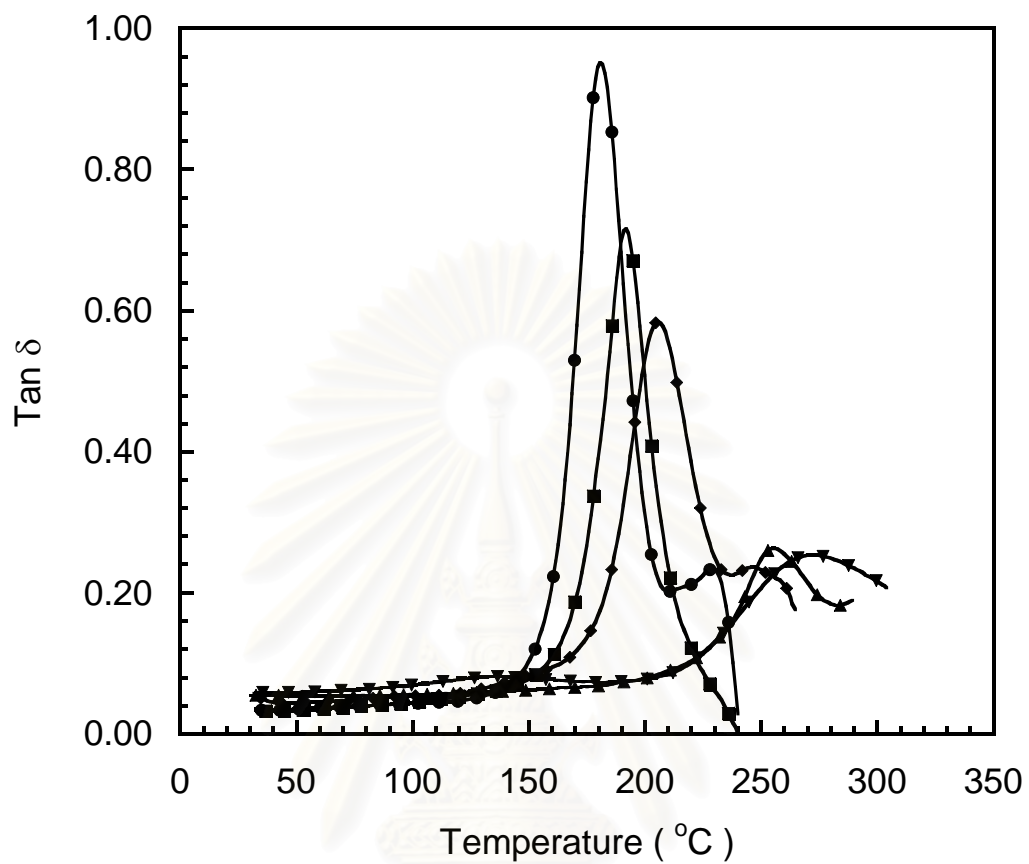


Figure 5.13 : Tan δ of BA:PU alloys using TDI at various compositions: (●) BA, (■) 90:10 BA:PU, (◆) 80:20 BA:PU, (▲) 70:30 BA:PU, (▼) 60:40 BA:PU.

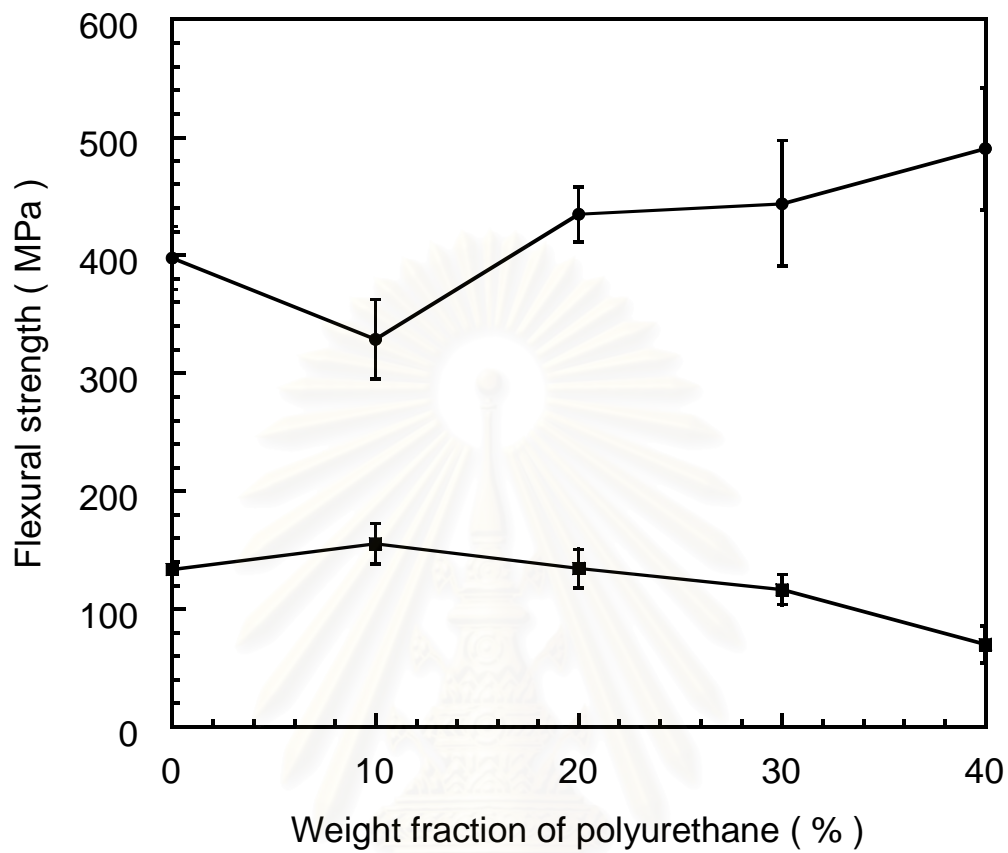


Figure 5.14: Flexural strength of carbon fiber reinforced BA:PU using TDI at various compositions comparing with BA:PU alloy using TDI:

- (●) Carbon fiber reinforced BA:PU using TDI,
- (■) BA:PU matrix alloys using TDI.

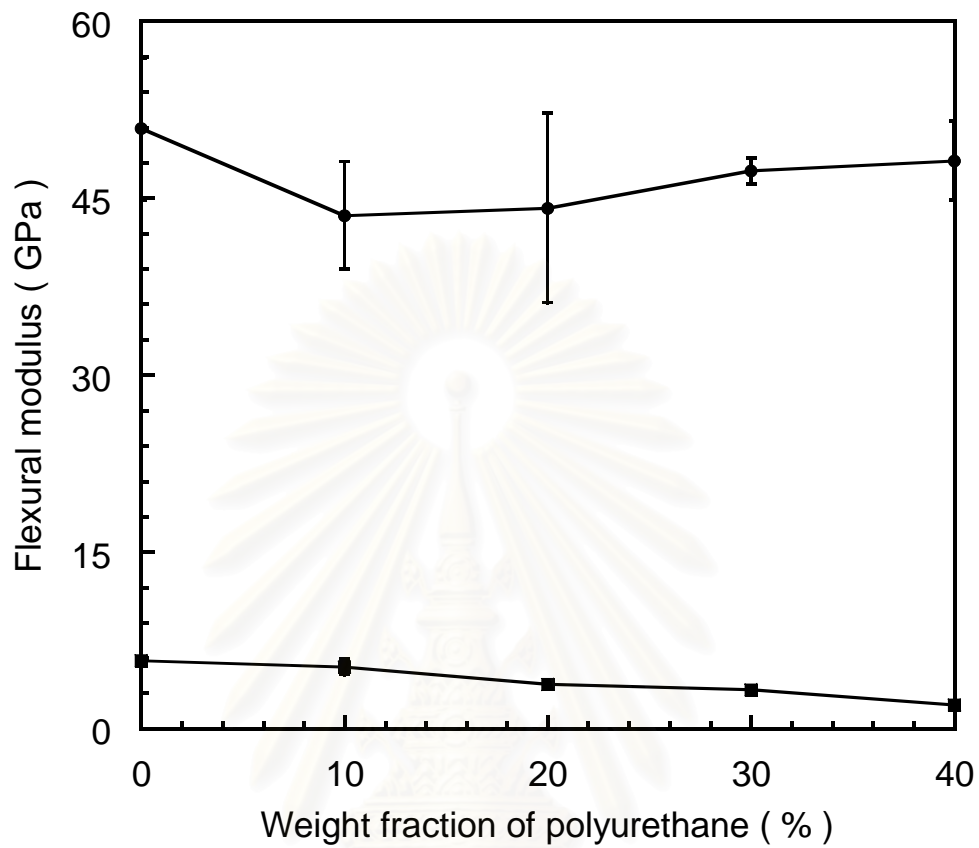


Figure 5.15: Flexural modulus of carbon fiber reinforced BA:PU using TDI at various compositions comparing with BA:PU alloy using TDI:

- (●) Carbon fiber reinforced BA:PU using TDI composites,
- (■) BA:PU matrix alloys using TDI.

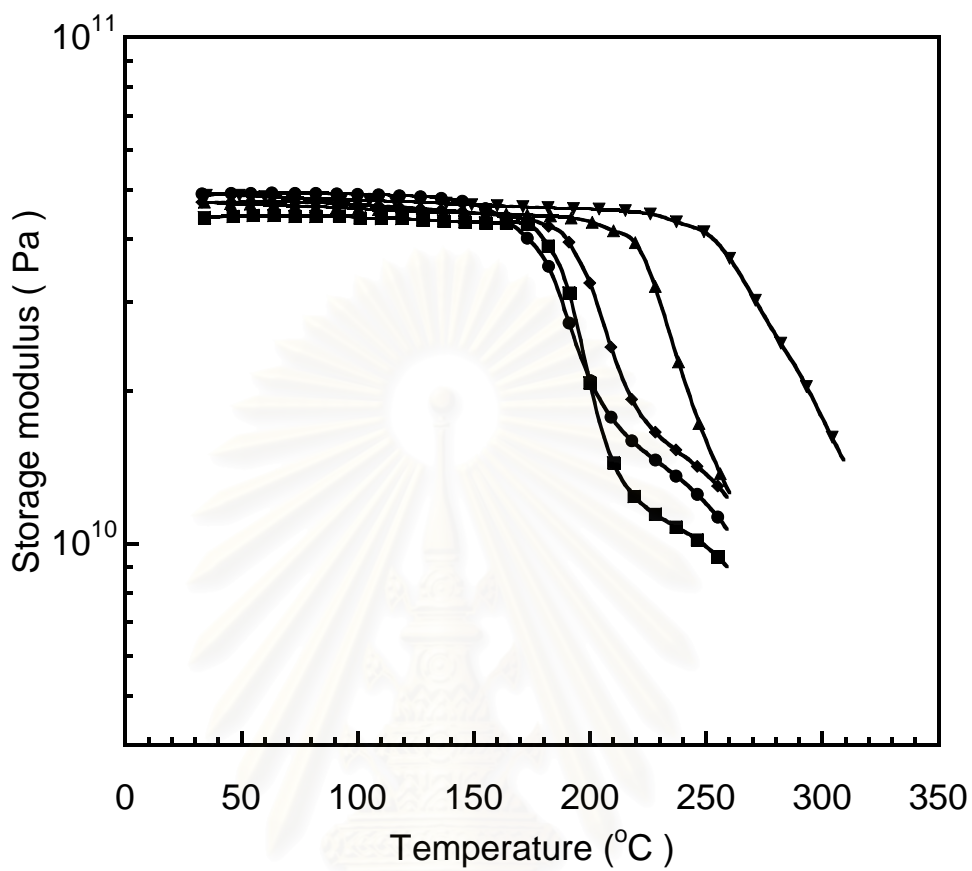


Figure 5.16: Storage modulus of carbon fiber reinforced BA:PU using TDI at various compositions: (●) BA, (■) 90:10 BA:PU, (◆) 80:20 BA:PU, (▲) 70:30 BA:PU, (▼) 60:40 BA:PU.

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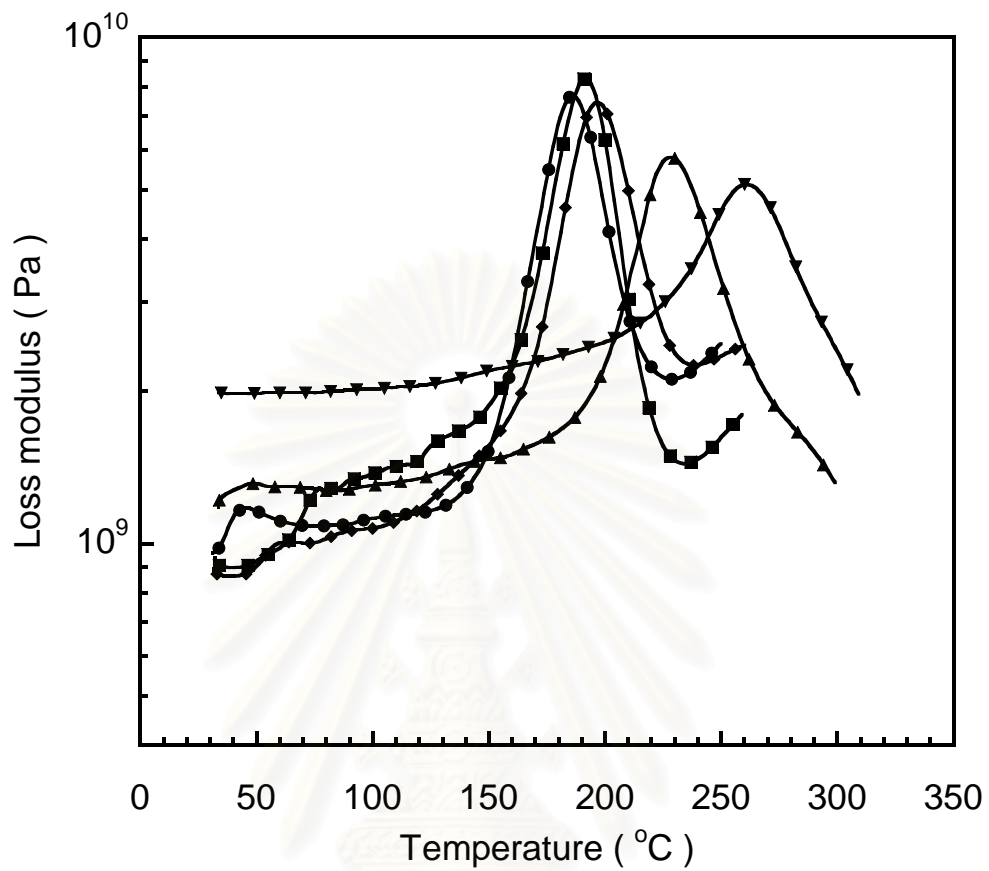


Figure 5.17: Loss modulus of carbon fiber reinforced BA:PU using TDI at various compositions: (●) BA, (■) 90:10 BA:PU, (◆) 80:20 BA:PU, (▲) 70:30 BA:PU, (▼) 60:40 BA:PU.

CHAPTER VI

CONCLUSIONS

The effect of different types of isocyanates used in the urethane resin preparation on properties of their polybenzoxazine alloys were examined. The presence of urethane resin in benzoxazine resin was observed to retard the curing reaction of the BA:PU resin mixture. Curing conditions of all BA:PU alloys were 150°C/1h, 170°C/1h, 190°C/1h, and 200°C/2h. Furthermore, the degradation temperature of BA/PU alloys was slightly higher than that of the neat polybenzoxazine. On the other hand, a synergistic behavior of flexural strength was observed at the BA:PU ratio of 90:10 for all three BA:PU alloys systems. Finally, the flexural modulus of the polybenzoxazine was found to systematically decrease with an addition of PU in the alloys. These polymer alloys were also proved to be useful as matrices of carbon fiber composites with relatively high mechanical properties while still maintaining high thermal stability of the polymer matrices.

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APPENDICES

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APPENDIX A

Thermal Properties of BA/PU Alloys

Appendix A-1 Glass transition temperature of BA/PU alloys at different types of isocyanates.(from DSC)

PU Content (wt.%)	T _{gs} (°C)		
	BA:PU based on TDI	BA:PU based on IPDI	BA:PU based on MDI
0	160	160	160
10	174	167	169
20	191	175	184
30	237	223	229
40	253	236	243

Appendix A-2 Degradation temperature (T_d) of BA/PU alloys at different types of isocyanates.

PU Content (wt.%)	T _d of BA:PU based on TDI (°C)		T _d of BA:PU based on IPDI (°C)		T _d of BA:PU based on IPDI (°C)	
	At 5 wt% loss	At 10 wt% loss	At 5 wt% loss	At 10 wt% loss	At 5 wt% loss	At 10 wt% loss
0	321	345	321	345	321	345
10	328	351	329	352	329	351
20	331	352	329	348	327	349
30	329	349	328	352	329	349
40	329	350	327	351	327	351

Appendix A-3 The char yield of BA:PU alloys at different types of isocyanates.

PU Content (wt.%)	Char Yield of BA:PU based on TDI (%)	Char Yield of BA:PU based on IPDI (%)	Char Yield of BA:PU based on MDI (%)
0	31	31	31
10	24	23	27
20	23	20	24
30	21	19	23
40	20	18	21



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APPENDIX B

Mechanical Properties of BA/PU Alloys

Appendix B-1 Flexural modulus of BA:PU alloys at different types of isocyanates.

PU Content (wt.%)	Flexural modulus of BA:PU based on TDI (GPa)	Flexural modulus of BA:PU based on IPDI (GPa)	Flexural modulus of BA:PU based on MDI (GPa)
0	5.8±0.05	5.8±0.05	5.8±0.05
10	5.2±0.67	4.9±0.05	4.8±0.23
20	3.8±0.32	3.7±0.11	3.7±0.11
30	3.3±0.27	3.0±0.19	2.8±0.36
40	2.0±0.27	1.8±0.18	1.7±0.43

Appendix B-2 Flexural strength of BA:PU alloys at different types of isocyanates.

PU Content (wt.%)	Flexural strength of BA:PU based on TDI (GPa)	Flexural strength of BA:PU based on IPDI (GPa)	Flexural strength of BA:PU based on MDI (GPa)
0	133±0.06	133±0.06	133±0.06
10	155±17.27	146±4.47	137±18.11
20	134±16.66	130±4.58	111±8.05
30	116±12.64	104±10.22	98±6.50
40	70±15.46	57±15.29	40±3.67

APPENDIX C

Dynamic Mechanical Properties of BA/PU Alloys Based on TDI

Appendix C-1 Storage modulus of BA:PU alloys based on TDI at 30 °C

PU Content (wt.%)	Storage modulus of BA:PU based on TDI (GPa)
0	5.4
10	4.7
20	3.7
30	2.6
40	1.7

Appendix C-2 Glass transition temperature of BA/PU alloys based on TDI (from DMA)

PU Content (wt.%)	Glass transition temperature of BA:PU based on TDI (°C)
0	166
10	180
20	202
30	239
40	251

APPENDIX D

Density Determination of Carbon Fiber Reinforced BA/PU Alloys Based on TDI.

Appendix D-1 Density of carbon fiber composites of BA/PU alloys based on TDI
(80 wt% of fiber content).

PU Content (wt%)	Theoretical density (g/cm ³)	Actual density (g/cm ³)
0	1.477	1.459
10	1.467	1.456
20	1.457	1.440
30	1.448	1.431
40	1.438	1.422

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APPENDIX E

Mechanical Properties of Carbon Fiber Reinforced BA/PU Alloys Based on TDI.

Appendix E-1 Flexural properties of carbon fiber reinforced BA/PU alloys based on TDI at 80 vol% fiber content.

PU Content (wt.%)	Flexural modulus of Carbon fiber and BA:PU based on TDI (GPa)
0	51±6.0
10	43±4.5
20	44±8.1
30	47±1.1
40	48±3.3

Appendix E-2 Flexural strength of carbon fiber reinforced BA/PU alloys based on TDI at 80 vol% fiber content.

PU Content (wt.%)	Flexural Strength of Carbon fiber and BA:PU based on TDI (MPa)
0	398±26.6
10	329±33.8
20	434±23.8
30	444±53.2
40	490±51.7

APPENDIX F

Dynamic Mechanical Properties of Carbon Fiber Reinforced BA/PU Alloys Based on TDI

Appendix F-1 Storage modulus of carbon fiber reinforced BA/PU alloys based on TDI at 30 °C

PU Content (wt%)	Storage modulus of BA:PU based on TDI (GPa)
0	49
10	44
20	47
30	47
40	48

Appendix F-2 Glass transition temperature of carbon fiber reinforced BA/PU alloys based on TDI (from DMA)

PU Content (wt%)	Glass transition temperature of BA:PU based on TDI (°C)
0	173
10	186
20	200
30	238
40	253

VITA

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