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ศูนย์วิทยุทรัพยากร

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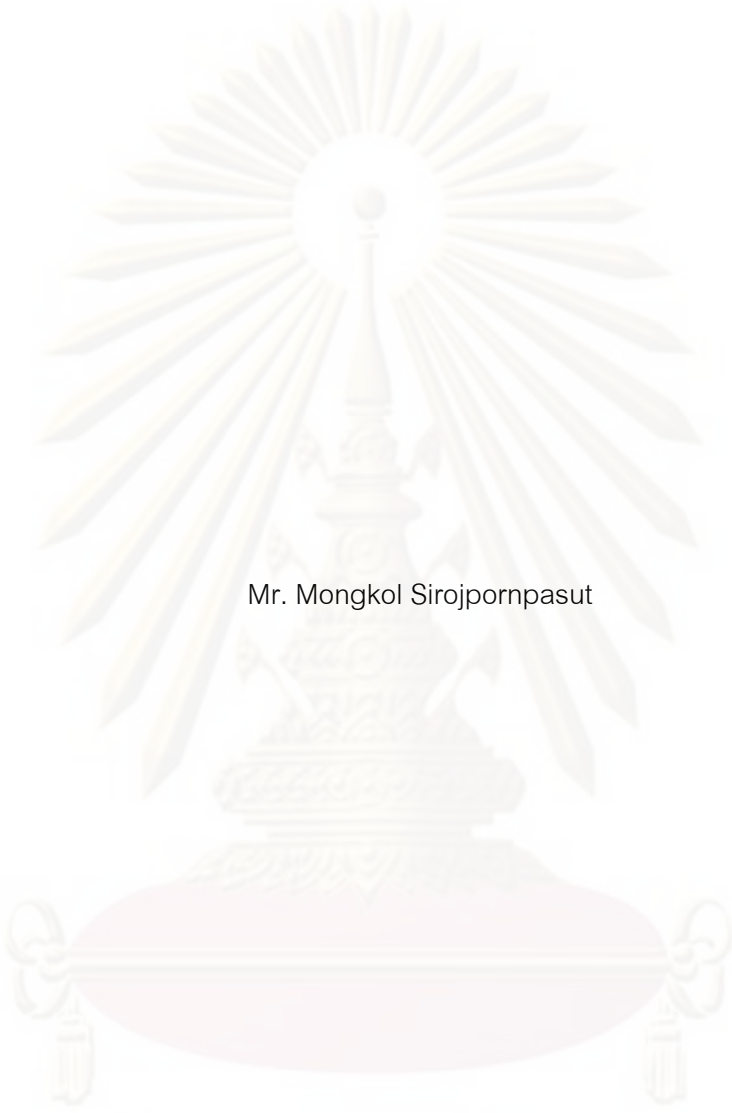
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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

EFFECTS OF CTBN RUBBER ON MECHANICAL PROPERTIES AND MORPHOLOGY OF  
BISPHENOL EPOXY RESINS



Mr. Mongkol Sirojpornpasut

A Thesis Submitted in Partial Fulfillment of the Requirements  
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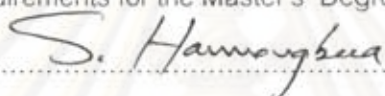
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By Mr.Mongkol Sirojpornpasut  
Field of Study Petrochemistry and Polymer Science  
Advisor Assistant Professor Sirilux Poompradub, Ph.D.

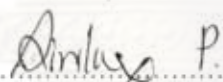
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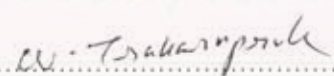
Accepted by the Faculty of Science, Chulalongkorn University in Partial  
Fulfillment of the Requirements for the Master's Degree

..... Dean of the Faculty of Science  
(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITTEE

..... Chairman  
(Professor Pattarapan Prasassarakich, Ph.D.)

..... Thesis Advisor  
(Assistant Professor Sirilux Poompradub, Ph.D.)

..... Examiner  
(Associate Professor Wimonrat Trakarnpruk, Ph.D.)

..... External Examiner  
(Jutharat Saelao, Ph.D.)

ศูนย์วิทยุทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

มงคล ศิริโรตม์พรพศุตม์: ผลของยางซีทีบีเอ็นต่อสมบัติเชิงกลและสัณฐานวิทยาของบิสฟีนอลอีพ็อกซีเรซิน. (EFFECTS OF CTBN RUBBER ON MECHANICAL PROPERTIES AND MORPHOLOGY OF BISPHENOL EPOXY RESINS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร. ศิริลักษณ์ พุ่มประดับ, 111 หน้า.

งานวิจัยนี้ศึกษาอิทธิพลของยางซีทีบีเอ็นที่มีต่ออีพ็อกซีเรซิน โดเรซินที่ใช้มีสองชนิด คือ Epon 828 และ Epon 862 และสารทำแข็งแบ่งเป็น 3 ชนิด คือ Jeffamine T-403 Imicure EMI-24 และ DCA221 ซึ่งทำการศึกษาอัตราส่วนที่เหมาะสมในการเติมสารทำแข็งลงในเรซิน จากการทดลองพบว่าก่อนที่จะใส่ยางซีทีบีเอ็นลงไปให้อีพ็อกซีเรซินและสารทำแข็ง ชิ้นงานที่เตรียมขึ้นเพื่อศึกษาสมบัติเชิงกลให้ค่าสมบัติเชิงกลที่ดี โดยจากการทดลองสามารถคัดเลือกสูตรที่มีสมบัติเชิงกลเหมาะสมที่สุดสำหรับนำไปศึกษาผลของยางซีทีบีเอ็นที่มีต่อเรซินและสารทำแข็ง แต่ละชนิดเป็นดังนี้ Epon 828 กับ Jeffamine T-403 ในอัตราส่วน 100 ต่อ 80 โดยน้ำหนัก และ Epon 862 กับ Jeffamine T-403 ในอัตราส่วน 100 ต่อ 40 โดยน้ำหนัก ซึ่งสูตรที่เลือกเป็นสูตรที่ให้ค่าสมบัติเชิงกลที่สูง เพื่อที่จะได้เห็นการเปลี่ยนแปลงของสมบัติเชิงกลได้อย่างชัดเจน หลังจากนั้นทำการเตรียมอีพ็อกซีเรซินที่ผสมกับยางซีทีบีเอ็นที่อัตราส่วนต่างๆกัน เมื่อใส่ยางซีทีบีเอ็นเข้าไปแล้วพบสมบัติเชิงกลของชิ้นงานที่เตรียมขึ้นมีค่าลดลงในช่วงที่มีปริมาณยางซีทีบีเอ็นน้อย เนื่องจากเกิดการแยกวัฏภาคระหว่างส่วนของเรซินกับสารทำแข็งและยางซีทีบีเอ็น และสมบัติเชิงกลมีค่ามากขึ้นเมื่อมีปริมาณยางซีทีบีเอ็นเพิ่มมากขึ้น เนื่องจากวัฏภาคของยางซีทีบีเอ็นที่แยกจากส่วนของเรซินกับสารทำแข็งที่มีขนาดใหญ่ขึ้น จากผลการทดลองที่ได้มีการติดตามการแยกวัฏภาคระหว่างเรซินกับสารทำแข็ง และยางซีทีบีเอ็นโดยวิธีการถ่ายภาพด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด พบว่าการแยกวัฏภาคระหว่างยางซีทีบีเอ็นและส่วนของเรซินกับสารทำแข็งเกิดขึ้นอย่างชัดเจน ซึ่งสรุปได้ว่ายางซีทีบีเอ็นเข้ากับส่วนของเรซินและสารทำแข็งได้น้อยมาก

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์  
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ลายมือชื่อนิสิต มงคล ศิริโรตม์พรพศุตม์  
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MONGKOL SIROJPORNPASUT : EFFECTS OF CTBN RUBBER ON MECHANICAL  
PROPERTIES AND MORPHOLOGY OF BISPHENOL EPOXY RESINS. THESIS  
ADVISOR : ASST. PROF. SIRILUX POOMPRADUB, Ph.D., 111 pp.

In this research, the effect of CTBN rubber on epoxy resin had been investigated. Two types of resins (Epon 828 and Epon 862) and three kinds of hardeners are Jeffamine T-403, Imicure EMI-24 and DCA221 used for found optimum ratio between resin and hardener. From results, epoxy resin without CTBN rubber had the high mechanical properties. The best mechanical properties were obtained at 100 to 80 wt% for Epon 828/Jeffamine T-403 and 100 to 40 wt% for Epon 862/Jeffamine T-403. These formulae gave the high mechanical properties. After that, the various concentrations of the CTBN rubber that added to epoxy resin were prepared. Addition of small amount CTBN rubber led to the decrease of mechanical properties of the materials. This was due to the phase separation between epoxy resin phase and CTBN rubber phase. In contrast, when high amount of CTBN rubber was added to epoxy resin, the mechanical properties increased. This may be due to the increase of particle size of CTBN rubber in epoxy resin. Scanning Electron Microscope was used to study the phase separation between epoxy resin with hardener and CTBN rubber. The phase separation of CTBN rubber in epoxy resin with hardener matrix was observed. It can be concluded that CTBN rubber was less compatible with epoxy resin with hardener.

Field of Study : Petrochemistry and Polymer Science..

Academic Year : 2009.....

Student's Signature

Advisor's Signature

*Mongkol O.*

*Sirilux P.*

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## LIST OF ABBREVIATIONS

AFM	: Atomic Force Microscopy
ATBN	: Amine-terminated acrylonitrile butadiene
BDMA	: Benzyl dimethyl amine
BGE	: n-butyl glycidyl ether
CTBN	: Carboxyl terminated acrylonitrile butadiene
CTPEHA	: Carboxy-terminated poly(2-ethyl hexyl acrylate)
°C	: Celcius degree
cPs	: Centipoises
DETA	: Diethylene triamine
DGA	: Diglycidyl aniline
DGEBA	: Diglycidyl ether of bisphenol A
DGEBF	: Diglycidyl ether of bisphenol F
DGEHQ	: Diglycidyl ether of hydroquinone
DMP 30	: Tris(dimethylaminomethyl) phenol
DSC	: Differential Scanning Calorimeter
ENR	: Epoxidized natural rubber
FTIR	: Fourier Transform Infared Spectroscopy
HDT	: Heat distortion temperature
ISO	: International standard
IPA	: Isopropanol
KBr	: Potassium bromide
kN	: Kilo Newton
MDA	: 4,4'-methylene dianiline
ml	: Milliliter
mm	: Millimeter
$M_n$	: Number average molecular weight
MPa	: Megapascal
MPDA	: m- Phenylene diamine

Pa.s	: Pascal second
phr	: Part per hundred part
SEM	: Scanning Electron Microscopy
TEPA	: Tetraethylene pentamine
$T_g$	: Glass transition temperature



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## CHAPTER I

### INTRODUCTION

#### 1.1 The Purpose of the Investigation

Adhesives are substances capable of holding materials together in a useful manner by surface attachment. The principal attribute of adhesives is to form strong bonds with surfaces of wide range of materials and retain bond strength under expected use conditions. Although most adhesives do not have excellent bulk properties, they are important to keep adhesive thin film. Some materials such as epoxies have bulk properties which qualify them as engineering materials and thus they can be used in multifunctional applications.

Epoxy resins have found widespread use in adhesives, sealants, paints and electrical applications. The versatility of epoxy resin systems arise from the large number of combination of epoxy resins and curing agents, each of which results in a different molecular structure in the resulting polymer. Even with a greatly variable molecular structure, epoxies generally share adhesion to a wide range of substrates, resistance to a wide range of chemicals and excellent mechanical properties.

Modification of epoxy resins by additives, modifiers, fillers, plasticizers and other

polymers offers vast opportunities to further customize the attributes of these materials. However, the general epoxy systems usually suffer the shortage of toughness because of their highly crosslinked but brittle structure.

Several methods have been proposed to increase the toughness of epoxy resin and one of the most successful method involves the addition of a suitable rubber to the uncured epoxy resin. The popular reactive rubbers e.g. acrylic rubber [1], hydroxyl-terminated acrylonitrile butadiene, epoxy-terminated acrylonitrile butadiene [2], hydroxyl-terminated butadiene [3, 4], carboxyl-terminated acrylonitrile butadiene (CTBN) [5-27] and amine-terminated acrylonitrile butadiene (ATBN) [28-29] rubbers were added to epoxy resin. When polymerization reactions of epoxy and liquid rubber proceed under controlled sets of conditions, the rubber domains are separated from the epoxy matrix. The rubber domains in epoxy matrix can improve the toughness by absorbing the impact energy. This present thesis aimed therefore to study the incorporation of CTBN rubber as toughening agent onto epoxy resin. Two types of resins and three types of hardeners are used in this study to investigate mechanical properties and morphology. Diglycidyl ether of bisphenol A (DGEBA) and diglycidyl ether of bisphenol F (DGEBF) are used as resin. Amine and imidazole are used as the hardener for this study.

## 1.2 The Objectives

The objectives of this research can be summarized as follows:

1. Study the chemical reactions that possibly take place during modification of epoxy resins by FTIR technique.
2. Study the morphology of epoxy resins with CTBN rubber.
3. Study the mechanical properties of the epoxy resin with/without CTBN rubber.

## 1.3 The Scope of Investigation

1. Literature survey and in-dept study for this research work.
2. Prepare various types of epoxy resins (bisphenol A and bisphenol F acted as resins and amine and imidazole acted as hardeners). The chemical reactions that possibly took place were investigated and the thermal properties were also studied.
3. Investigate the mechanical properties of epoxy resins without CTBN rubber.
4. Prepare the CTBN modified epoxy resins at different CTBN contents.
5. Investigate the mechanical properties and morphology of CTBN modified epoxy resins.

6. Summarize the results and suggest future work.
7. Literature survey and in-dept study for this research work.
8. Prepare various types of epoxy resins (bisphenol A and bisphenol F acted as resins and amine and imidazole acted as hardeners). The chemical reactions that possibly took place were investigated and the thermal properties were also studied.
9. Investigate the mechanical properties of epoxy resins without CTBN rubber.
10. Prepare the CTBN modified epoxy resins at different CTBN contents.
11. Investigate the mechanical properties and morphology of CTBN modified epoxy resins.
12. Summarize the results and write thesis.

## CHAPTER II

### THEORY AND LITERATURE REVIEWS

#### 2.1 Adhesive Bonding

Adhesives have been widely used in industry for many years. Today, there are probably as many adhesives formulations as there are applications. With the availability of new polymers, additives, modifiers, curing agents and new advances in polymer processing technology, adhesives can be tailored to meet requirements in very demanding applications such as microelectronics [30], aerospace and biomedical. One of the major reasons for using adhesive joining is the simplicity in its operation. It can conveniently join dissimilar materials, regardless of size and shape, and at the same time providing structural integrity. Moreover, adhesives can bond substrates of different nature and with greatly different thermal expansion coefficient, hardness, texture and configurations. For structural bonding, adhesives offer better strength to weight ratio than mechanical fastening resulting in overall weight saving. This is extremely important in the automotive and aerospace.

Although there are many theories being able to explain the adhesion phenomenon in certain adhesive/substrate/environment combination [31, 32], there is still no unified theory on adhesion, nor is there unanimity on even the fundamental notion

of what causes materials to stick together. For the strong, durable bond, the adhesive and adherend must be compatible. In the other words, the adhesive must be able to wet and spread on the adherend surface. Surface preparation is one parameter that will affect to bond strength. Although clean metal surfaces are easily wetted due to their high critical surface tensions, common metal surfaces are rarely clean, nor smooth. They usually have an oxide layer, conversion coating, oil or grease film. Therefore surface treatment is essential to achieve good bonding. For plastic surfaces, they can also be treated to improve their wettability. Methods used include: mechanical roughening, coating, chemical etching, flame oxidation, corona discharge, radiation and plasma.

## 2.2 Chemistry of Epoxy Resin

Epoxy resins are a group of reactive compounds that are characterized by the presence of the oxirane group as shown in Figure 2.1. They are capable of reacting with suitable hardeners to form crosslinked matrices of great strength and with excellent adhesion to a wide range of substrates. This makes them ideally suited to adhesive applications in which high strength under adverse conditions is a prerequisite. Their unique characteristics include negligible shrinkage during cure, an open time equal to

the usable life, excellent chemical resistance, ability to bond nonporous substrates and great versatility.

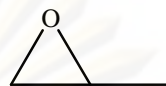


Figure 2.1 Chemical structure of oxirane group

Although the work on epoxy resins started in the mid-1920s, the first commercially useful epoxy resins were based on the diglycidyl ether of bisphenol A (usually referred to as DGEBA resins), and today these resins, in a range of molecular weights, constitute the majority of all epoxy resins used. By contrast, however, hardeners come in a variety of shapes and sizes, including amines [5, 7-8, 13, 28-29], amides [1, 2], mercaptans, anhydrides [9, 10] and Lewis acids and bases [12]. Choice of hardener depends on the application requirements, and the wide range of hardeners available increases the versatility of adhesives based on epoxy resins.

Epichlorohydrin is capable of reacting with hydroxyl groups, with the elimination of hydrochloric acid. The most widely used epoxy resins are the family products produced by the reaction between epichlorohydrin and bisphenol A as shown in Figure

2.2.

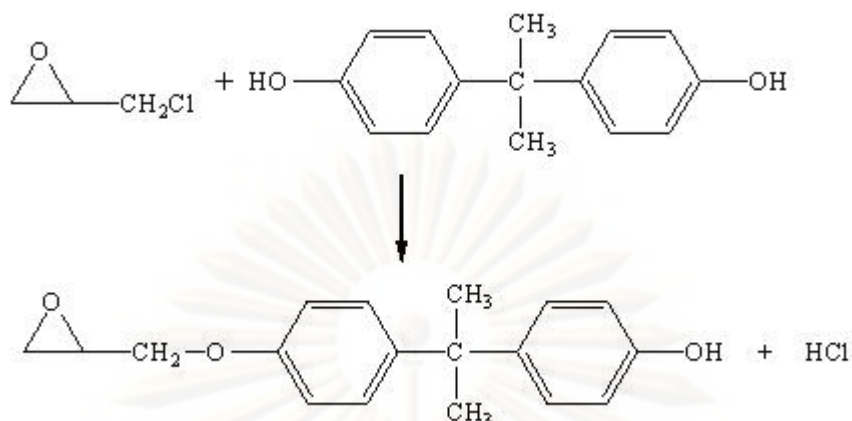


Figure 2.2 Chemical reaction between epichlorohydrin and Bisphenol A

The two crosslinking reactions are external by reaction of the oxirane group with active hydrogen and internal by homopolymerization through the oxirane oxygen. The former is typical of crosslinking by hardeners and catalysts are referred to as curing agents. The classic epoxy curing mechanism is illustrated by the reaction between a primary amine and epoxy group as shown in Figure 2.3. The product can react with an additional epoxy group to continue the crosslinking process as shown in Figure 2.4. This reaction is characteristic of hardeners having active hydrogens available, including amines, amides and mercaptans. The reaction is catalyzed by hydroxyl group, especially phenolic hydroxyls and tertiary amines. The excellent properties of epoxy resin, such as durability and adhesiveness, depend largely on its structure. From Figure 2.5, the relationship between the chemical structure of epoxy resin and their properties are described below:



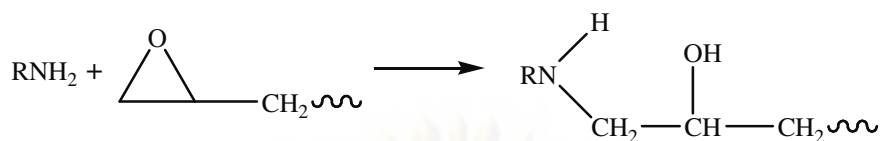


Figure 2.3 Chemical reaction between oxirane ring of epoxy and primary amine

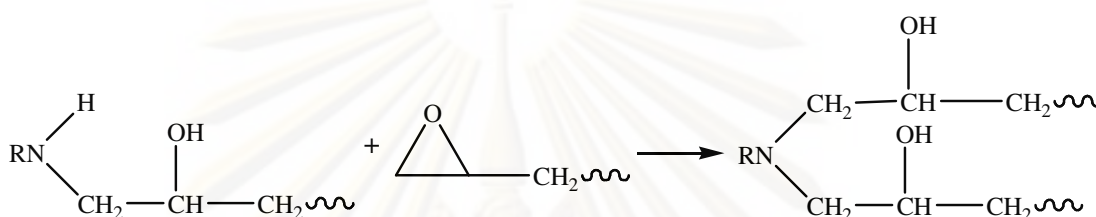


Figure 2.4 Crosslink reaction of epoxy resin

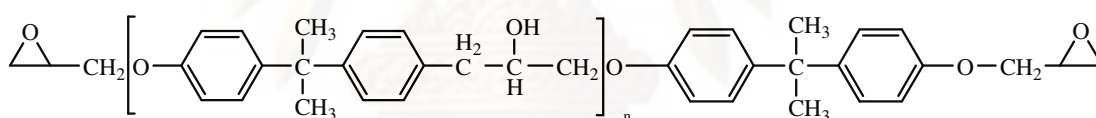


Figure 2.5 Chemical structure of DGEBA epoxy resin (Epon 828)

1. The epoxy groups at both terminals of molecule and hydroxyl groups at mid point of the molecule are highly reactive allowing room temperature and high temperature curing using suitable curing agents, and a wide range of modification. In addition, the resin is cured by ring opening polymerization, and as a result has a smaller degree of cure shrinkage other than other thermosetting resins.

2. The ether linkages included in the main chain improve the chemical resistance and elasticity.
3. The benzene rings provide chemical resistance, adhesiveness, durability, heat resistance and excellent electrical properties.
4. The coexistence of hydrophilic groups with hydrophobic groups in the molecule significantly increases the adhesion to various adherends.

As describe above, many properties are ascribable to the structure, but such properties are largely dependent on the curing agents that cause the curing reaction, resulting in widely selectively of epoxy resin.

### 2.3 Compounding Ingredients of Epoxy Resin

Epoxy resins offer a unique combination of properties for adhesive applications. These include the ability to formulate liquid systems without solvents or carriers, the ability to convert these systems to cured products without the production low molecular weight by products, the ability to bond dissimilar or nonporous surfaces, and the ability to produce thick sections without subsequent stress cracking due to shrinkage. Although epoxy resin and hardener may be used in unmodified form in adhesive systems, most systems will consist of components that have been modified by incorporation of various additives to achieve specific effects. Formulators will add

catalysts or blend hardeners to obtain a specific usable life of the mix and to control the curing temperature. Reactive diluents may be added to modify viscosity or flexibility. Fillers impart improved compression strength and reduce shrinkage and cost. Solvents may be used to reduce viscosity or improve adhesion. Various additives may be added, usually at a low percentage, to reduce aeration, improve adhesion to difficult surfaces, or minimize settlement of fillers. Depending on the application, particular properties such as flame retardant, electrical insulation or conductivity, or chemical resistance may be improved by formulating.

### 2.3.1 Resins

Most epoxy resins are composed of the basis of three types of resins (DGEBA: Epon 828, DGEBF: Epon 862 and Bisphenol A D types). The chemical structures of these resins are shown in Figures 2.5 and 2.6, respectively. Although DGEBA resins provide the backbone of most epoxy formulations, they may be blended with other types to achieve modifications. Epoxy novolacs (as shown in Figure 2.7), having higher functionality, increase the crosslink density, which improve heat resistance but decrease impact resistance. Incorporation of epoxidized oils increases flexibility at the expense of heat and chemical resistance. Low viscosity polyfunctional epoxies based on polyols or polyhydric phenols reduce viscosity and can increase functionality without impairing cured properties. Monofunctional reactive diluents will also decrease viscosity and form

part of the polymer backbone, to impart a measure of flexibility without the possibility of migration.

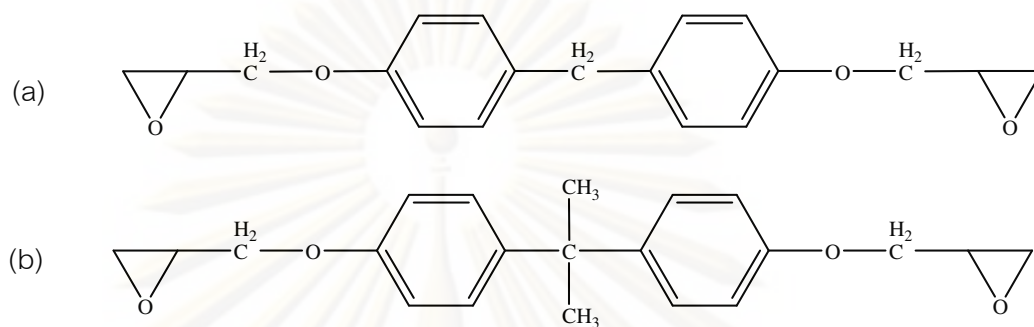


Figure 2.6 Chemical structures of (a) DGEBA (Epon 862) and (b) Bisphenol A D Types

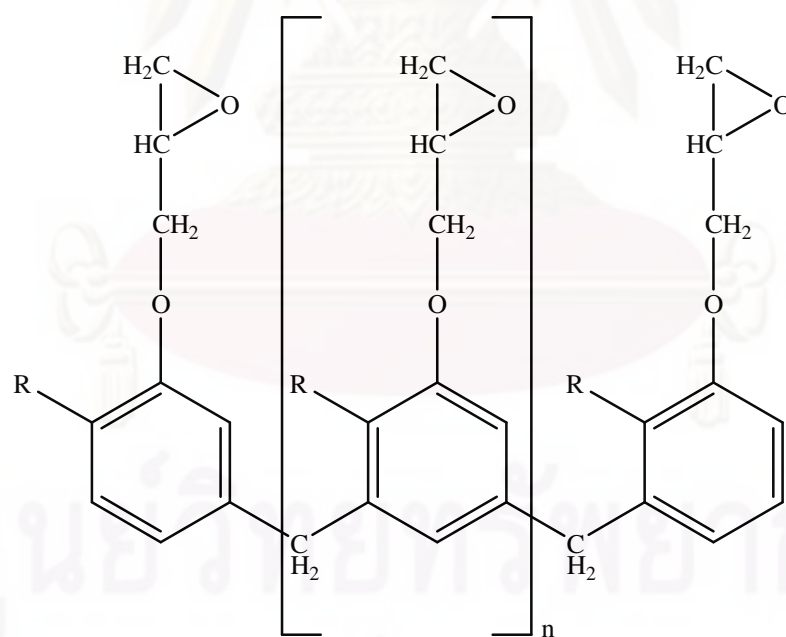


Figure 2.7 Chemical structure of epoxy novolac resin

### 2.3.2 Hardeners

There are various types of hardeners for epoxy resin. Hardeners may be blended to achieve properties intermediate to the individual components [2], to reduce exotherm or accelerate cure, to modify the cured properties, or simply to arrive at a more convenient mix ratio. Several classes of curing agents each having distinctive characteristics may be used [31].

**a) Aliphatic primary amines:** Common examples are diethylene triamine (DETA), tetraethylene pentamine (TEPA), n-aminoethyl piperazine, and isophorone diamine. They give good room temperature cure at stoichiometric ratios, but have poor heat distortion temperature (HDT), inconvenient mix ratios, high peak exotherm, and are strongly irritant. Isophorone diamine produces very light colored mixes with good color stability.

**b) Aromatic primary amines:** These offer improved heat and chemical resistance and longer pot life with reduced exotherm, but poor color stability and sluggish cure. They are generally solids and require some formulating to produce easily handleable products. Reactions proceed best at elevated temperatures, where their irritancy can be a problem. For room temperature cures they should be used with catalysts, of which phenols,  $\text{BF}_3$  complex, and anhydrides are the best. m-Phenylene diamine (MPDA) and methylene dianiline (MDA) are the best examples.

c) **Amine adducts:** Both aliphatic and aromatic amines can be adducted with small amount of mono or diglycidyl epoxies to produce amine adducts of medium to high viscosity that have decreased volatility and irritancy, more convenient mix ratios, and often better reactivity.

d) **Tertiary amines:** Although their primary use is as catalysts with other hardeners, tris(dimethylaminomethyl) phenol (DMP 30) is an effective curing agent on its own, at both room and elevated temperatures.

e) **Amides** [1, 2, 33]: Although amides on their own are too unreactive, reaction products of polyamines with fatty acids to produce amidopolyamides provide the largest group of commercial hardeners for adhesive applications. Reduced volatility and irritancy and a convenient mix ratio offer the compounder ease of handling. The mix ratio is relatively noncritical, increasing hardener levels yield increased flexibility and adhesion but reduced HDT and chemical resistance. Initially, amidoamides have poor compatibility and an induction period is necessary to allow the reduction to start. Pot life is relatively long and exotherm slow, but low temperature cure is poor. Small quantities of imadazoline improve adhesion to metal. Dicyandiamide is a special example of an amide that can be used on its own. Its low reactivity yields a usable life in excess of 6 months, but at elevated temperatures it reacts quickly.

f) **Mercaptans:** Most mercaptans on their own are unreactive, but with catalysts produce flexible cures. Certain mercaptans in conjunction with DMP 30 provide extremely rapid cure, with low exotherm, making them ideally suited to retail applications.

g) **Acids and anhydrides** [9, 10]: This group of curing agents provides the best high temperature performance. Boron trifluoride monoethylamine, oxalic acid, and maleic and phthalic anhydride are used for electrical or high temperature applications, often with catalysts such as benzyldimethyl amine (BDMA) or DMP 30.

### 2.3.3 Diluents

As previous mentioned, when various materials are added to epoxy resin in order to improve its properties, the viscosity of the composition correspondingly increases. So it inevitably requires adjustment (reduction) of its viscosity. For this purpose, diluents are used. The influence of diluents on performance must be minimized, and thus the preferably used filler are those that can have a significant effect with as small amount as possible. Diluents are divided into two groups: unreactive one having no epoxy group and reactive one having epoxy groups. The chemical structure of reactive diluents are shown in Figure 2.8. Most one part epoxy resins are used reactive diluents that have a low vapor pressure, as it undergoes a heating process.

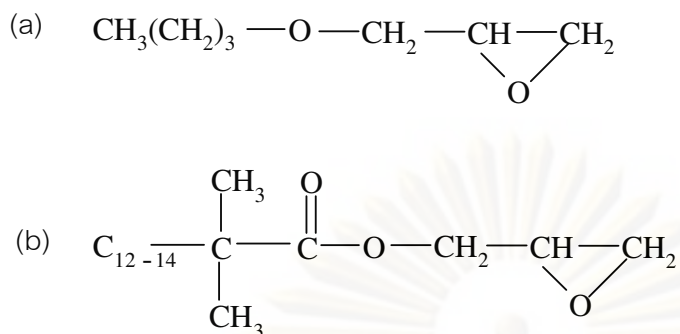


Figure 2.8 Examples of reactive diluents (a) BGE and (b) Carjula E

### 2.3.4 Plasticizers

Conventional plasticizers may be used in formulated products. Phthalate esters are the preferred plasticizers. They exhibit little tendency to migrate and have good compatibility with both resin and hardener. Chlorinated plasticizers may be used to reduce flammability, especially in conjugation with antimony trioxide. The effect of plasticizer additions is generally to degrade most physical properties, although at low additions the effect is usually small. Addition of plasticizers will affect on various important properties such as pot life extension, increasing the impact resistance, decreasing the tensile strength, chemical resistance and heat distortion. It should be noted that plasticizers do not introduce marked flexibility into epoxy resin systems. Nor is this generally a desirable attribute in adhesive applications, where epoxies are usually selected because of their great strength.



### 2.3.5 Fillers

Two types of fillers may be incorporated into formulated epoxy systems. Powder fillers are added to increase viscosity, improve abrasion resistance and gap-filling properties, impart specific electrical or mechanical properties, or reduce cost and shrinkage. Addition levels may be 50 to 300 parts per weight of resin (phr). Although the most fillers will increase the density of the cured product, certain lightweight fillers will decrease density. Viscosity increases depend on surface area, oil absorption and filler type. Chemical resistance may be improved or made worse, depending on fillers selected. Highly alkali fillers should be avoided, especially with acid cured systems, as they may retard setting. Fibrous fillers may be added to impart specific rheological properties or to reinforce the system. They will usually improve both tensile strength and impact resistance. Addition levels are much lower at 10 to 50 phr. as they usually cause much more rapid thickening. Table 2.1 shows list of the common fillers.

Table 2.1 Type of Fillers

Filler	Specific gravity	Oil absorption (%)	Relative cost	Usage level	Purpose
Silica	2.5-2.7	20-30	Low	50-500	Bulk, price
Quartz	2.5-2.7	15-30	Low	50-300	reduction,
CaCO <sub>3</sub>	2.6-2.8	15-25	Low	50-300	stability and reduce exotherm
Carbon	2.0-2.2	-	Medium	5-50	Thermal and
Aluminum powder	2.5-2.7	-	High	20-100	electrical conductivity
Silica carbide	3.2	-	Medium	50-200	Abrasion resistance
Glass fiber	2.4-2.6	-	Medium	10-50	Reinforcement

Settlement of fillers during storage depends primarily on the particle size of the filler and its density, and the viscosity of the formulated product. Settlement can be reduced or eliminated by proper formulation. Fine particle fillers with relatively low specific gravity in high viscosity products will settle much less, especially if the product is at all thixotropic. Where coarse fillers must be used, an approach toward a fully filled voidless system where the volume of liquid is such as just to fill the voids will solve the problem. Incorporation of fine fillers, use of a pigment dispersing aid, and where application permits, use of a thixotropic agent will help to reduce or eliminate settlement. Depending on addition levels, fillers will generally increase the usable life and extend the cure time of the mix. Tensile and compressive strength usually increase maximally then decrease on further additions. Most fillers have relatively little effect on HDT. Chemical resistance will vary from filler to filler. Shrinkage is usually reduced.

### 2.3.6 Solvents

Although a major advantage of epoxy adhesives is their ability to be formulated without solvent, under certain circumstances solvents may be included. On porous substrates solvents may be added to reduce viscosity and assist penetration. On certain nonporous substrates, particularly some plastics, addition of a small percentage (1 to 3%) of a suitable solvent will improve adhesion. Common solvents are low boiling aromatic solvent, ketone or ester.

### 2.3.7 Additives

Additives are typically products added at levels of 0.1 to 0.5% to modify specific properties. Most commonly used additives are defoamers, antisetling or wetting agents, thixotropes, and adhesion promoters. Use of antioxidants or preservatives is rare. Because of their minimal shrinkage, compressive strength of cured epoxies is very high. Since aeration will reduce this substantially, use of defoamers, especially in heavily filled systems, is quite common. Many defoamers are suitable, but silicone-based defoamers should be avoided on surfaces where adhesion is critical. Addition levels of 0.05 to 0.2% usually suffice.

Antisetling agents, pigment dispersers, or wetting agents may be included in filled formulations. Depending on the formula, particularly the selection of fillers, such as products may reduce or eliminate settlement. Usage will generally be at a level of 0.1 to 0.3% of formulation. These agents are best added prior to incorporation of the fillers. Various thixotropes are used in epoxy formulations to reduce or eliminate flow in products designed for use on vertical surfaces, to improve gap-filling properties, or to reduce settlement of fillers. Fumed silica is widely used at levels of 0.1 to 3%. At low levels, the effect on viscosity is small except in high viscosity systems, but settlement will be reduced. At higher addition levels, even low viscosity products can be converted to firm pastes. To improve the efficiency of fumed silica, especially in the resin component, small quantities of polar liquids may be added.

Other thixotroping agents include bentones and tixogels, of which a number of grades are available, and China clay or kaolin, usually added as a filler, but which imparts thixotropy to the formulated product. Organofunctional silanes are extremely effective adhesion promoters. Added at levels of 0.05 to 0.2%, they can improve adhesion to certain nonporous substrates, such as glass, metals, and certain plastics. Formulators can select from a number of different functional groups, but generally epoxy functional types will be used in the resin component and amine functional grades in the hardener.

### 2.3.8 Elastomers

Despite its high strength, cured epoxy resin has the problem of brittleness due to its poor elasticity. Thus, the addition of elasticated agent to epoxy resin is necessary to improve these properties. The purposes of adding elasticated agents include, i.e., improvements in mechanical strength, prevention of cracks due to thermal distortion and reduction of distortion, and improvements in adhesiveness particularly improvements in peel strength by imparting elasticity to disperse stresses.

The method of compounding elasticated agent is that: an elastic structure is introduced to the main chain polymer, side chain or terminal of bisphenol type resin (see Figure 2.9). However, the introduction of polymers having a rubber structure or a straight chain inevitably causes a significant increase in the viscosity of material and

deterioration of the properties of the material, such as heat resistance, due to decrease in the crosslink density. To avoid such deteriorations in properties, elastomers may be added. CTBN (carboxyl terminated butadiene acrylonitrile copolymer) is a popular reactive rubber that added to epoxy resin. During the final cure, the CTBN rubber must precipitate out of solution into discrete particles within the epoxy resin matrix. The rubber acts as the crack inhibitors as shown in Figure 2.10. These results in a general increase in toughness and impact strength.

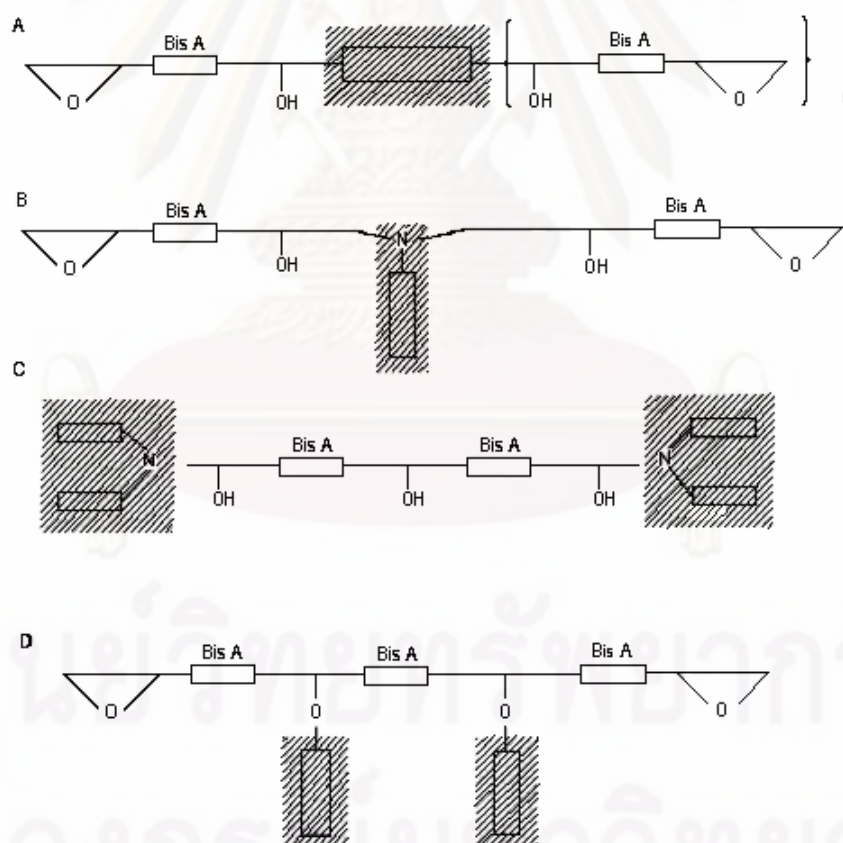


Figure 2.9 Schematic structures of modified resins

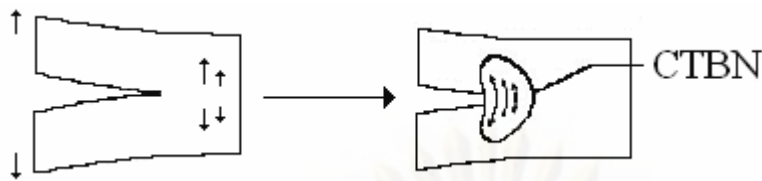


Figure 2.10 Effect of CTBN rubber on cracking process

## 2.4 Applications

Epoxy resins are used in various applications such as construction, metal bonding, wood bonding, film adhesive and electrical application. Due to the high strengths that can be achieved and the relatively high costs, they are generally used in structural applications in both concrete and metal bonding. Their good electrical properties allied to low shrinkage and good durability suit them for potting and encapsulating. Low shrinkage and good gap filling make epoxy ideal for applications where clamping is difficult, while the fact that both components are generally liquid up to the moment of cure means that they can be used where applications constraints require long open or assembly times. Conversely, systems with very short cure times are perfect for consumer applications. Good adhesion to nonporous surfaces allows them to be used in demanding situations. They find major outlets in the construction, automotive and electronics industries.

## 2.5 Literature Reviews

Epoxy resins are widely applied in adhesives, composites and molding compounds due to their outstanding versatility and mechanical properties. However, the general epoxy systems usually suffer the shortage of toughness because of their highly crosslinked but brittle structure. Several methods have been proposed to increase the toughness of epoxy resin and one of the most successful involves the addition of a suitable rubber to the uncured epoxy resin. The popular reactive rubbers e.g. acrylic rubber, hydroxyl-terminated acrylonitrile butadiene, epoxy-terminated acrylonitrile butadiene, hydroxyl-terminated butadiene, epoxy-terminated butadiene, carboxyl-terminated acrylonitrile butadiene (CTBN) and amine-terminated acrylonitrile butadiene (ATBN) rubber were added to epoxy resin. When polymerization reactions of epoxy and liquid rubber proceed under controlled sets of conditions, there induced a phase separation between the particles of epoxy matrix and rubber.

The toughening mechanisms of rubber in epoxy resin, especially CTBN, ATBN and ENR, have been well studied in the past. S.-G. Hong and C.-K. Chan [2] studied the curing behaviors of the epoxy/dicyanamide/2-methyl imidazole system modified with epoxidized natural rubber. They found that the reaction order of epoxy system can be changed by the presence of ENR because of the participation of ENR in the curing reaction system. The SEM result indicated that the particle size of the rubber phase



increased with increase in the curing temperature and ENR content. The lap shear strengths obtained from different specimens increased with increase in the curing temperature due to a better cure at higher temperature, but decrease with increasing the ENR content resulting from an inferior structure formed in the presence of ENR.

Cure kinetics of diglycidyl ether of bisphenol A (DGEBA)/4,4'-methylene dianiline (MDA) system with various content of MDA-encapped carboxyl-terminated butadiene acrylonitrile (CTBN) were studied by J.-Y. Lee et al. [7]. With increasing MDA-encapped CTBN content, the exothermic heat decreased due to the diffusion control induced by rubber domain produced in the epoxy matrix, which disturbed the diffusion of functional groups, and the maximum exothermic peak value and the activation energy decreased due to the increasing content of amine group in rubber compound, which reacted with epoxy group and formed a hydroxyl group acted as a catalyst [2].

For CTBN modified epoxy resins, G. Tripathi and D. Srivastava [6] studied the effect of carboxyl-terminated poly(butadiene-co-acrylonitrile) (CTBN) concentration on thermal and mechanical properties of binary blends of diglycidyl ether of bisphenol A (DGEBA) epoxy resin. The morphology study of the cured system revealed a two-phase region where the liquid rubber particles are distributed in the epoxy matrix. There was slight reduction in  $T_g$  on the addition of CTBN. The incorporation of CTBN rubber of about 20 phr showed better-toughened properties. A further increase in the concentration of the elastomer led to phase inversion. The mechanical properties like

tensile and flexural strength showed reduction, whereas impact strength increased with higher concentration of CTBN. Dynamic mechanical analysis further established two-phase morphology. The elastomeric phase showed better adherence to the epoxy matrix.

Moreover, R. Thomas and coworkers [10] also studied the cure kinetic, morphology and miscibility of modified DGEBA-based epoxy resin with CTBN inclusion. The curing analysis and morphology were followed by DSC and SEM, respectively. The addition of liquid rubber did not change the mechanism of cure. However, on the lowering temperature, the rate and the extent of reaction decreased. The extent of reaction decreased after attaining the gelation point. This was due to the phase separation of rubber from the epoxy matrix. Addition of higher wt% of rubber increased particle size but decreased the rate and conversion. This was due to the dilution effect and the increase of viscosity. Good fits are obtained between the autocatalytic model and the experimental data up to the vitrification state. Afterwards the reaction became diffusion controlled.

Autocatalytic model was also used to describe the curing process of two epoxy resins with different structures (DGEBA and DGEHQ), in the presence of DGA, as a reactive diluent and TETA as hardener [34]. From results, the reactive diluent decreased both the activation energy and the cure kinetic parameters. Non-isothermal DSC

thermograms obtained using the experimental data show a good agreement with that theoretically calculated.

The addition of two CTBN and ATBN on amine cured epoxy resin was studied by C.W. Wise et al. [5]. The CTBN carboxyl end groups strongly enhanced the curing rate through the impurity catalysis mechanism, however, the amino-terminated ATBN only retarded the reaction, possibly by dilution effect or owing to change in the dielectric constant of the reaction medium. The glass transition temperature of epoxy matrix was slightly depressed for the CTBN-filled system, probably due to the plasticizing action of small levels of rubber dissolved in the matrix. The  $T_g$  of rubbery CTBN phase was also lower than  $T_g$  of neat CTBN. The height of DMTA rubber was linear function of the level of CTBN. From SEM micrograph, the surface of epoxy sample with 5% rubber clearly showed a spherical second phase. The size of rubber particles was smaller for the more polar CTBN rubber possibly due to its greater solubility in the matrix.

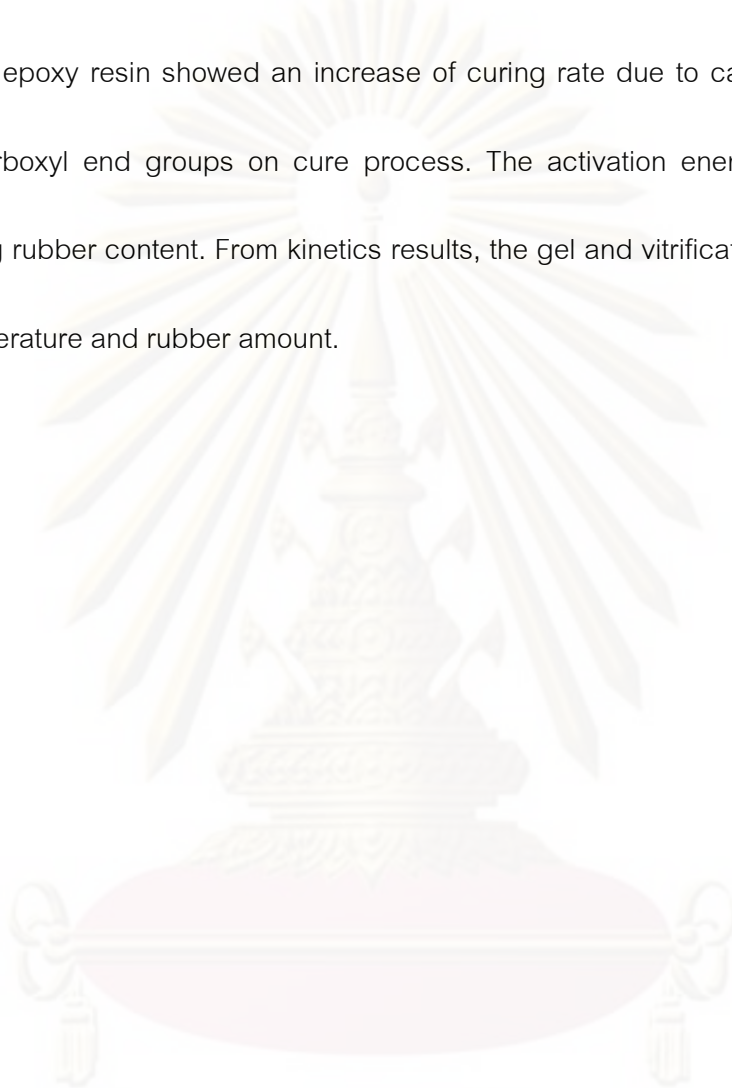
Phase separation behavior of carboxy-terminated poly(2-ethyl hexyl acrylate) (CTPEHA) liquid rubber modified epoxy mixture have been studied by D. Ratna [35]. The CTPEHA was incorporated into epoxy matrix by a preheat method. The delay in polymerization for modified mixtures with respect to that of the neat resin can be explained by lower reactivity of chain extended resin and viscosity effect. The  $T_g$  of epoxy matrix decreased with increase in rubber concentration and cure temperature. The  $T_g$  of rubbery CTPEHA phase was also lower than that of neat CTPEHA. The flexural

and impact properties have been discussed in term of morphological behavior for and epoxy matrix modified with various amount of CTPEHA. Optimum impact performance was achieved for the mixture containing 10 phr of CTPEHA and cured at 140°C, which contain both phase separated rubber as well as dissolved rubber.

B. Russell and R. Chartoff [8] used SEM and AFM techniques to study the influence of cure conditions on the morphology and phase distribution in CTBN rubber-modified diglycidyl ether of bisphenol A (Epon 828). They found that % acrylonitrile content of rubber affected both rubber particle size and volume fraction. The curing temperature strongly affected the rubber particle volume fraction and modulus, while larger volume fractions of CTBN rubber improved toughness, but the toughness was greatest when modulus values did not exceed 6.2 MPa. Thus, the increased volume fraction by itself may not always result in increased toughness.

Amine-terminated butadiene acrylonitrile (ATBN) copolymer was also added to diglycidyl ether of bisphenol A epoxy resin using polyaminoimidazoline as a curing agent. With ATBN incorporation, all reactivity characteristic (gel time and temperature, cure time and exotherm peak) decreased. From FTIR results, the occurrence of chemical reaction between ATBN and epoxy resin led to improve compatibility and decreased  $T_g$ . On adding ATBN, the stress at break decreased accompanied by an increase in elongation at break with the appearance of yielding [28].

L. Calabrese and A. Valenza [9] investigated the effect of CTBN rubber inclusions on the curing kinetic of DGEBA-DGEBF epoxy resin. The addition of CTBN rubber to epoxy resin showed an increase of curing rate due to catalytic effect of the CTBN carboxyl end groups on cure process. The activation energy decreased with increasing rubber content. From kinetics results, the gel and vitrification time decreased with temperature and rubber amount.



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## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials

##### 3.1.1 Epoxy Resin

Two types of epoxy resins; Epon 862 and Epon 828 (from Miller-Stephenson Chemical Co., Ltd.), were used for this study. The specifications of each resin are shown in Table 3.1.

**Table 3.1** Properties of epoxy resins that used in the experiment

Properties	Epon 828	Epon 862
Epoxy Based	Diglycidyl ether of bisphenol A	Diglycidyl ether of bisphenol F
Viscosity at 25°C (Pa.s)	110-150	25-45
Epoxide Equivalent Weight (g/eq.)	185-192	165-173

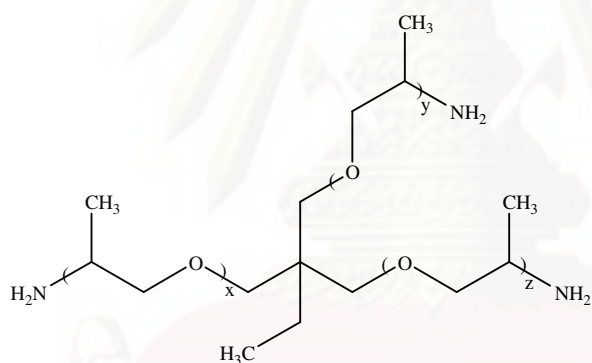
##### 3.1.2 Hardener

Three kinds of hardeners used in this study were Jeffamine T-403 Polyetheramine (Huntsman), DCA221 (Dixie Chemical Company, Inc.) and Imicure EMI-

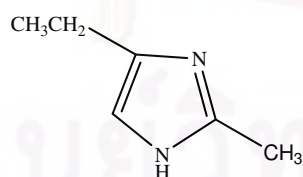
24 (Air Products and Chemicals, Inc.). The chemical structures of hardeners used are shown in Figure 3.1. The specifications of all materials are shown below:

- a) Jeffamine T-403 is a trifunctional primary amine having an average molecular weight of approximately 440. Total amine is 6.1-6.7 meq/g, viscosity is 72 cPs at 25°C.
- b) DCA221 is polyglycoldiamine having amine equivalent 8.6-9.16 meq/g, viscosity is about 9.5-15.8 cPs at 25°C.
- c) Imicure EMI-24 is poly(ethyl-4-methyl-1h-imidazole)

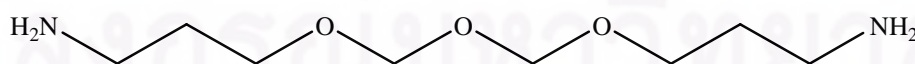
(a) Jeffamine T-403



(b) Imicure EMI-24



(c) DCA221



**Figure 3.1** Chemical structures of (a) Jeffamine T-403, (b) Imicure EMI-24 (Main composition) and (c) DCA221 (Main composition)

### 3.1.3 Rubber

Carboxyl terminated butadiene acrylonitrile copolymer (trade name: Hycar 1300x13) was supplied by BF Goodrich with molecular weight,  $M_n$ , of 3150 g/mol containing 26% acrylonitrile content. The viscosity of CTBN used in this study was about 625,000 mPas at 27°C. The chemical structure of CTBN is shown in Figure 3.2.

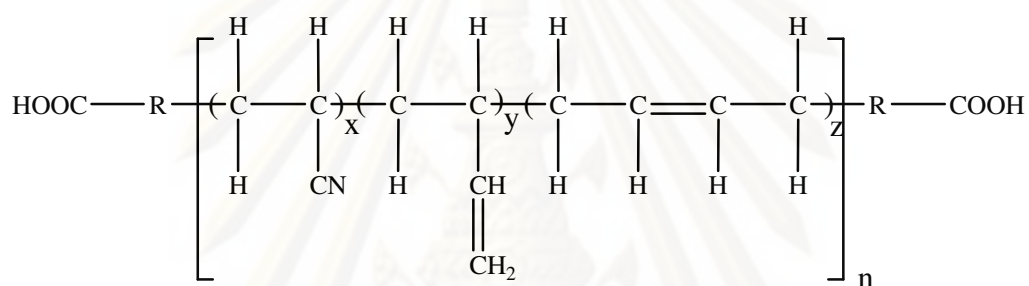


Figure 3.2 Structure of carboxyl terminated butadiene acrylonitrile copolymer (CTBN)



### 3.2 Instruments

The instruments which used in this study were summarized in Table 3.2

**Table 3.2** Instruments

Instrument	Model
Centrifuge	Nuve
Fourier Transform Infrared Spectrometer	Perkin Elmer Spectrum 2000
Differential Scanning Calorimeter	Mettler Toledo DSC 822e
Test Stand	Chatillon TCD 200
Force Gauge	Mecmesin
Cone and Plate Viscometer	Brookfield HBDV-II+CP51
Scanning Electron Microscope	Jeol JSM-5900 LV
Tensile Tester	Lloyd LR 10K Plus
Gold Coating Apparatus	Polaron CA7625

### 3.3 Sample Preparation

The formulations of epoxy resins are given in Table 3.3. DGEBA (Epon 828: sample A, C and E) or DGEBF (Epon 862: sample B, D and F) resins and hardeners were weighed in a 100 ml beaker. The mixtures were stirred by hand for 10 minutes. Then the homogeneous mixture was observed. It was next placed in a vacuum desiccator to degas at room temperature until the bubble was disappeared. Finally, the mixture was cured under condition in oven as seen in Table 3.4.

For the compositions including CTBN rubber (sample G and H), in formulation the epoxy resins and hardeners were mixed until the homogeneous mixture was obtained. After that CTBN rubber was slowly mixed and the mixture was degassed to remove bubble from the mixture. Finally, the mixture was cured under condition in oven as seen in Table 3.4.

#### Sample preparation for shear strength test

The aluminum plates and rods were cleaned by ultrasonic process with isopropyl alcohol. The adhesive formulation was applied on aluminum plate by using micro dispenser. Five drops of adhesives were added to each plates, each drop of adhesive has volume about 0.2 ml. The cleaned rods were placed on adhesive droplet.

Two plates for each formulation were used for this study. The samples were then cured in oven at different conditions as shown in Table 3.4.

#### Sample preparation for tensile strength test

The aluminum plates were cleaned by ultrasonic process with isopropyl alcohol. The adhesive formulation was applied on an aluminum plate. Each drop of adhesive has weight about 0.2 g. The cleaned plates were placed on adhesive area. Five plates for each formulation were used for this study. The samples were then cured in oven at different conditions as shown in Table 3.4.

Table 3.3 Formulation of epoxy resins

Sample	Resin			Hardener (phr)		CTBN (phr)
	Epon 828	Epon 862	Jeffamine T-403	DCA221	Imicure EMI-24	
A1	100	-	20	-	-	-
A2	100	-	40	-	-	-
A3	100	-	60	-	-	-
A4	100	-	80	-	-	-
A5	100	-	100	-	-	-
B1	-	100	20	-	-	-
B2	-	100	40	-	-	-
B3	-	100	60	-	-	-
B4	-	100	80	-	-	-
C1	100	-	-	20	-	-
C2	100	-	-	40	-	-
C3	100	-	-	60	-	-
C4	100	-	-	80	-	-
D1	-	100	-	20	-	-
D2	-	100	-	40	-	-
D3	-	100	-	60	-	-
D4	-	100	-	80	-	-
E1	100	-	-	-	10	-
E2	100	-	-	-	20	-
E3	100	-	-	-	40	-
E4	100	-	-	-	60	-
F1	-	100	-	-	10	-
F2	-	100	-	-	20	-
F3	-	100	-	-	40	-
F4	-	100	-	-	60	-
G1	100	-	80	-	-	5
G2	100	-	80	-	-	10
G3	100	-	80	-	-	15
G4	100	-	80	-	-	20
G5	100	-	80	-	-	25
H1	-	100	40	-	-	5
H2	-	100	40	-	-	10
H3	-	100	40	-	-	15
H4	-	100	40	-	-	20
H5	-	100	40	-	-	25

**Table 3.4** Curing condition for each formulation

Hardeners	Curing condition
Jeffamine T-403	120°C for 60 min
DCA221	100°C for 120 min following with 150°C for 120 min
Imicured EMI-24	120°C for 60 min

### 3.4 Characterization and Mechanical Properties

#### 3.4.1 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectrophotometer had been used to monitor the functional group in order to determine the chemical reaction which occurred when hardeners and CTBN rubber were added to epoxy resins. A small portion of the cured epoxy system was grinded to a fine powder, mixed with potassium bromide (KBr) powder and pressed into a pellet by hand press. FTIR were recorded by Perkin Elmer Spectrum 2000 with 16 scans at the resolution of  $4\text{ cm}^{-1}$  in the range of  $4000\text{-}600\text{ cm}^{-1}$ .

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### 3.4.2 Viscosity Test

Viscosity of epoxy resin mixed with hardener before curing was measured by Cone and Plate Brookfield Viscometer (HBDV-II+CP51 model). 0.5 ml of epoxy mixture was dispensed to center of plate. Hold the sample in cone and plate viscometer for 2 minutes at setting temperature (25°C). Viscosity was measured every one minute for three times. The average viscosity was reported.

### 3.4.3 Shear Strength Test

Cured samples were employed shear strength by Mecmesin force gauge that fixed on Chaltillon TCD200 test stand at speed 0.02 inch/minutes, the test instrument is shown in Figure 3.3.



Figure 3.3 The shear strength test instrument

#### 3.4.4 Tensile Test

The tensile properties were measured by a Lloyd Universal Testing Machine (model LR 10K Plus) according to ISO4587. The samples used were 70 mm in gauge length, 25 mm in width and 16 mm in thickness. The crosshead speed was set at 1 mm/min and load cell 1 kN. The test was operated at room temperature. The values reports for each sample were based on an average of five measurements.

#### 3.4.5 Scanning Electron Microscopy (SEM)

The blend morphology was investigated with scanning electron microscope on small pieces of molded samples. The samples after curing were fractured under liquid nitrogen and the dispersed rubber phase in epoxy resin sample was extracted using toluene for 10 hours at ambient temperature. The dried samples were sputter-coated with gold prior to SEM examination. JEOL JSM-5900 LV model was used to view the specimen. Several micrographs were taken for each sample.

#### 3.4.6 Differential Scanning Calorimetry (DSC)

Mettler Toledo DSC 822e was used to measure the glass transition temperature ( $T_g$ ) of cured samples. The instrument was calibrated with indium. Sample (8-10 mg) was weighed and put in an aluminum pan. After that samples were cured at

condition as showed in Table 3.4. The sample was inserted into the DSC cell. The temperature was increased from 25°C to 220°C at a heating rate of 10°C/min.



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## CHAPTER IV

### RESULTS AND DISCUSSION

The present thesis aims to investigate the properties of various epoxy resins with/ without CTBN rubber. This work was divided into two parts. The first part was the investigation of the suitable formulation for mixing of Epon 828 and Epon 862 based materials with three kinds of hardeners in order to give the optimum mechanical properties. In the second part, the effect of CTBN that added to epoxy resins on mechanical properties and morphology was studied.

#### Part I Epoxy Resins without CTBN Rubber

##### 4.1 Characterization of Chemical Structure of Raw Materials

In this section, epoxy based materials (Epon 828 and Epon 862) and three types of hardeners (Jeffamine T-403, DCA221 and Imicure EMI-24) were analyzed by FTIR technique in order to identify the chemical functional group as follows:

#### 4.1.1 FTIR Analysis of Epoxy Resins

The FTIR spectra in 4000-600  $\text{cm}^{-1}$  regions for Epon 828 and Epon 862 are shown in Figure 4.1. The assignments of IR absorption bands of two based resins are summarized in Table 4.1. From FTIR spectra of Epon 828 (DGEBA) and Epon 862 (DGEBF), the main absorption band at 915  $\text{cm}^{-1}$  is the characteristic of oxirane ring of the epoxy resin that found on both kinds of epoxy resins. Absorption signals of O-H stretching and C-O stretching of ether function were also observed on both spectra at 3530, 1247 and 1035  $\text{cm}^{-1}$ , respectively. From Figure 4.1, extra absorption signal at 1385  $\text{cm}^{-1}$ , which can be assigned to C-H bending of methyl group was detected on FTIR spectrum of Epon 828. But methyl function was not found on spectrum of Epon 862. This evidence can therefore be used to confirm the chemical structure of both neat resins.

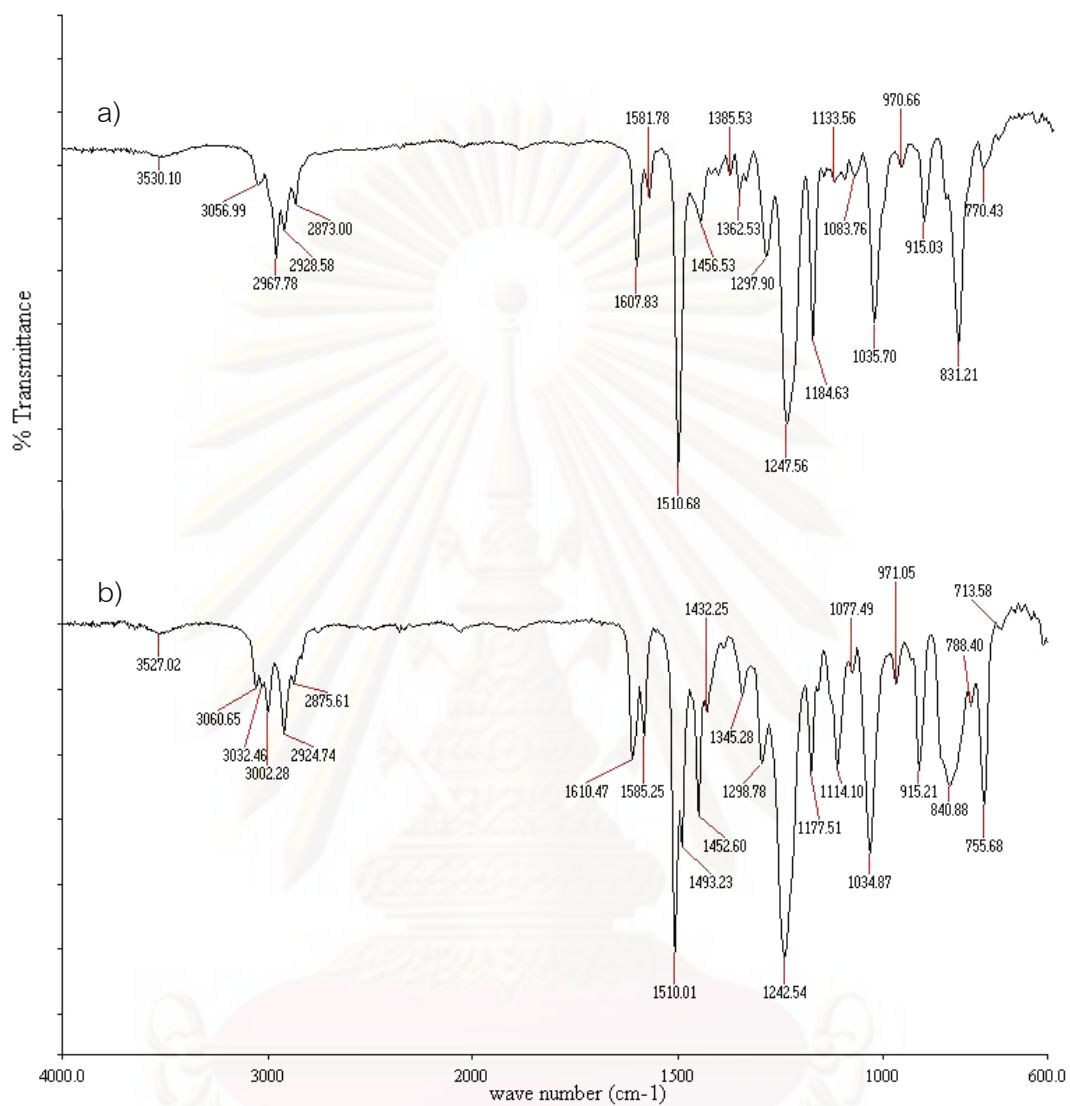


Figure 4.1 FTIR spectra of a) Epon 828 and b) Epon 862

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**Table 4.1** Assignment of IR absorption bands of Epon 828 and Epon 862

Vibration	Wave number (cm <sup>-1</sup> )	
	Epon 828	Epon 862
O-H stretching	3530	3527
=C-H stretching	3056	3060
C-H (aliphatic) stretching	2967, 2928, 2873	3002, 2924, 2875
C=C (aromatic) stretching	1607, 1581, 1510, 1456	1610, 1585, 1510, 1452
CH <sub>2</sub> (C-H bending)	1456	1452
CH <sub>3</sub> (C-H bending)	1385	-
C-O (ether) stretching	1247, 1035	1242, 1034
oxirane group of epoxy	915, 831	915, 840

#### 4.1.2 FTIR Analysis of Hardeners

Chemical functional groups on Jeffamine T-403, Imicure EMI-24 and DCA221 were analyzed by FTIR technique, the results are shown in Figures 4.2, 4.3 and 4.4, respectively. The assignments of IR absorption bands of three types of hardener are shown in Table 4.2. From Figure 4.2, the absorption signals of amine function of Jeffamine T-403 were detected at 3363 and 3292 cm<sup>-1</sup>. The absorption signals of methyl and ether groups were also observed at 1374 and 1106 cm<sup>-1</sup>, respectively. FTIR

spectrum of Imicure EMI-24 was showed in Figure 4.3. The signal of amine function was not detected, but the signals of C=N stretching and C=C aromatic stretching were observed. Figure 4.4 can be used to confirm that DCA221 consisted of amine and ether functional groups.

**Table 4.2** Assignment of IR absorption bands of Jeffamine T-403, Imicure EMI-24 and DCA221

Vibration	Wave number (cm <sup>-1</sup> )		
	Jeffamine T-403	Imicure EMI-24	DCA 221
N-H stretching	3363, 3292	-	3369
C-H (aliphatic) stretching	2968, 2931, 2878	2975, 2939, 2879	2921, 2872
=C-H stretching	-	3080	-
CH <sub>2</sub> (C-H bending)	1461	1447	1484
CH <sub>3</sub> (C-H bending)	1374	1383	-
N-H bending	1580	-	1572
C-O (ether) stretching	1106	-	1110
O-H stretching	-	-	3369
C=C (aromatic) stretching	-	1604, 1583, 1514, 1447	-
C=N stretching	-	1604	-

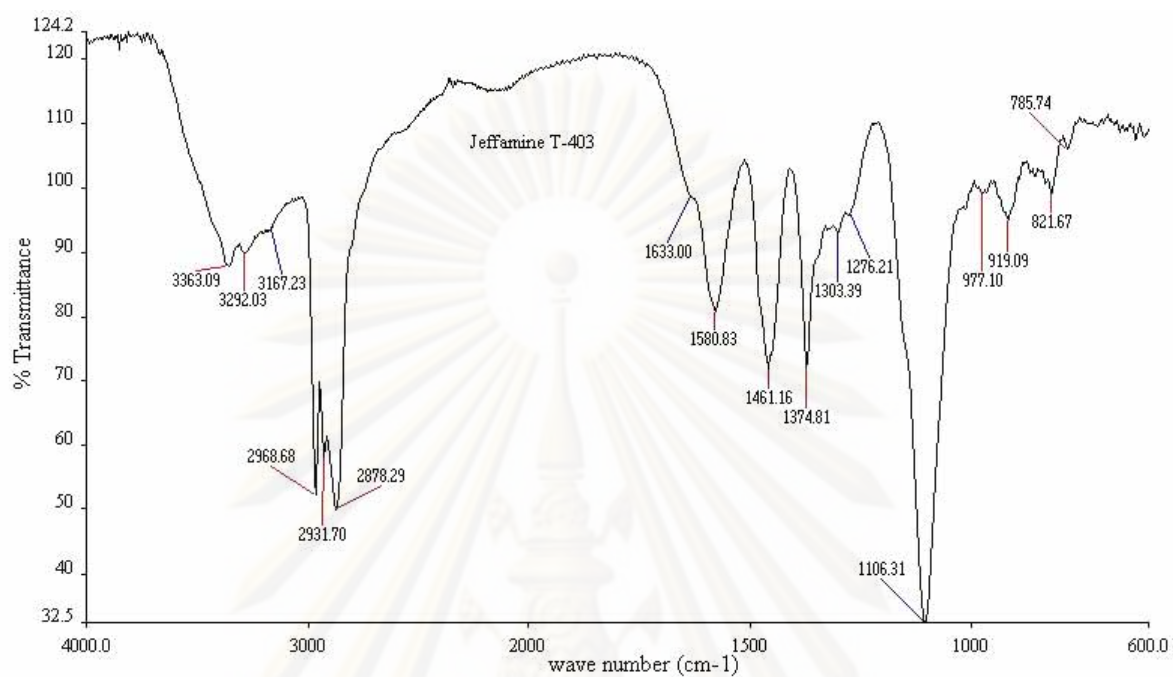


Figure 4.2 FTIR spectrum of Jeffamine T-403

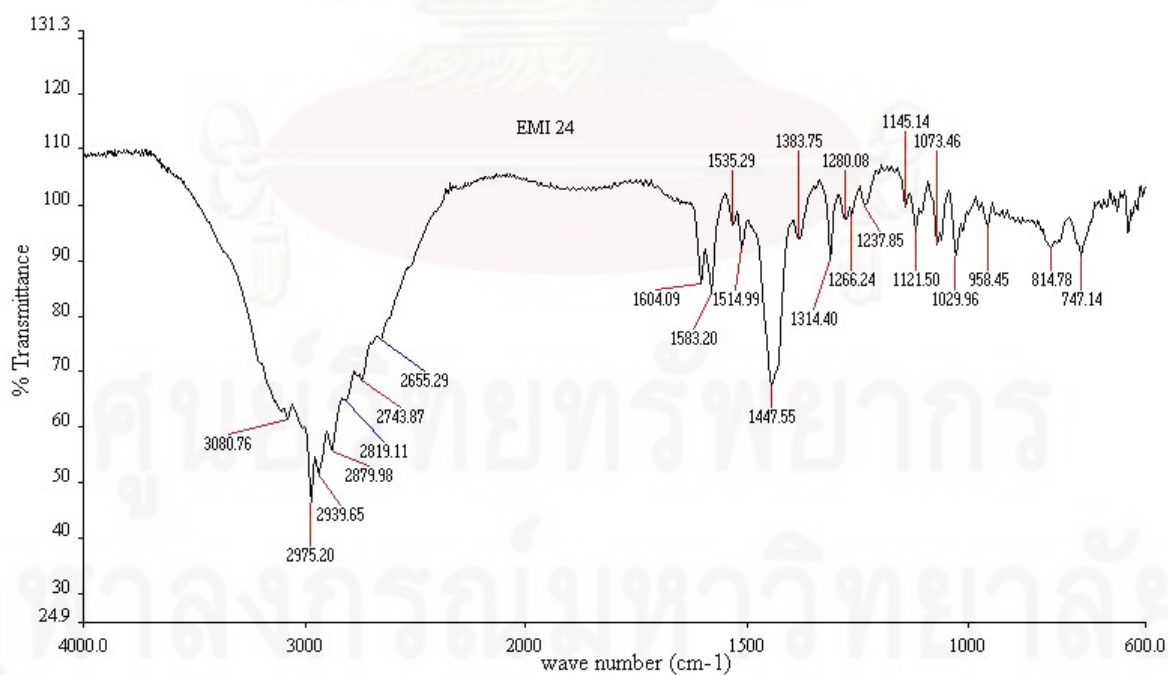


Figure 4.3 FTIR spectrum of Imicure EMI-24

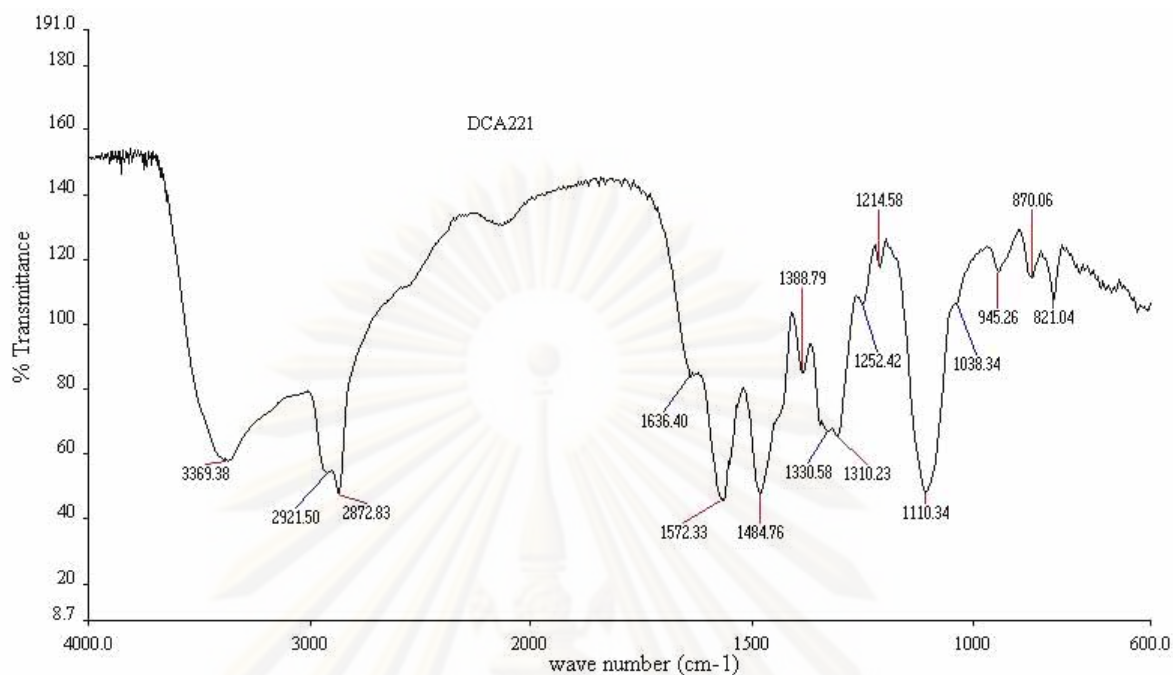


Figure 4.4 FTIR spectrum of DCA221

#### 4.2 Characterization of Epon 828 mixed with Different Kinds of Hardeners

The incorporation of three kinds of hardeners (Jeffamine T-403, Imicure EMI-24 and DCA221) into Epon 828 resin was done at different compositions according to the formulation as seen in Table 3.3. The mixtures were then determined the viscosity, mechanical properties, chemical structure and thermal properties as follows:

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#### 4.2.1 Viscosity Testing

The viscosities of the mixture of Epon 828 and three kinds of hardeners before curing were measured by cone and plate viscometer at room temperature. The results are shown in Figure 4.5. When Jeffamine T-403 content increased, the viscosity of epoxy mixture decreased which was because Jeffamine T-403 acts as the diluents for this mixture. The similar tendency was also obtained in the case of DCA221 system. This was possibly due to the low viscosity of DCA221 (9.5-15.8 cPs). The viscosity increased when Imicure EMI-24 hardener concentration increased. It may be due to the the hydrogen bonding that occurred between Epon 828 with Imicure EMI-24.

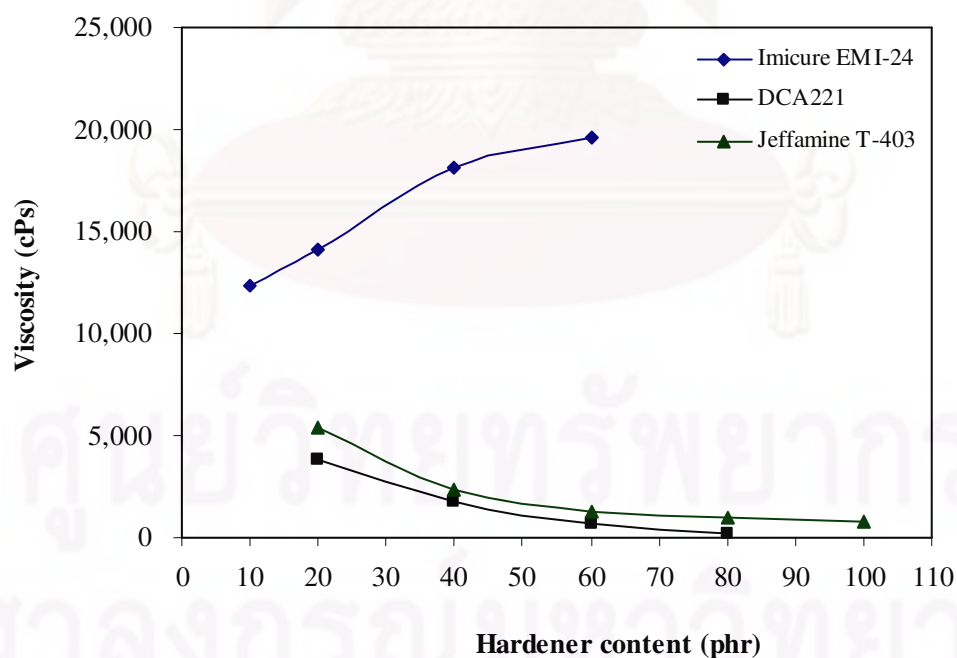


Figure 4.5 Viscosity of Epon 828 with three kinds of hardeners

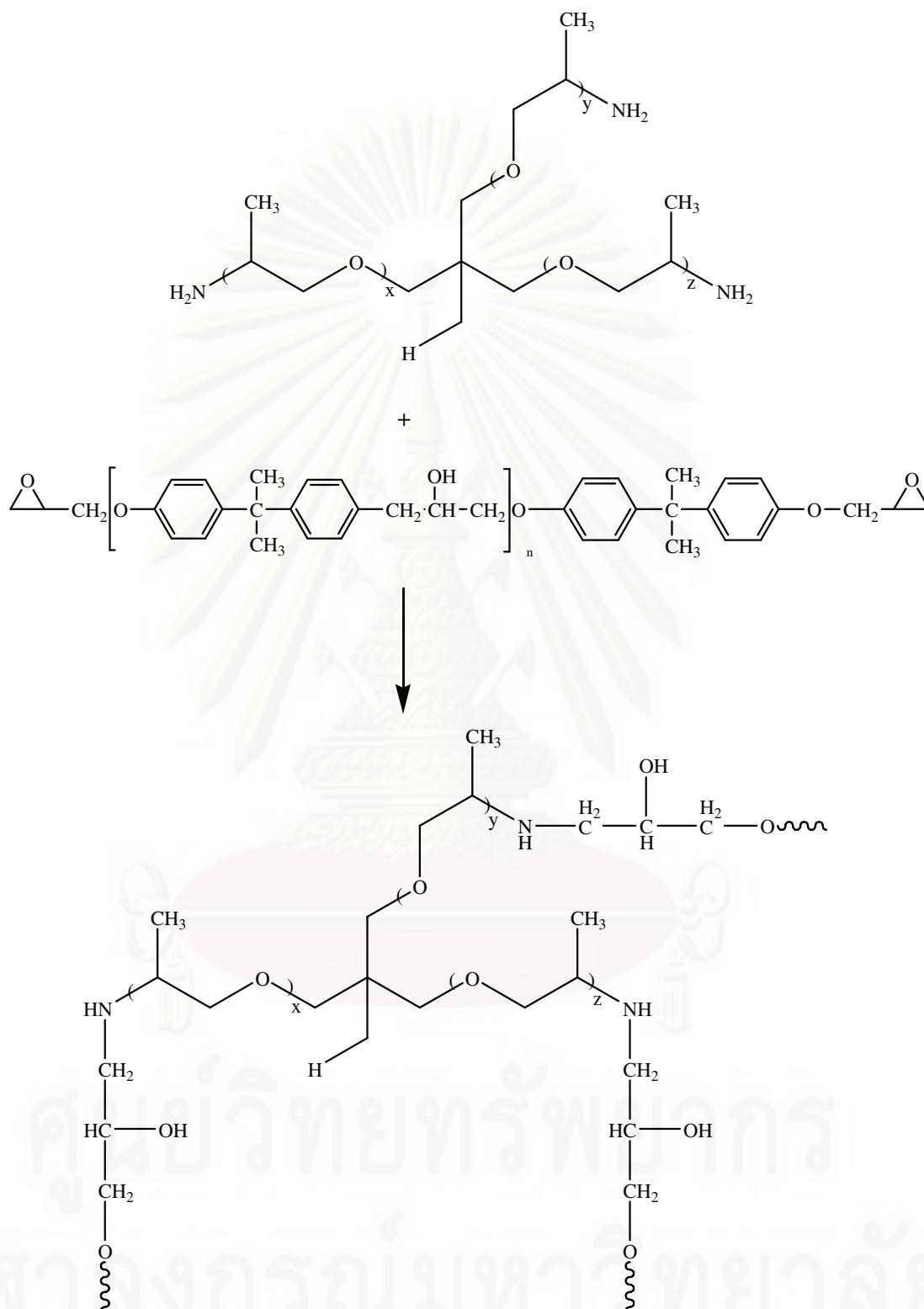


#### 4.2.2 Mechanical Properties

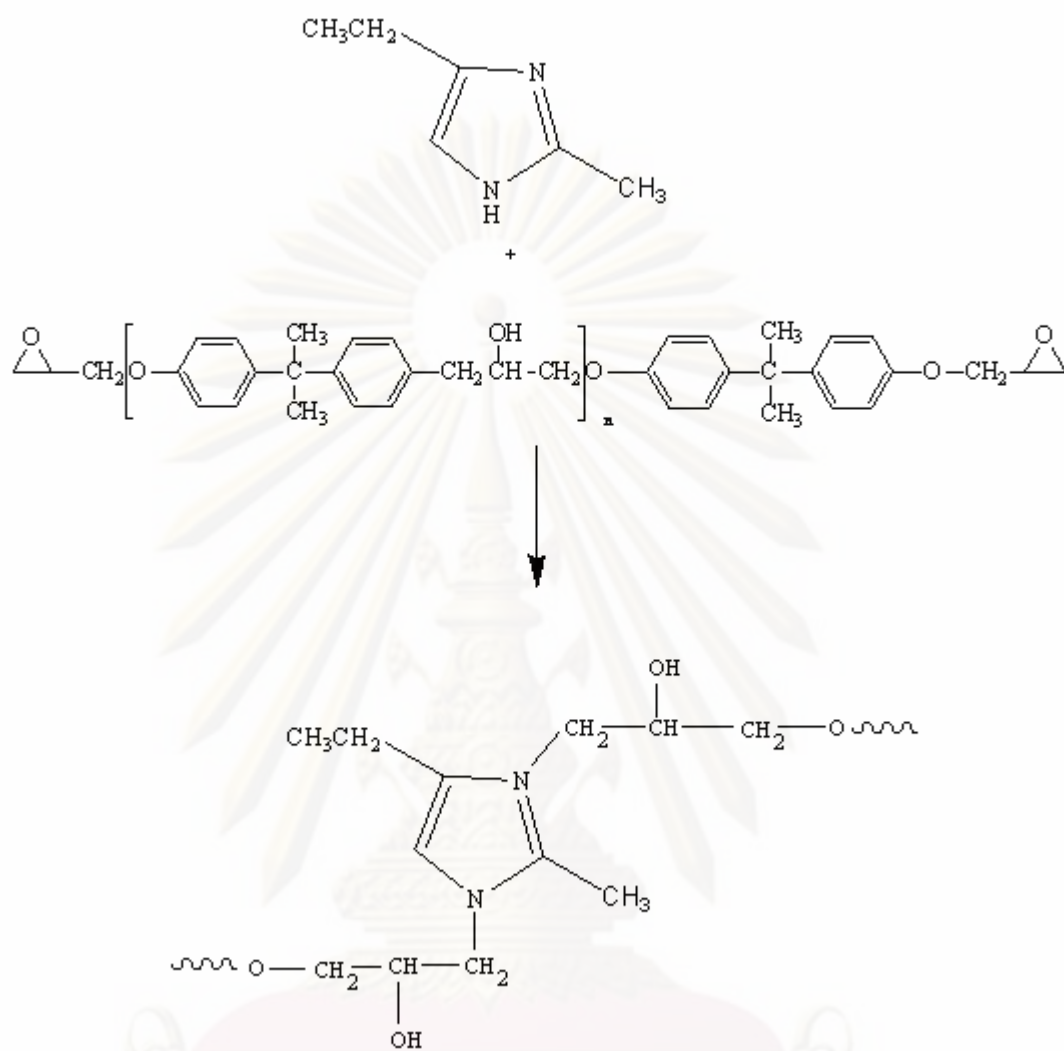
The results of shear strength and tensile strength of Epon 828 mixed with three kinds hardener after curing (Table 3.4) are shown in Figures 4.6 and 4.7, respectively. In Figure 4.6, when Jeffamine T-403 contents increased the shear strength of Epon 828 epoxy resins exhibited a bell shape curve with a maximum at 80 wt % of Jeffamine T-403. The increase of shear strength in the first region (20-80 wt % of Jeffamine T-403) was come from the reason that the increase of chemical reaction between oxirane rings of Epon 828 and amine function of Jeffamine T-403 (as seen in Scheme 4.1) leading to the increase of shear strength properties.

The shear strength of Epon 828 with Imicure EMI-24 increased with increasing Imicure EMI-24 contents from 10 wt% to 20 wt% due to the increase of interaction between resin and hardener (as seen in Scheme 4.2). Afterthat, the shear strength decreased when the hardener contents increased. It may be because the chemical structure of Imicure EMI-24 is in five membered ring, which showed the high stability and hardly to react with other functional groups. Therefore, the Imicure EMI-24 may be acted as the plasticizer for this system.

Due to the flexible segment in the chemical structure of DCA221 as shown in Scheme 4.3, the shear strength decreased when increased amount of DCA221 hardener as seen in Figure 4.6.

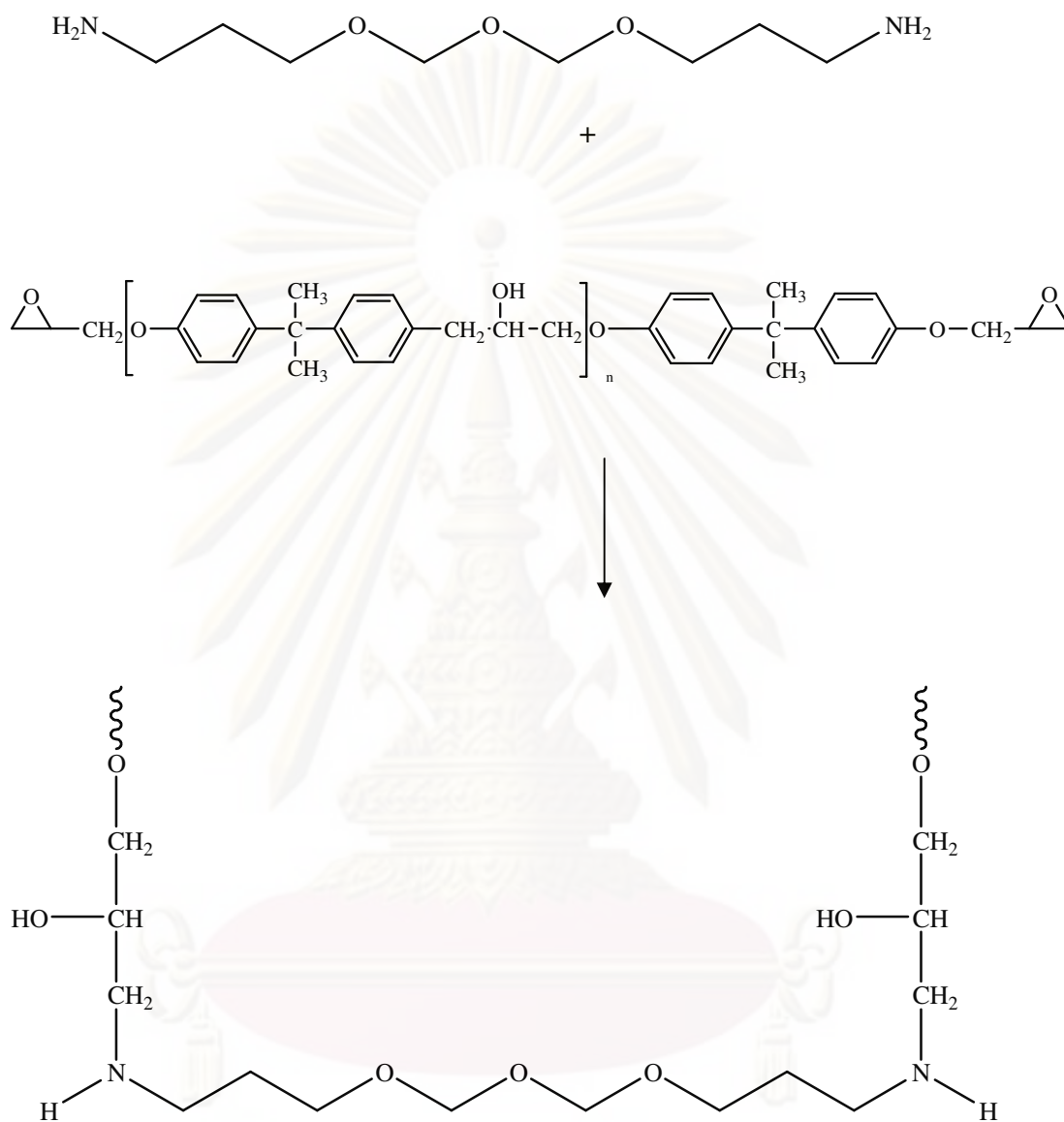


Scheme 4.1 Proposed chemical reaction between Epon 828 and Jeffamine T-403



Scheme 4.2 Proposed chemical reaction between Epon 828 and Imicure EMI-24

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Scheme 4.3 Proposed chemical reaction between Epon 828 and DCA221

According to the shear strength results for Epon 828 system, Jeffamine T-403 is the hardener that gives higher shear strength values when compared with Imicure EMI-24 and DCA221. Therefore, all ratios of mixing Jeffamine T-403 with Epon 828 was

subjected to measure the mechanical properties. From Figure 4.7, it is clearly observed that the relationship between tensile strength and Jeffamine T-403 contents shows the bell shape curve. This tensile result was similar to the shear strength result of Epon 828 with Jeffamine T-403. The highest tensile strength was obtained by using Jeffamine T-403 amount of 80 wt%. Accordingly, we decided to use this ratio for study the effect of CTBN rubber in the later section.

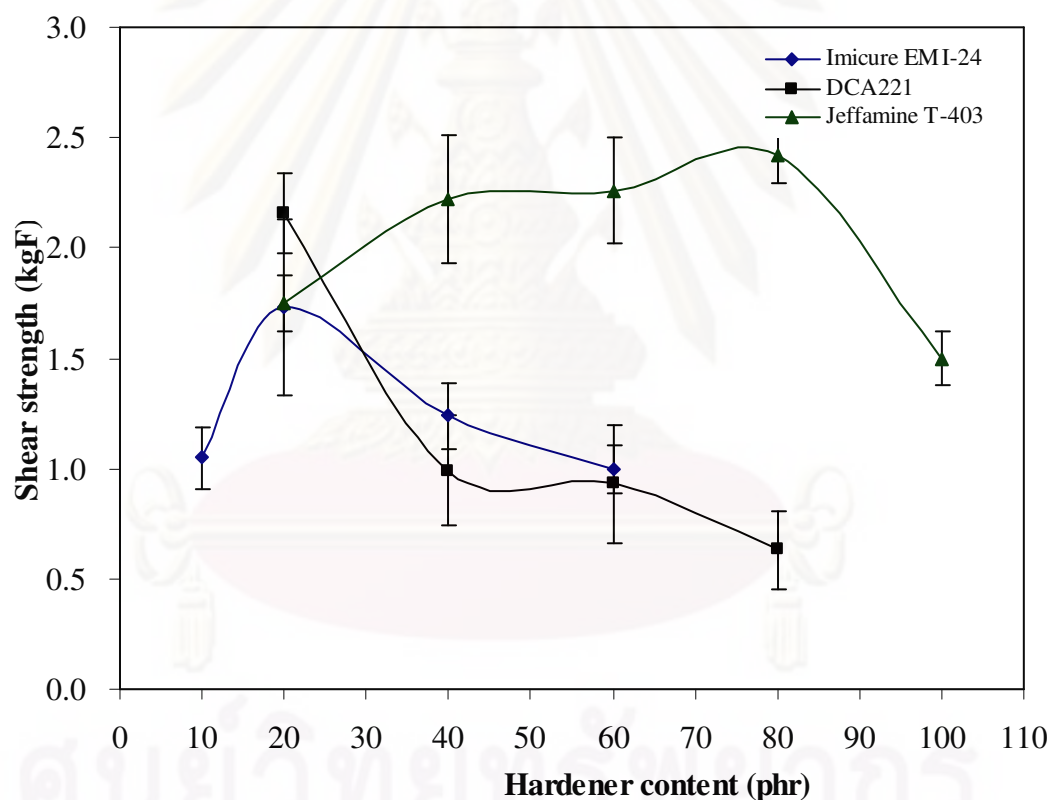


Figure 4.6 Shear strength of Epon 828 with three kinds of hardeners

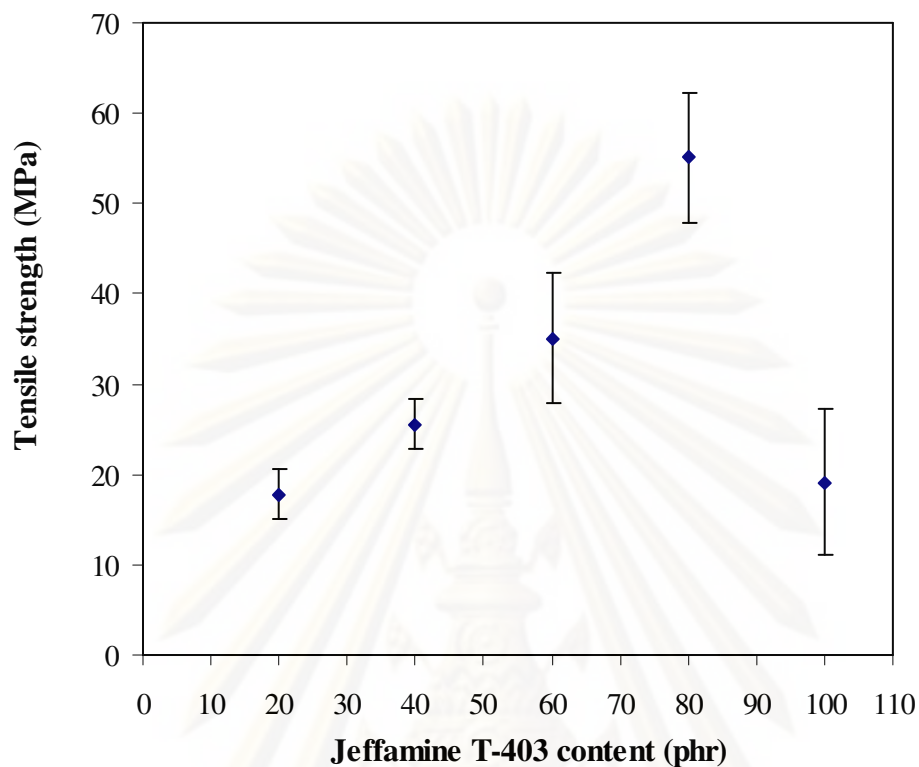


Figure 4.7 Tensile strength of Epon 828 with Jeffamine T-403

#### 4.2.3 Chemical Structure Characterization

Epon 828 was mixed with Jeffamine T-403 at different compositions and cured in the oven at 120°C for 1 hour. The cured samples were then analyzed the chemical structure using FTIR technique. The FTIR results are shown in Figure 4.8. The intense C-H stretching vibrations appeared at 2800-3000  $\text{cm}^{-1}$ . The absorption bands at 1607, 1582, 1510 and 1455  $\text{cm}^{-1}$  represented the C=C (aromatic) stretching. The signals of methylene ( $\text{CH}_2$ -) and methyl ( $\text{CH}_3$ -) carbons were also observed at 1458 and 1375  $\text{cm}^{-1}$ ,

respectively. Ring opening reaction occurred when of the oxirane ring of Epon 828 reacted with amine group of Jeffamine T-403, so the signal of O-H stretching was observed at 3200-3400  $\text{cm}^{-1}$  which overlapping with signal of N-H stretching. From these spectra, it was found that the signal at 3200-3400  $\text{cm}^{-1}$  increased when concentration of Jeffamine T-403 increased. This may be due to the increase of hydroxyl group from ring opening reaction and the remained of amine function of Jeffamine T-403. The signal of epoxy function was also observed on all samples at 915  $\text{cm}^{-1}$ . This indicated that the oxirane ring remained in all formulae.

Series of FTIR spectra (Figure 4.9) have been obtained to evidence the occurrence of any chemical interaction between Epon 828 epoxy resin and Imicure EMI-24. The absorption signals of all functional groups that found in spectrum of Epon 828 and Imicure EMI-24 were also observed on these spectra. The intense C-H stretching vibrations appeared at 2800-3000  $\text{cm}^{-1}$ . The absorption bands at 1607, 1582, 1510 and 1454  $\text{cm}^{-1}$  represented the C=C (aromatic) stretching. The signals of methylene ( $\text{CH}_2$ -) and methyl ( $\text{CH}_3$ -) carbons were also observed at 1454 and 1385  $\text{cm}^{-1}$ , respectively. When compared the results at different blend ratios, it was found that the signal of  $-\text{C}=\text{N}$  stretching (1454  $\text{cm}^{-1}$ ) increased but the epoxy signal (915  $\text{cm}^{-1}$ ) slightly decreased when increased hardener concentration. It is because Imicure EMI-24 is aromatic amine hardener that has high stability, so the reaction of Imicure EMI-24 with epoxy is hard to occur.

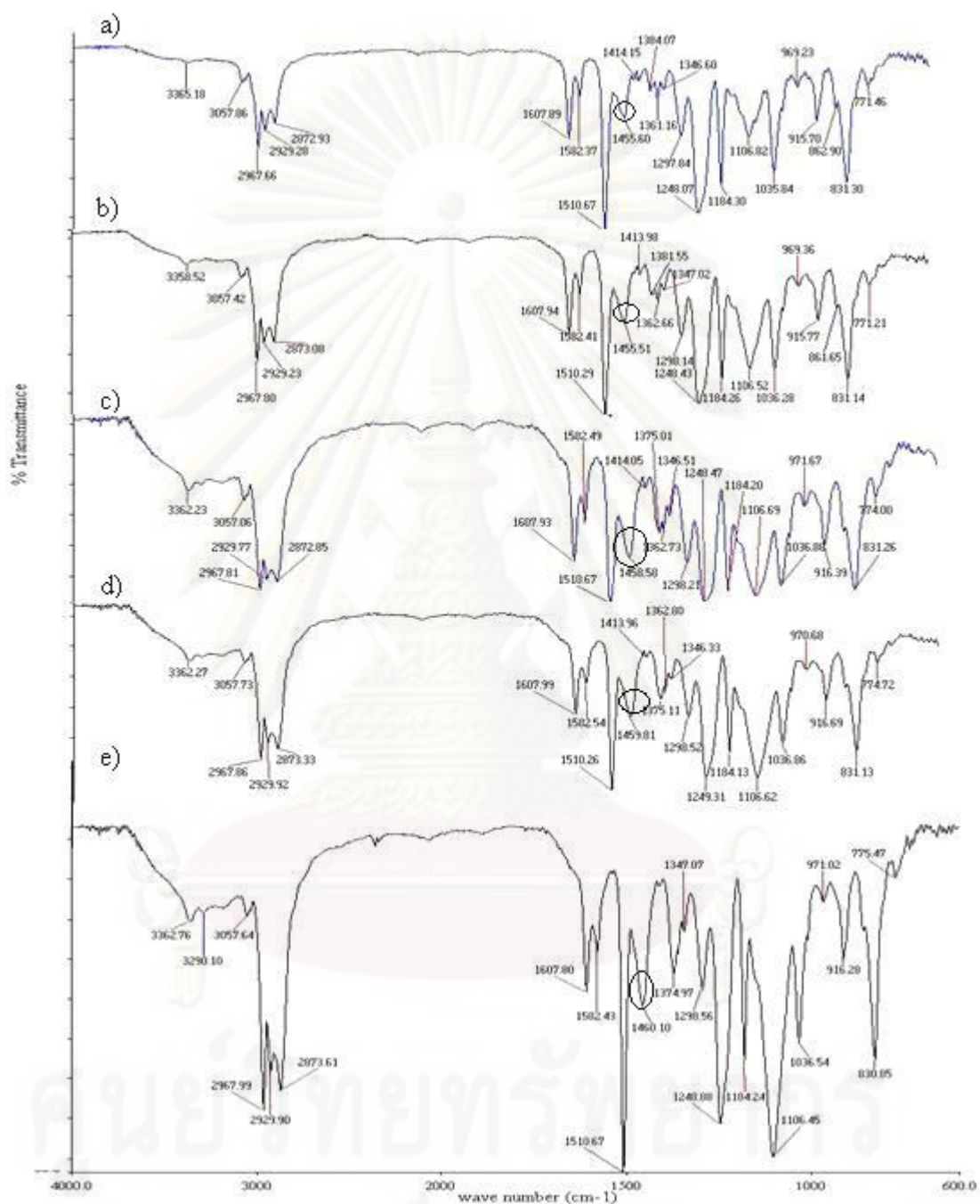


Figure 4.8 FTIR spectra of Epon 828 with Jeffamine T-403 at different ratios; a) 10:2, b)

10:4, c) 10:6, d) 10:8 and e) 10:10



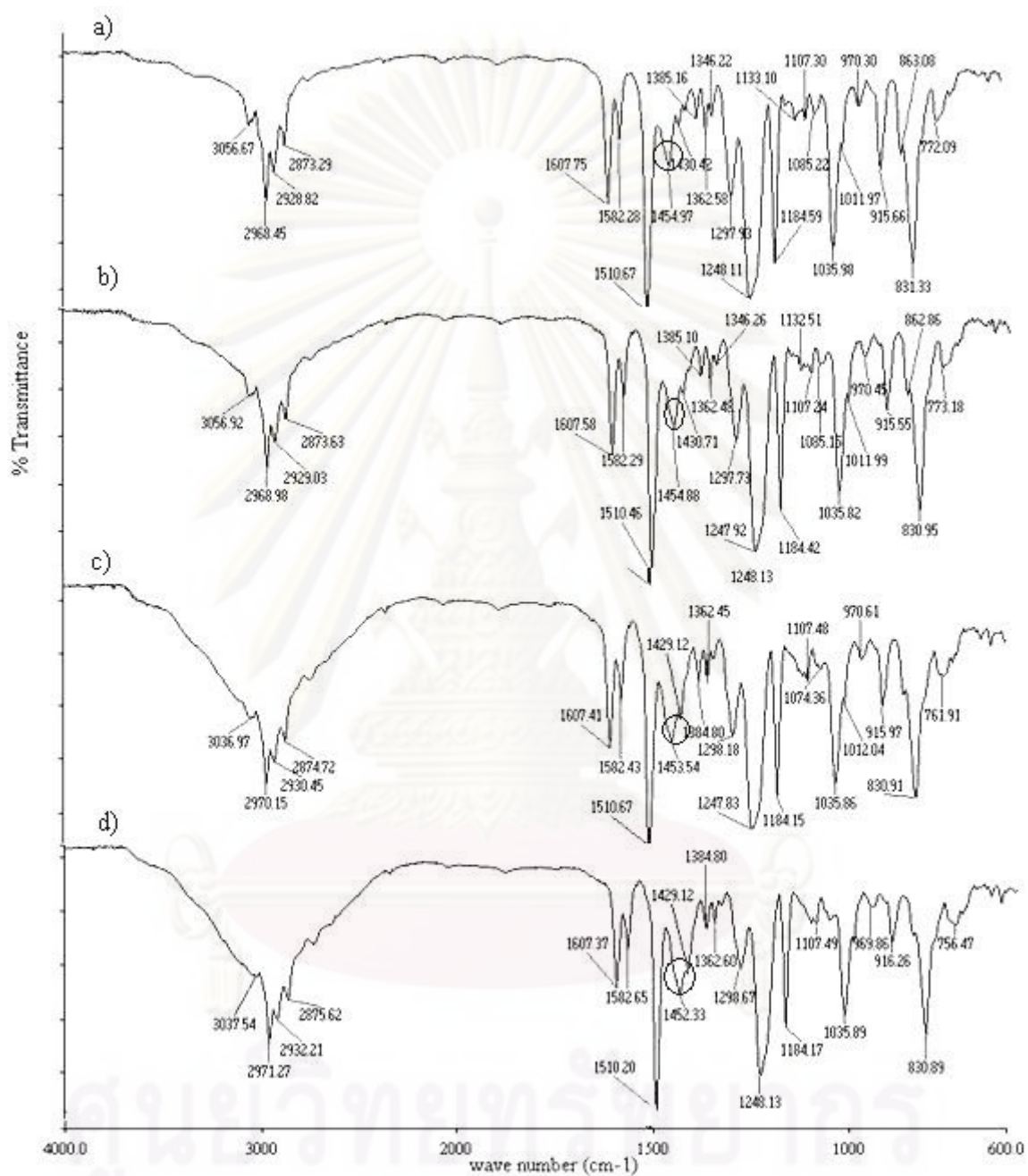


Figure 4.9 FTIR spectra of Epon 828 with Imicure EMI-24 at different ratios; a) 10:1, b)

10:2, c) 10:4 and d) 10:6

The FTIR spectra of Epon 828 mixed with DCA221 in the ratio of 10:2, 10:4, 10:6 and 10:8 are shown in Figure 4.10. The intense C-H stretching vibrations appeared at 2800-3000  $\text{cm}^{-1}$ . The absorption bands at 1607, 1581, 1510 and 1463  $\text{cm}^{-1}$  represented the C=C (aromatic) stretching. The signals of methylene ( $\text{CH}_2$ -) and methyl ( $\text{CH}_3$ -) carbons were also observed at 1463 and 1384  $\text{cm}^{-1}$ , respectively. The absorption signal of O-H stretching at 3360  $\text{cm}^{-1}$  increased with increased amount of DCA221. It is because the ring opening of oxirane ring happened as shown in Scheme 4.3. Moreover, the signals of N-H stretching of primary amine (1581  $\text{cm}^{-1}$ ) and C-O stretching of aliphatic ether (1108  $\text{cm}^{-1}$ ) increased when DCA221 hardener increased.

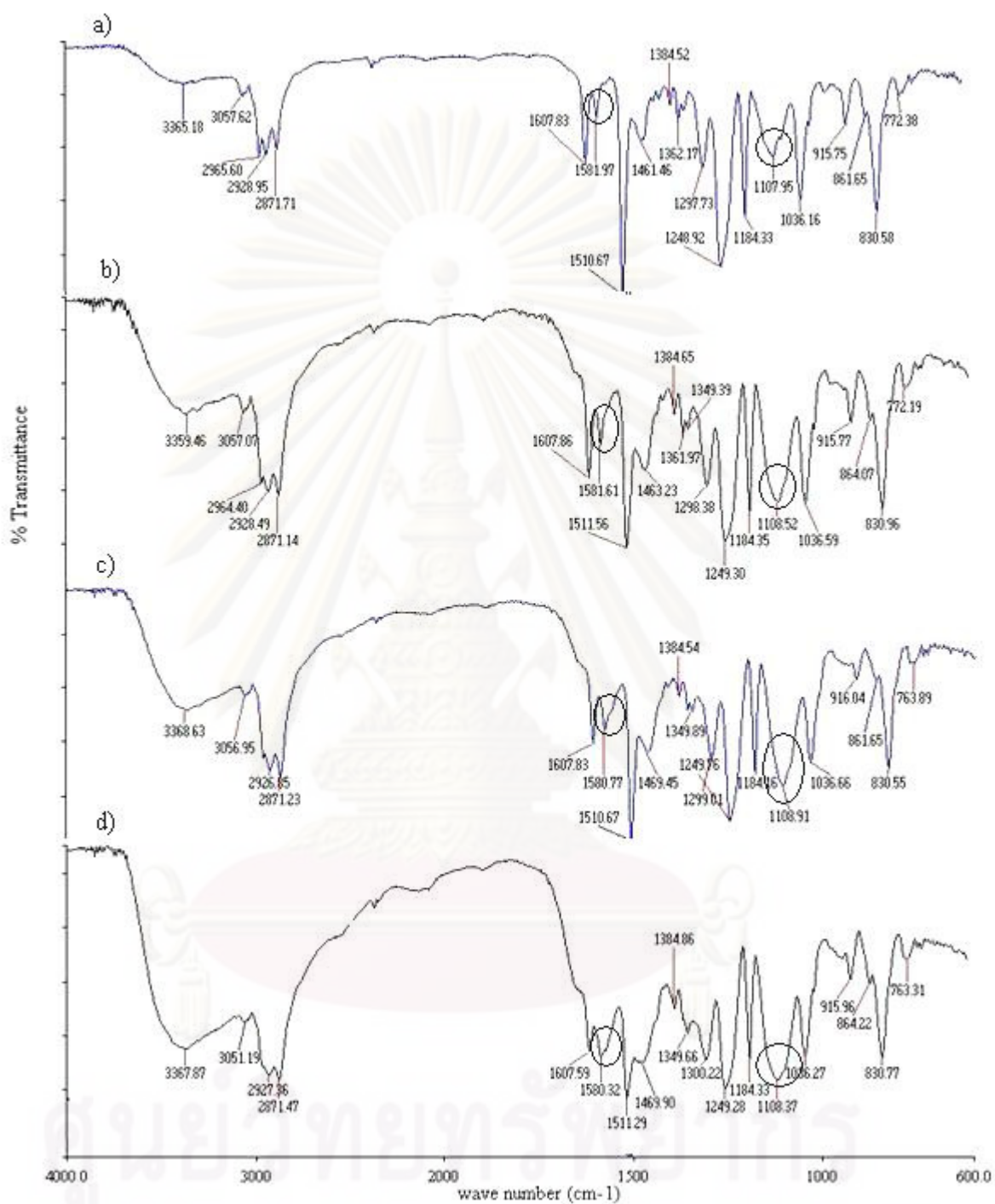


Figure 4.10 FTIR spectra of Epon 828 with DCA221 at different ratios; a) 10:2, b) 10:4, c)

10:6 and d) 10:8

#### 4.2.4 Thermal Properties

The cure of an epoxy resin was controlled by the temperature dependence of both diffusion rate and molecular collision rate which lead to the formation of the network. As cure proceeds, the increasing size and complexity of the epoxy oligomers restrict diffusion, as does the three dimensional connectivity. Glass transition temperatures of epoxy resin that have Epon 828 as based are shown in Table 4.3. It can be seen that the glass transition temperature decreased when hardener content increased. It may be due to the differences in crosslink density [5, 36, 37]. Low molecular weight of epoxy resin, hence the mixture of the Epon 828 with hardener, was obtained when increased hardener concentration. This was due to high amount of active sites of hardener that reaction can be occurred while the amount of resin was fixed. The excess amount of hardener will also act as plasticizing species that will affect to decrease the glass transition temperature. The glass transition temperatures of Epon 828 with three kinds of hardener were compared as shown in Table 4.3. It was found that the glass transition temperature of Epon 828 with Imicure EMI-24 gave the highest value. This was due to the smallest molecular structure of Imicure EMI-24 led to regularity in the structure when crosslink reaction was occurred. For DCA221 system, the glass transition temperature was lower than other hardener. It may be due to the flexible segment in the chemical structure of DCA221.

**Table 4.3** Glass transition temperatures of epoxy resin by using Epon 828 as based resin

Epon 828	Composition (phr)			T <sub>g</sub> (°C)
	Jeffamine T-403	Imicure EMI-24	DCA221	
100	40	-	-	75.17
100	60	-	-	63.00
100	-	40	-	95.97
100	-	60	-	63.98
100	-	-	40	50.45

#### 4.3 Characterization of Epon 862 mixed with Different Kind of Hardeners

Diglycidyl ether of bisphenol F (DGEBF or Epon 862) is one popular type of resin that used for adhesive application. The effect of hardener type and hardener concentration on viscosity, mechanical properties, chemical structure and thermal properties were also studied for Epon 862 system.

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### 4.3.1 Viscosity Testing

The influence of hardener concentration on viscosity of epoxy resin with different kind of hardeners (Jeffamine T-403, Imicure EMI-24 and DCA221) was studied. The results showed in Figure 4.11. The viscosity of mixtures in Jeffamine T-403 and DCA221 systems decreased when the hardener concentration increased. These results were similar to results of Epon 828. The higher amount of hardeners was acted as diluents. Viscosity of epoxy resin with Imicure EMI-24 hardener was increased when hardener content increased. This may be due to the hydrogen bonding that occurred between Epon 862 with Imicure EMI-24.

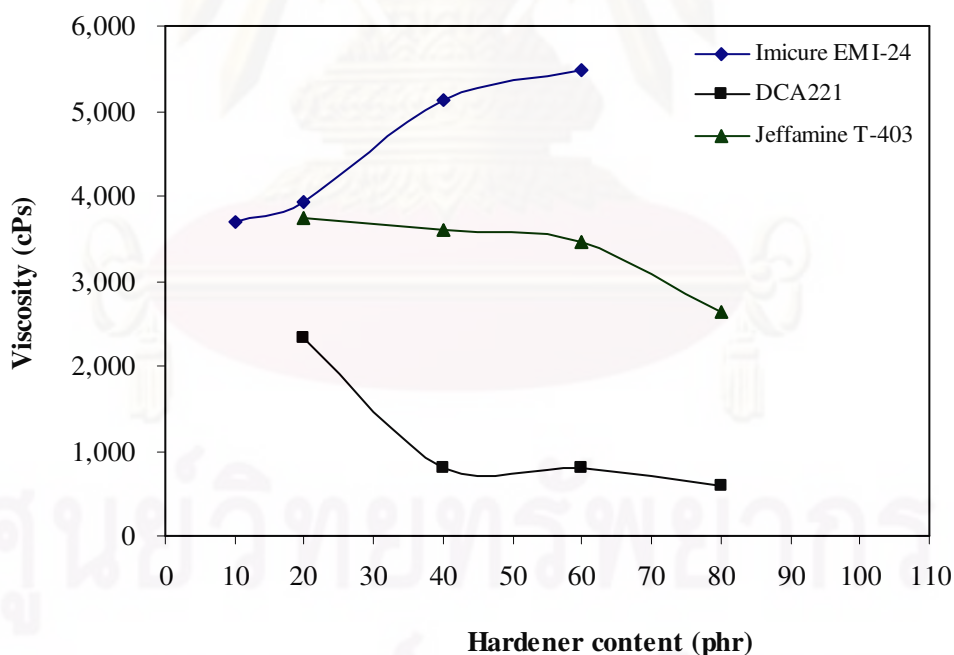


Figure 4.11 Viscosity of Epon 862 with three kinds of hardeners

### 4.3.2 Mechanical Properties

It is known that the mechanical properties of epoxy resin are usually related to the hardener concentration. For this reason, the shear strength of Epon 862 mixed with different hardeners was studied. The results of shear strength are showed in Figure 4.12. It is clearly seen that the shear strength of Epon 862 with Jeffamine T-403 and Imicure EMI-24 showed the bell shape curve with a maximum at 40 and 20 wt% hardener, respectively. For DCA221 system, the shear strength decreased when hardener content increased.

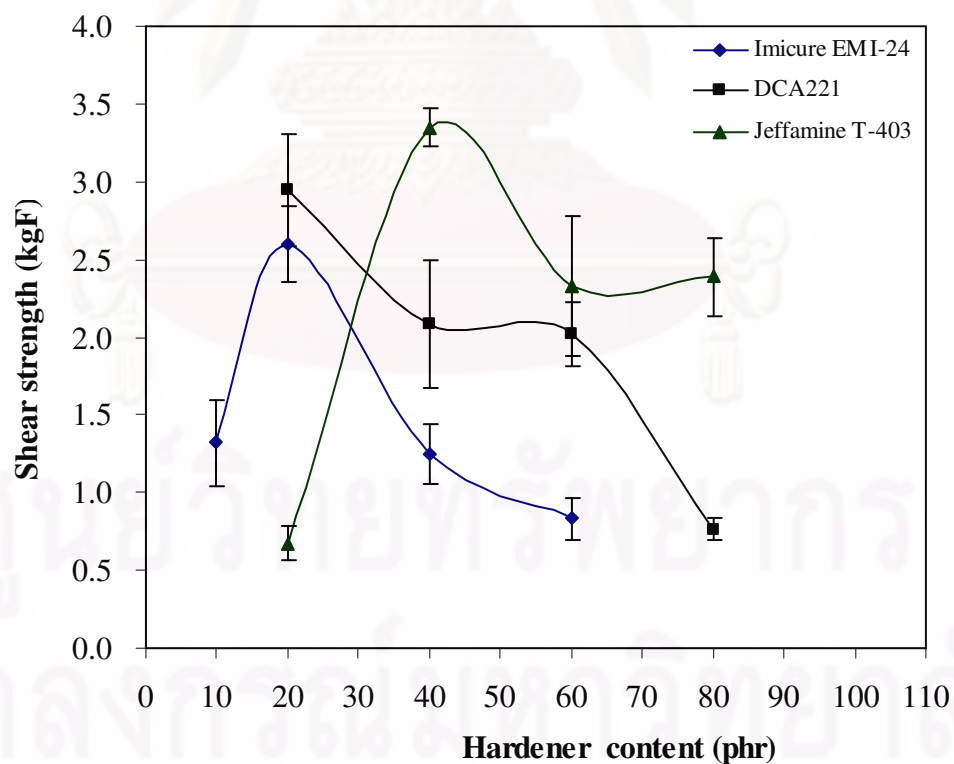


Figure 4.12 Shear strength of Epon 862 with three kinds of hardeners

From Figure 4.12, it can be summarized that Jeffamine T-403 is the hardener that gives the highest shear strength when compared with two other hardeners (Imicure EMI-24 and DCA221). Thus, tensile strength was also measured in Epon862/Jeffamine T-403 system for finding the optimization ratio. From Figure 4.13, it is clearly seen that the tensile strength of Epon 862 increased in the range of Jeffamine T-403 contents from 20 to 40 wt% with a maximum at 40 wt%. The tensile strength was decreased when Jeffamine T-403 content increased from 40 to 60 wt%. When the Jeffamine T-403 content increased up to 80 wt%, the tensile strength was increased. From these results, 40 wt% of Jeffamine T-403 was selected as optimum ratio for Epon 862 system, which was considered from the result of shear strength. This composition was used for further study about the effect of CTBN rubber on mechanical properties of Epon 862.

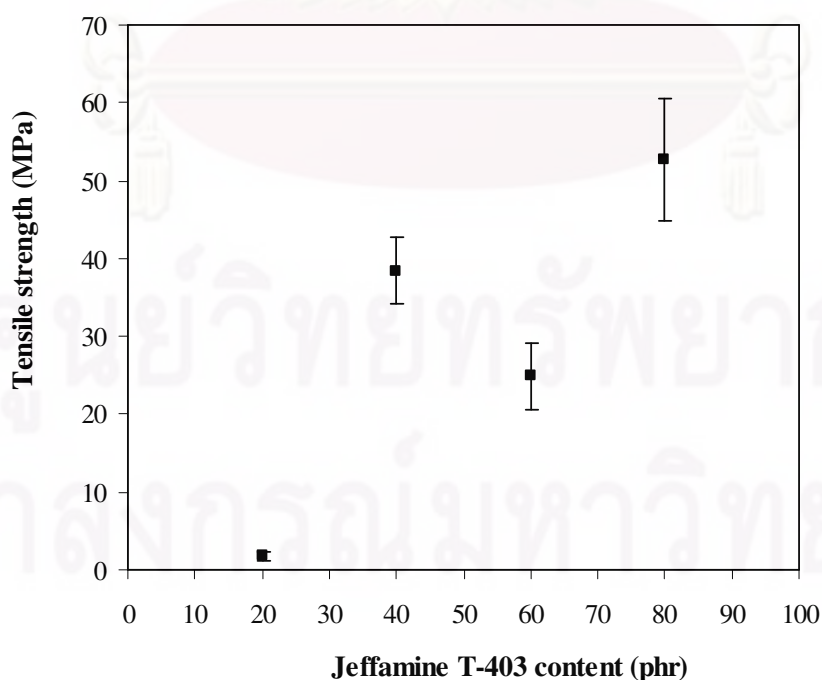


Figure 4.13 Tensile strength of Epon 862 with Jeffamine T-403



The standard deviation of tensile strength results showed the high values. It was due to the difficulty of controlling the spread of epoxy on aluminum plates. In addition, the air bubble that occurred during the curing process is one of the root cause of high standard deviation value of tensile strength values.

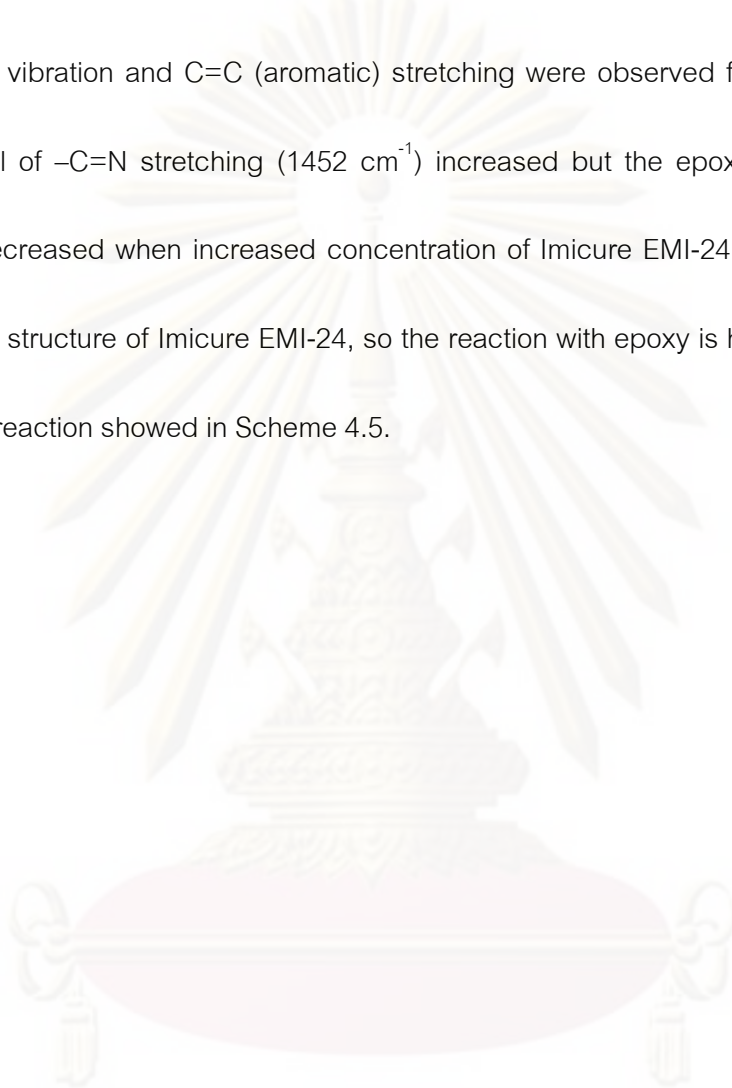
### 4.3.3 Chemical Structure Characterization

Figure 4.14 illustrated the FTIR spectra of neat epoxy resin further to its modification with different Jeffamine T-403 contents (10:2, 10:4, 10:6 and 10:8). The absorption bands at 2800-3000  $\text{cm}^{-1}$  can be ascribed to C-H stretching vibrations. The absorption bands at 1610, 1585, 1509 and 1453  $\text{cm}^{-1}$  represented the C=C (aromatic) stretching. The signal of methylene ( $\text{CH}_2$ -) from Epon 862 and Jeffamine T-403 was also observed at 1453  $\text{cm}^{-1}$ . The signal of methyl ( $\text{CH}_3$ -) group from Jeffamine T-403 hardener was also found 1375  $\text{cm}^{-1}$ . It is interesting to note that the absorption of hydroxyl group at 3200-3400  $\text{cm}^{-1}$  increased when hardener concentration increased. The increased in hydroxyl intensity peak has been attributed to the following factors: first the reaction between the amine group of Jeffamine T-403 and the oxirane ring of epoxy resin (as showed in Scheme 4.4), second the unreacted amine group of hardener absorbing at the same wave number as hydroxyl group. On the other hand, the absorption of unreacted epoxy group at about 916  $\text{cm}^{-1}$  was also detected.

The FTIR spectra of Epon 862 with Imicure EMI-24 are shown in Figure 4.15.

These results are similar to results of Epon 828 with Imicure EMI-24. The intense C-H stretching vibration and C=C (aromatic) stretching were observed for all compositions.

The signal of  $\text{-C=N}$  stretching ( $1452\text{ cm}^{-1}$ ) increased but the epoxy signal ( $915\text{ cm}^{-1}$ ) slightly decreased when increased concentration of Imicure EMI-24. It was due to high stability of structure of Imicure EMI-24, so the reaction with epoxy is hard to happen. The chemical reaction showed in Scheme 4.5.



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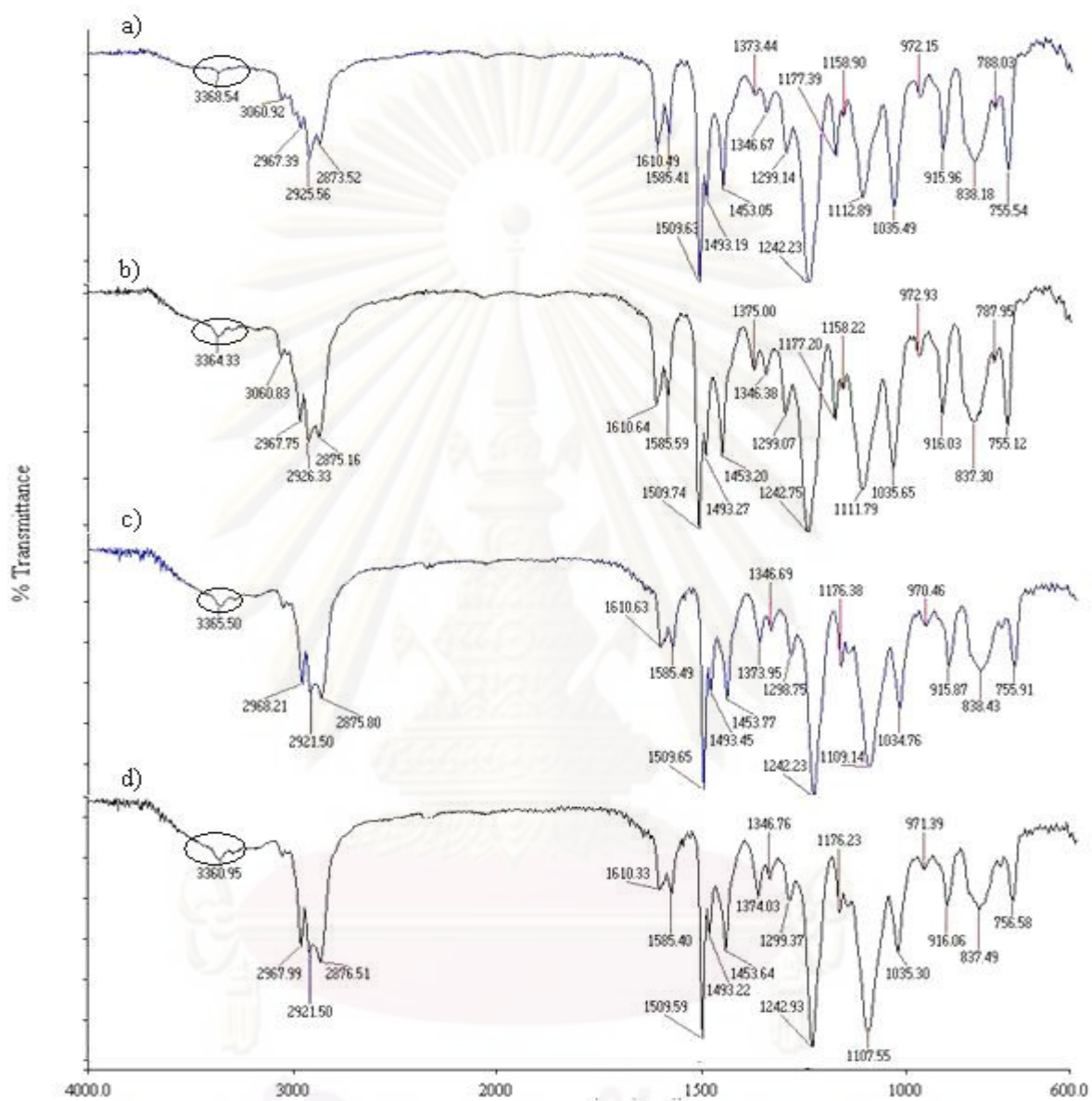
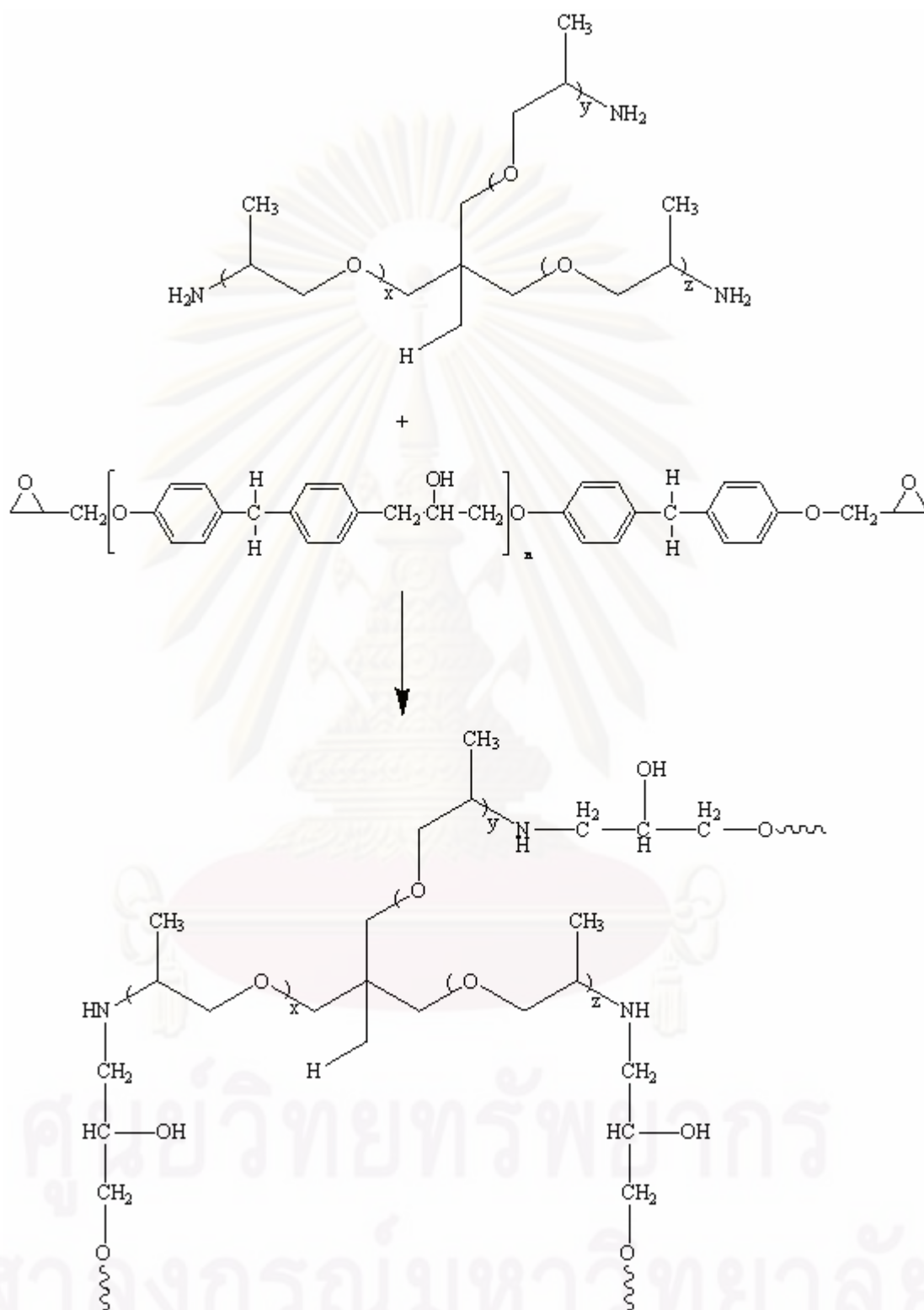


Figure 4.14 FTIR spectra of Epon 862 with Jeffamine T-403 at different ratios; a) 10:2, b)

10:4, c) 10:6 and d) 10:8



Scheme 4.4 Proposed chemical reaction between Epon 862 and Jeffamine T-403

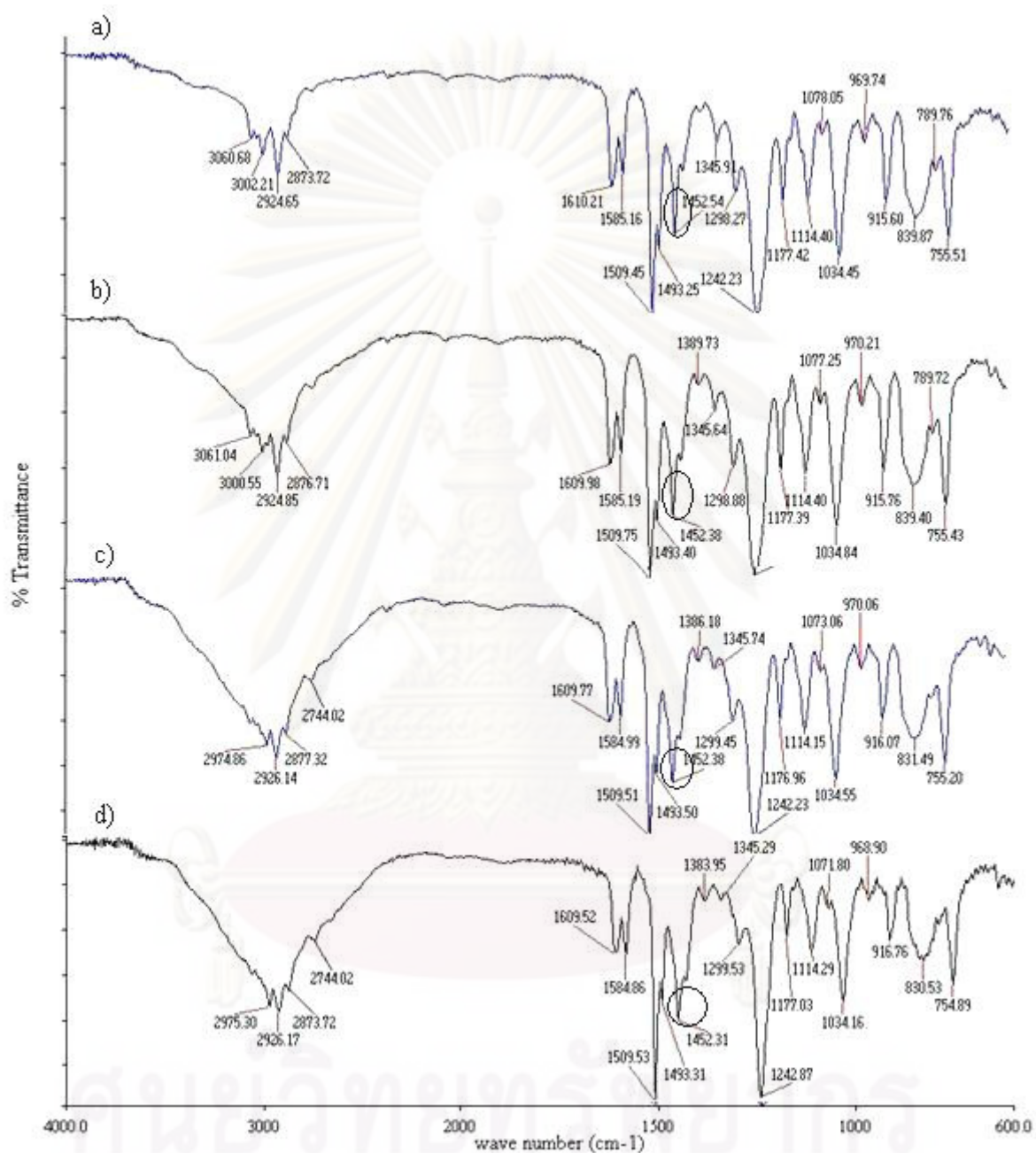
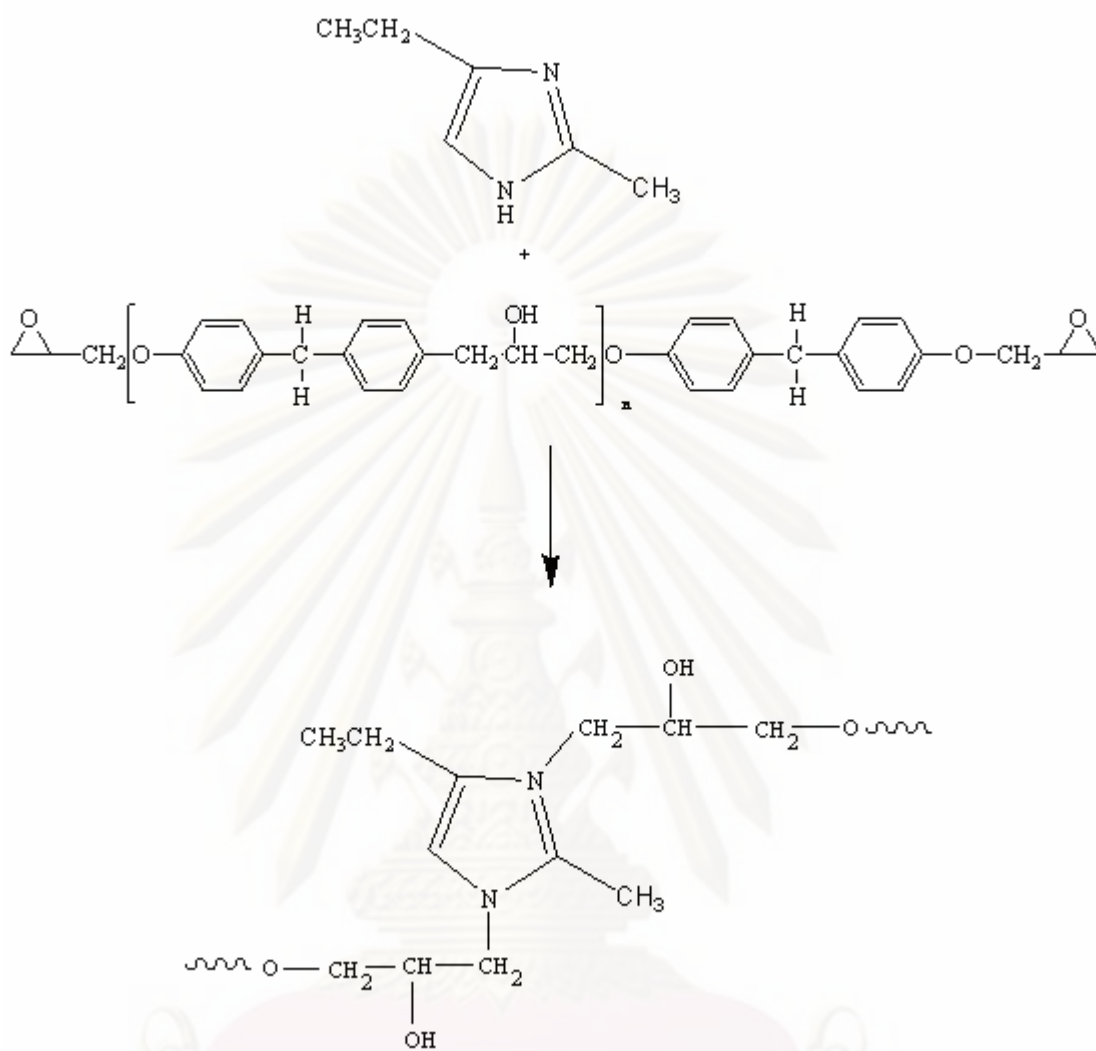


Figure 4.15 FTIR spectra of Epon 862 with Imicure EMI-24 at different ratios a) 10:1, b)

10:2, c) 10:4 and d) 10:6



Scheme 4.5 Proposed chemical reaction between Epon 862 and Imicure EMI-24

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The FTIR spectra for Epon 862 mixed with DCA221 are shown in Figure 4.16.

The C-H stretching, C=C (aromatic) stretching, methylene (CH<sub>2</sub>-) and methyl (CH<sub>3</sub>-) carbons were observed on all spectra. When increased DCA221 hardener content, the absorption signal of O-H stretching (at 3369 cm<sup>-1</sup>) increased, that might indicate the formation of chemical reaction between oxirane ring of epoxy and amine of hardener (as showed in Scheme 4.6). In addition, the signals of N-H stretching of primary amine (1581cm<sup>-1</sup>) and C-O stretching of aliphatic ether (1113 cm<sup>-1</sup>) were increased.



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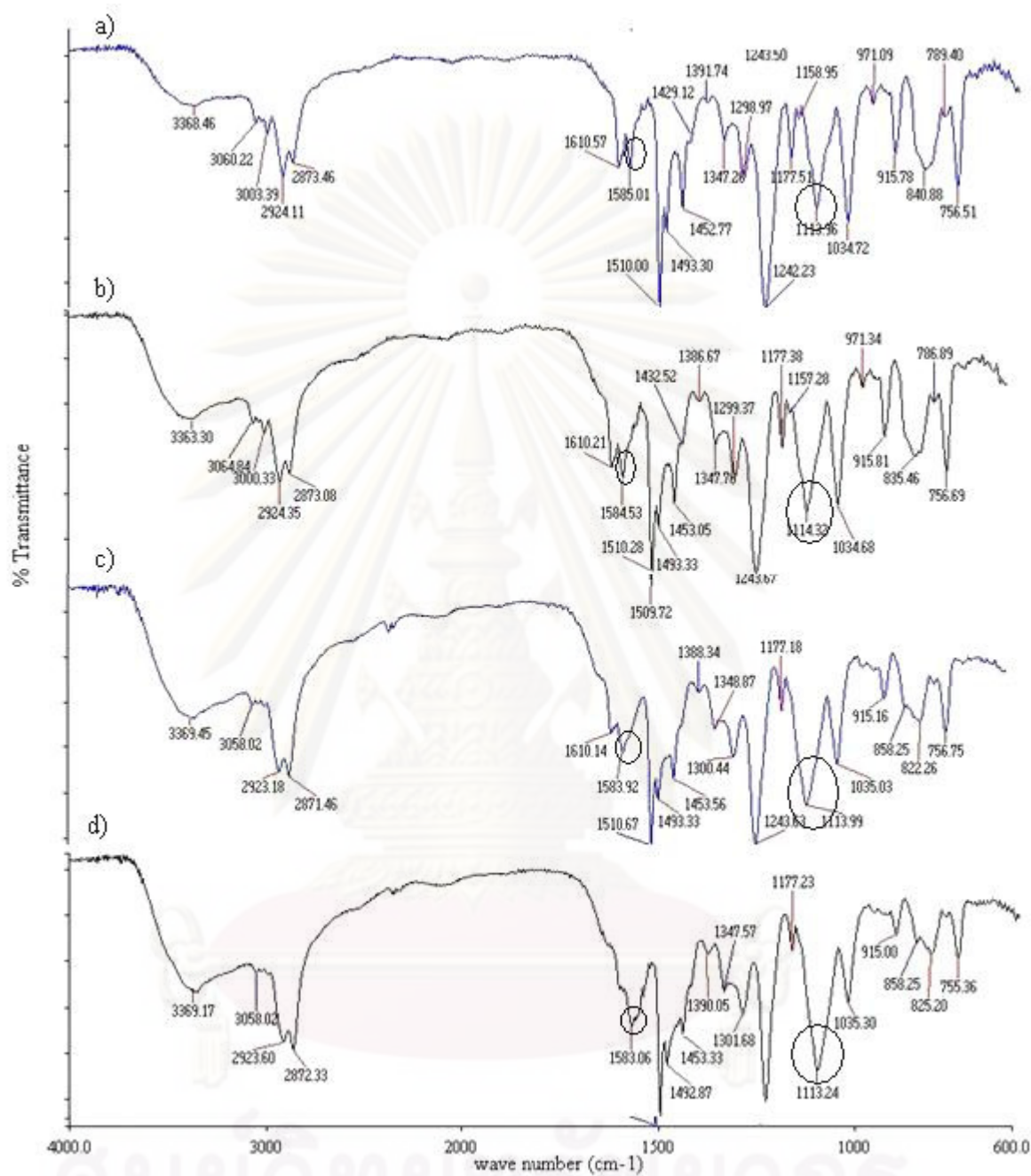
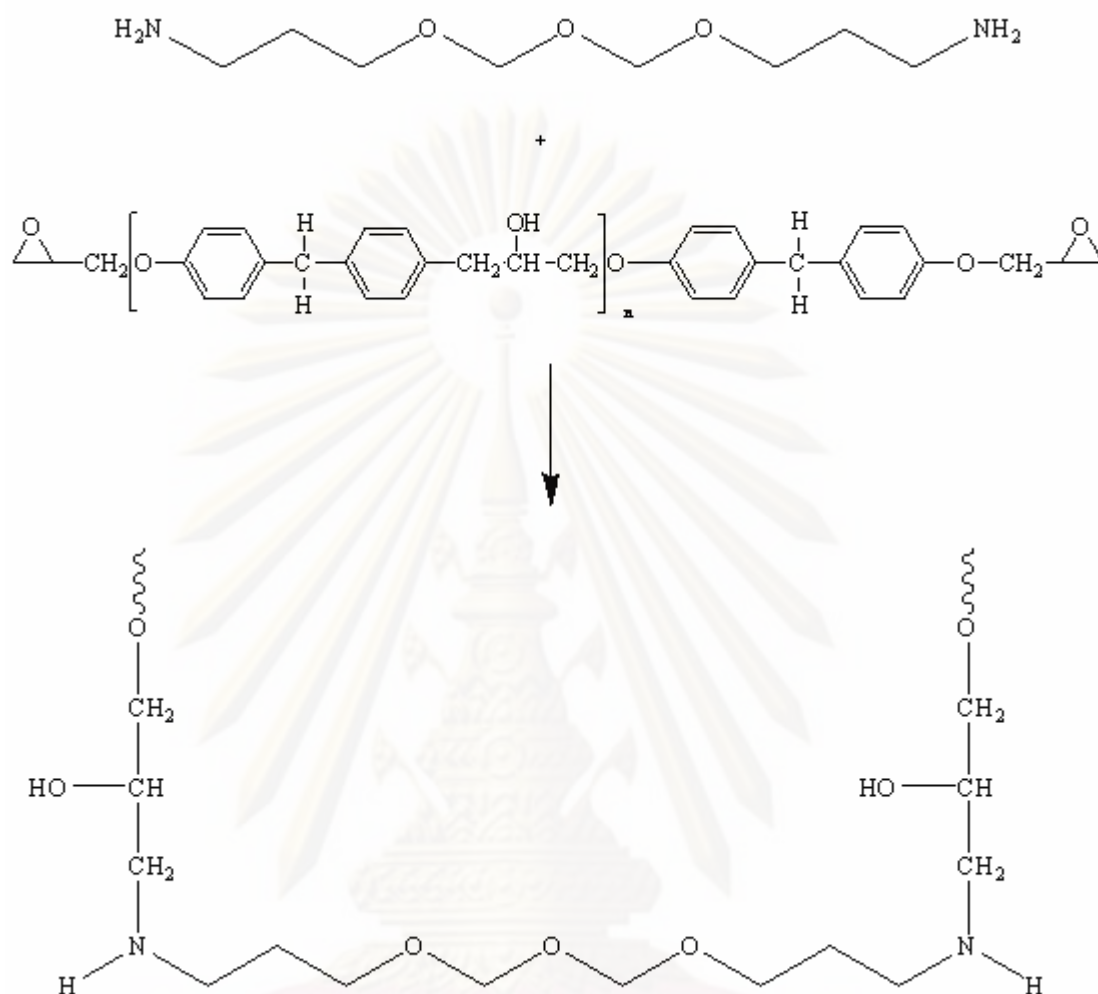


Figure 4.16 FTIR spectra of Epon 862 with DCA221 at different ratios; a) 10:2, b) 10:4, c) 10:6 and d) 10:8





Scheme 4.6 Proposed chemical reaction between Epon 862 and DCA221

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#### 4.3.4 Thermal Properties

Table 4.4 illustrates the dependence of glass transition temperature over a range of hardener concentration for Epon 862/Jeffamine T-403, Epon 862/Imicure EMI-24 and Epon 862/DCA221. The results show same trend as Epon 828 system. The decrease of glass transition temperature was due to low molecular weight of epoxy resin that occurred when hardener concentration increased. The increase of excess amount of hardener was also act as plasticizer. The glass transition temperatures of Epon 862 with three kinds of hardener were compared as shown in Table 4.4. It was found that the glass transition temperature of Epon 862 with Imicure EMI-24 gave the highest value. This was due to the smallest molecular structure of Imicure EMI-24 led to regularity in the structure when crosslink reaction was occurred. For DCA221 system, the glass transition temperature was lower than that other hardener. It may be due to the flexible segment in the chemical structure of DCA221. The results show same trend as Epon 828 system.

According to the results in Part I, Jeffamine T-403 was the best hardener for both types of resins (Epon 828 and Epon 862). The optimum ratio of Epon 828 to Jeffamine T-403 is 100: 80 wt%, while the optimum ratio of Epon 862 to Jeffamine T-403 is 100: 40 wt%, respectively. This optimum composition showed good mechanical properties were different for both types of resins.

Table 4.4 Glass transition temperatures of epoxy resin by using Epon 862 as based resin

Epon 862	Composition (phr)			Tg (°C)
	Jeffamine T-403	Imicure EMI-24	DCA221	
100	40	-	-	57.88
100	60	-	-	54.84
100	-	20	-	128.68
100	-	40	-	95.63
100	-	60	-	66.32
100	-	-	20	50.31
100	-	-	40	49.08

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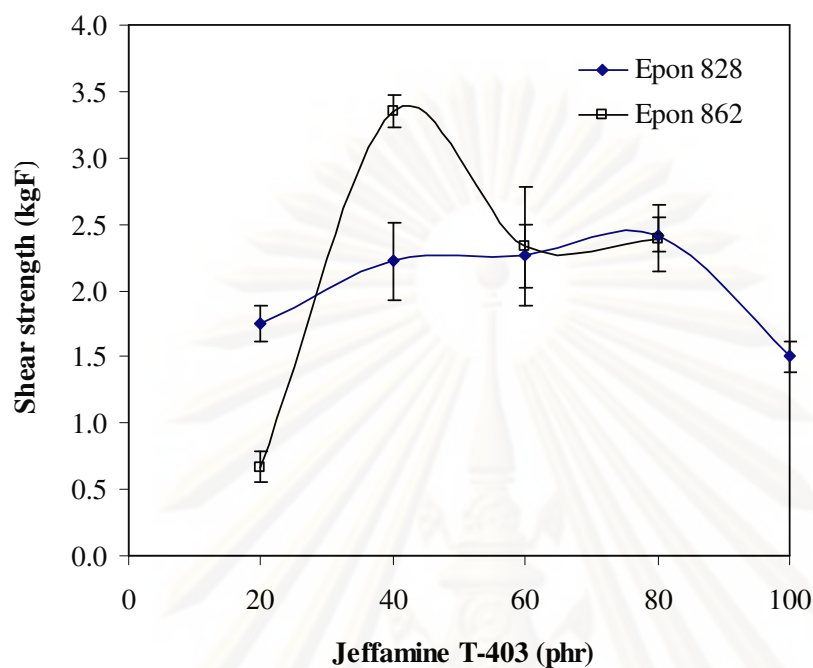


Figure 4.17 The comparison of shear strength between Epon 828 with Jeffamine T-403 and Epon 862 with Jeffamine T-403

For electronic and fiber optic applications, shear strength is the main property that used to select type of epoxy resin for bonding. From previous results, Jeffamine T-403 is the hardener that gives the highest shear strength for both epoxy resins. The best shear strength was obtained at 40 wt% for Epon 862/Jeffamine T-403. The comparison of shear strength between Epon 828 with Jeffamine T-403 and Epon 862 with Jeffamine T-403 shows in Figure 4.17. In the future, EU will ban Bisphenol F compound which include Epon 862. Thus Epon 828 (Bisphenol A) is the other choice that can use instead of Epon 862.

## Part II Epoxy resins with CTBN Rubber

Rubbers generally affect to the mechanical properties of epoxy resins depending on their compatibility with epoxy matrix, the surface area of contact, particle size, shape and content as well as the intrinsic strength of the rubber phase [28]. It is also well known that in order to toughen epoxy resin with liquid polymer, first, the liquid polymer should form a rubbery second phase which is dispersed throughout the matrix and second, the rubbery second phase should be bonded to the matrix through the functional groups of the liquid polymer. In this work, we analyze the effect of CTBN rubber content that added to Epon 828 and Epon 862 epoxy resin on the mechanical properties, morphology and thermal properties.

### 4.4 Viscosity of CTBN Modified Epoxy Resin

Figure 4.18 shows a comparison of the viscosity of CTBN modified two types epoxy resins (Epon 828 and Epon 862) with different rubber concentrations at 25°C. The presence of CTBN rubber into the both epoxy matrices induced an increase of viscosity of unmodified resins. These results are similar to the works carried out with CTBN modified DGEBA-DGEBF (Epikote 235) mixed epoxy resin [9] and carboxyl-terminated poly(2-ethyl hexyl acrylate) (CTPEHA) liquid rubber modified DGEBA (Araldite LY 556)

[35]. They also proposed that the polymerization rate should be increased when rubber content increased, which influence negatively the wetting resin [9].

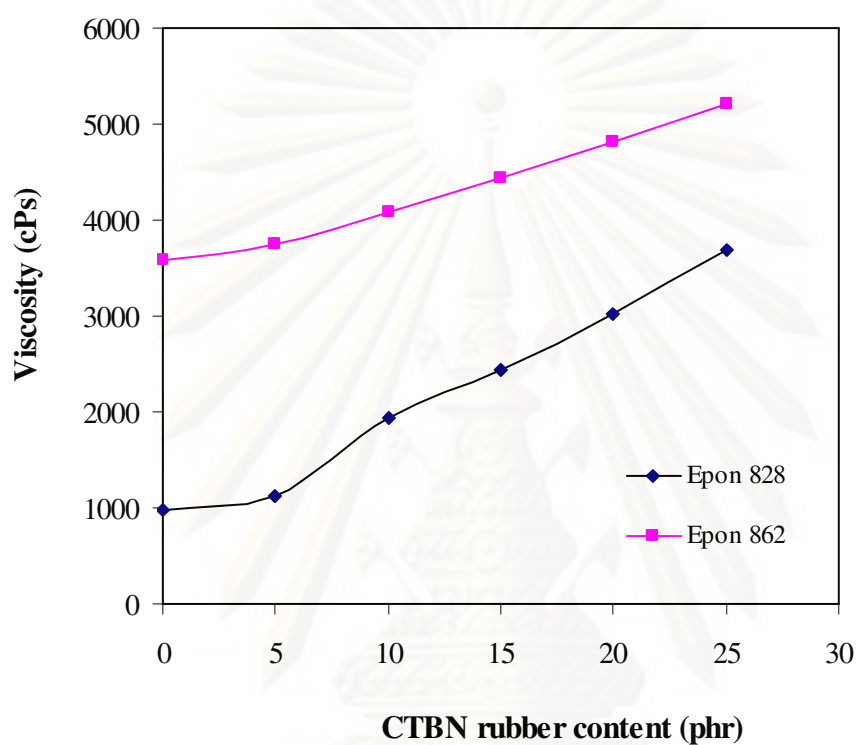


Figure 4.18 Viscosity of CTBN modified Epon 828 and Epon 862

#### 4.5 Mechanical Properties of Epoxy Resin with CTBN Rubber

Shear strength and tensile strength of Epon 828 and Epon 862 with Jeffamine T-403 and CTBN rubber (liquid rubber) blend are plotted with the variation of CTBN content in the blend samples as seen in Figures 4.19 and 4.20, respectively. The shear strength and tensile strength of modified resins decreased when CTBN rubber was

added in blend systems. This was due to the phase separation of CTBN rubber from epoxy matrix (as seen in the section 4.7 observed by SEM technique). From Figure 4.19, at the 20 phr of CTBN, the shear strength showed the highest value, which means that it likely absorbed greater shear force. It was due to CTBN particles acting as a shear force absorber. Higher amount of CTBN rubber, higher shear strength values were observed. However, CTBN rubber content increased up to 25 phr, the shear strength decreased clearly for Epon 862 system. It may be due to the liquid rubber flexibilized the epoxy matrix and reduced the crosslink density. A gradual fall in tensile strength was noted as CTBN rubber was added to blend system as shown in Figure 4.20. The results of the mechanical properties indicated that the cured resin containing CTBN ranging in between 15 to 20 phr showed the best balance of properties. The optimum shear strength was found at 20 phr of CTBN rubber whereas CTBN rubber increased from 15 to 20 phr, the tensile strength was slightly decreased.

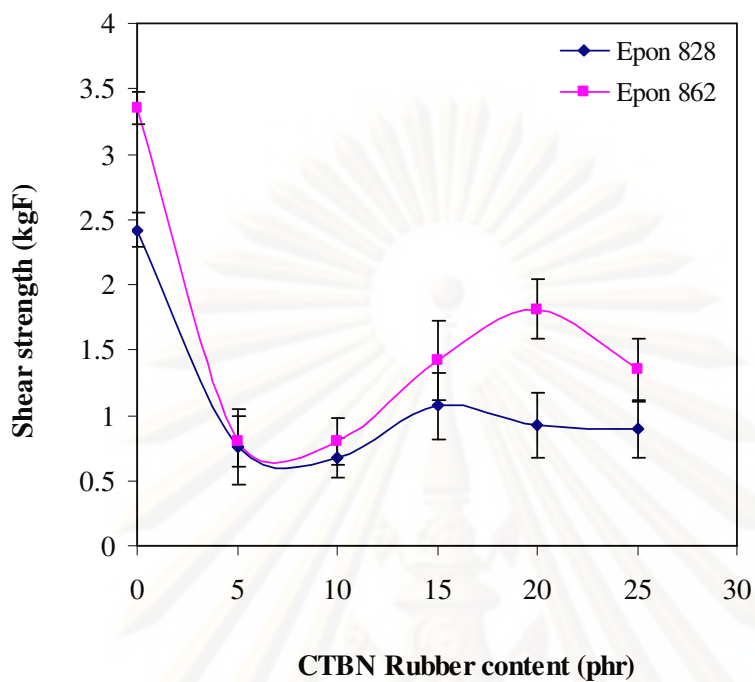


Figure 4.19 Shear strength of epoxy resin with Jeffamine T-403 and CTBN rubber

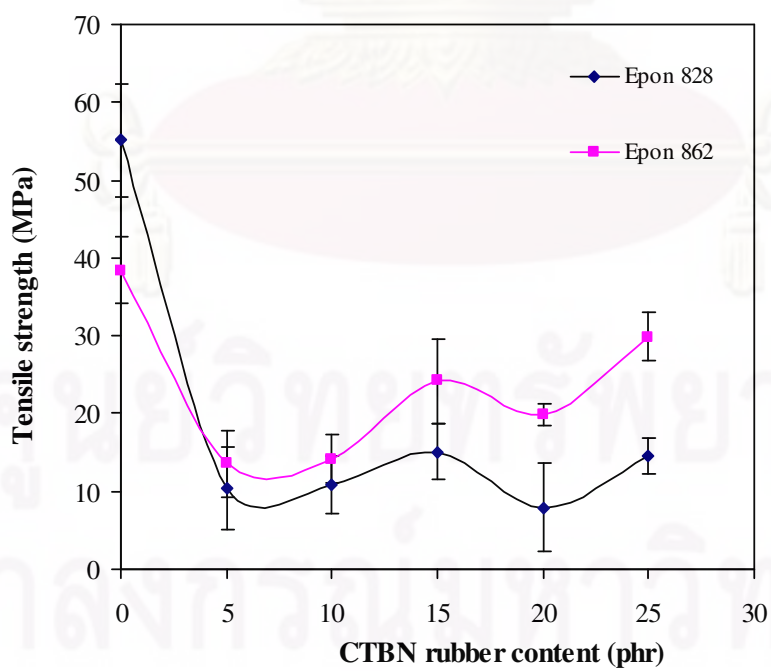


Figure 4.20 Tensile strength of epoxy resin with Jeffamine T-403 and CTBN rubber



#### 4.6 FTIR Analysis of Epoxy Resin with CTBN Rubber

Chemical structure of CTBN rubber that used in this study was clarified by FTIR technique. The FTIR spectrum of CTBN rubber was compared with FTIR spectra of epoxy resins as showed in Figures 4.21 and 4.22. A sharp  $\text{-C}\equiv\text{N}$  peak was observed at  $2237\text{ cm}^{-1}$ . Absorption signals of C-H stretching were detected at  $2922$  and  $2847\text{ cm}^{-1}$ . Extra absorption signals at  $1739$  and  $1712\text{ cm}^{-1}$ , can be assigned to C=O stretching. This evidence can therefore be used to confirm the chemical structure of CTBN rubber.

The FTIR spectra of Epon 828 and Epon 862 with Jeffamine T-403 at different CTBN rubber concentrations were showed in Figures 4.21 and 4.22, respectively. It was found that the addition of CTBN rubber into both epoxy resins (either Epon 828 or Epon 862) caused the chemical interaction between oxirane ring of epoxy and carboxyl functional group of CTBN rubber as showed in Scheme 4.7. The signals of cyano function ( $\text{-C}\equiv\text{N}$ ) and carboxyl (C=O) stretching were not detected on Figures 4.21 and 4.22, which is similar to result obtained for CTBN rubber added to diglycidyl ether of bisphenol A (DGEBA) epoxy resin that has 4,4'-diamino diphenyl sulphone (DDS) as hardener [6]. It has been reported that the complete disappearance of these peaks is possibility due to the utilization of cyano function in the network modification [38]. From Scheme 4.7, the carboxyl functionality of CTBN reacted with the secondary hydroxyl groups of the epoxy resin to form diester. Similarly, the carboxyl groups can also react

with the epoxide group to generate a diester. Thus, a large excess of bisepoxy resin resulted and the rubber being encapped at both ends by one unit of epoxy. Further reaction of the rubber containing diepoxide may be occurred with the unreacted epoxy. A three dimensional network structure was obtained due to the overall reactions.



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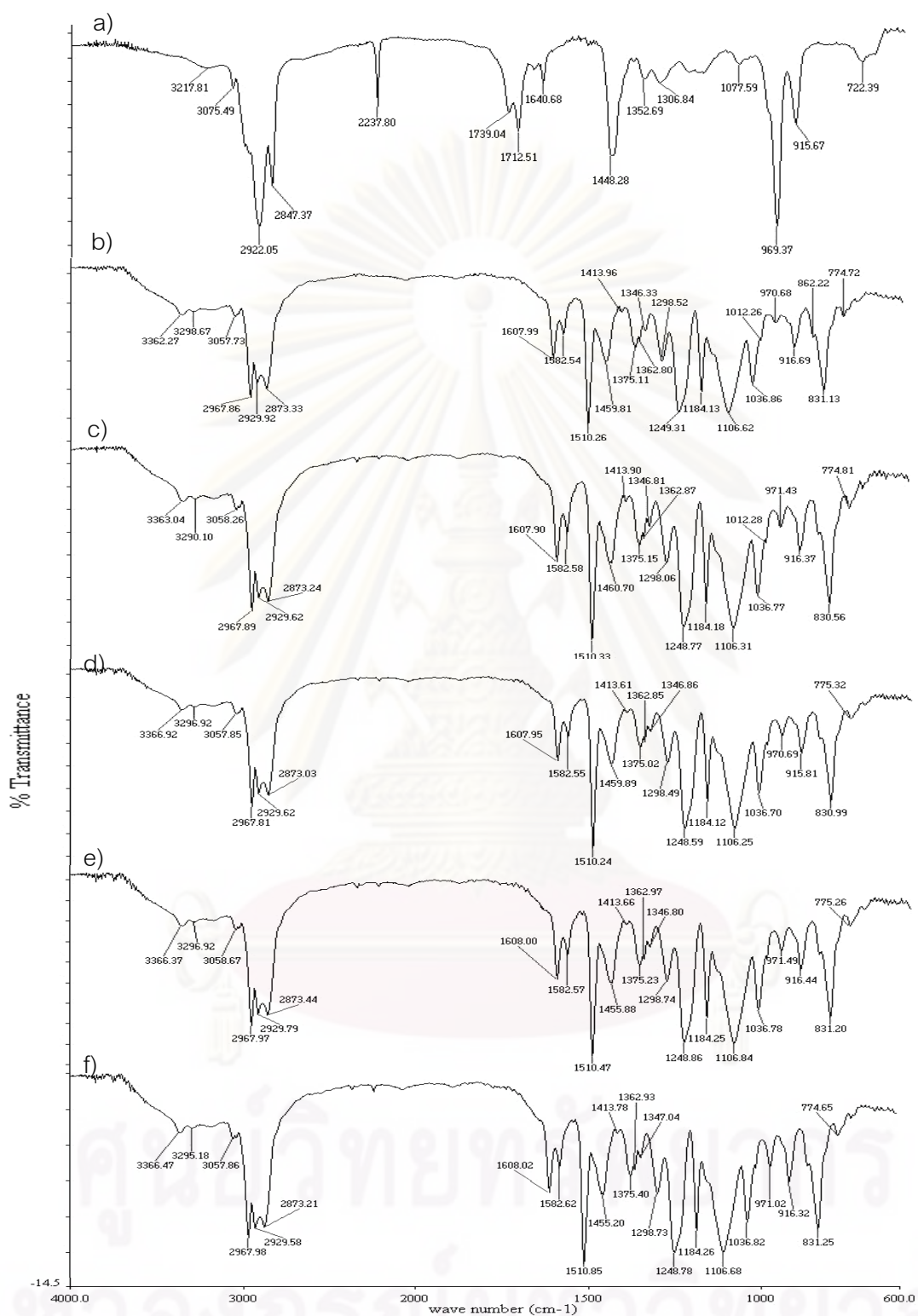


Figure 4.21 FTIR spectra of a) CTBN rubber and Epon 828 with Jeffamine T-403 (10:8) and CTBN rubber at different ratios: b) 5 phr, c) 10 phr, d) 15 phr, e) 20 phr and f) 25 phr

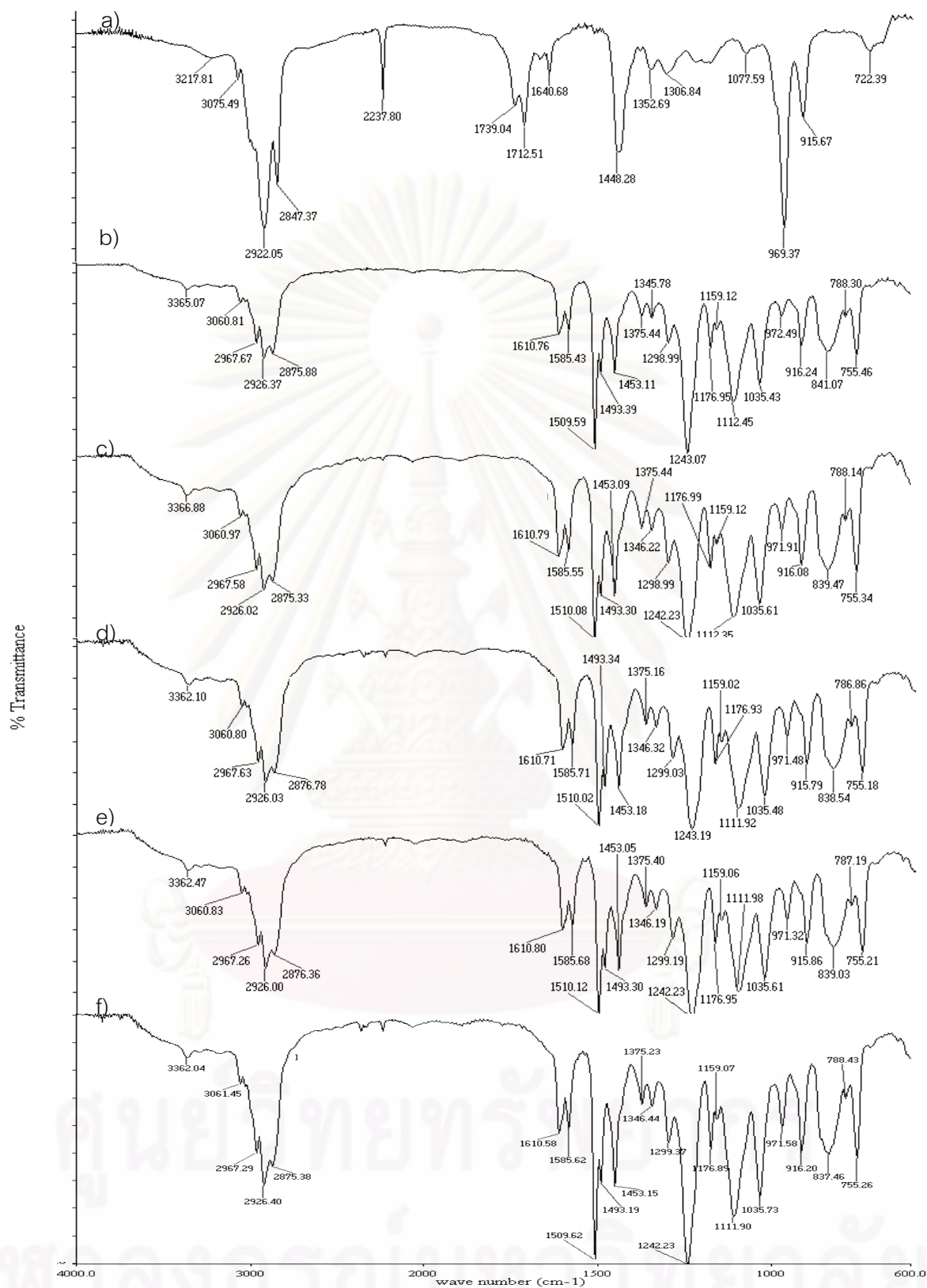
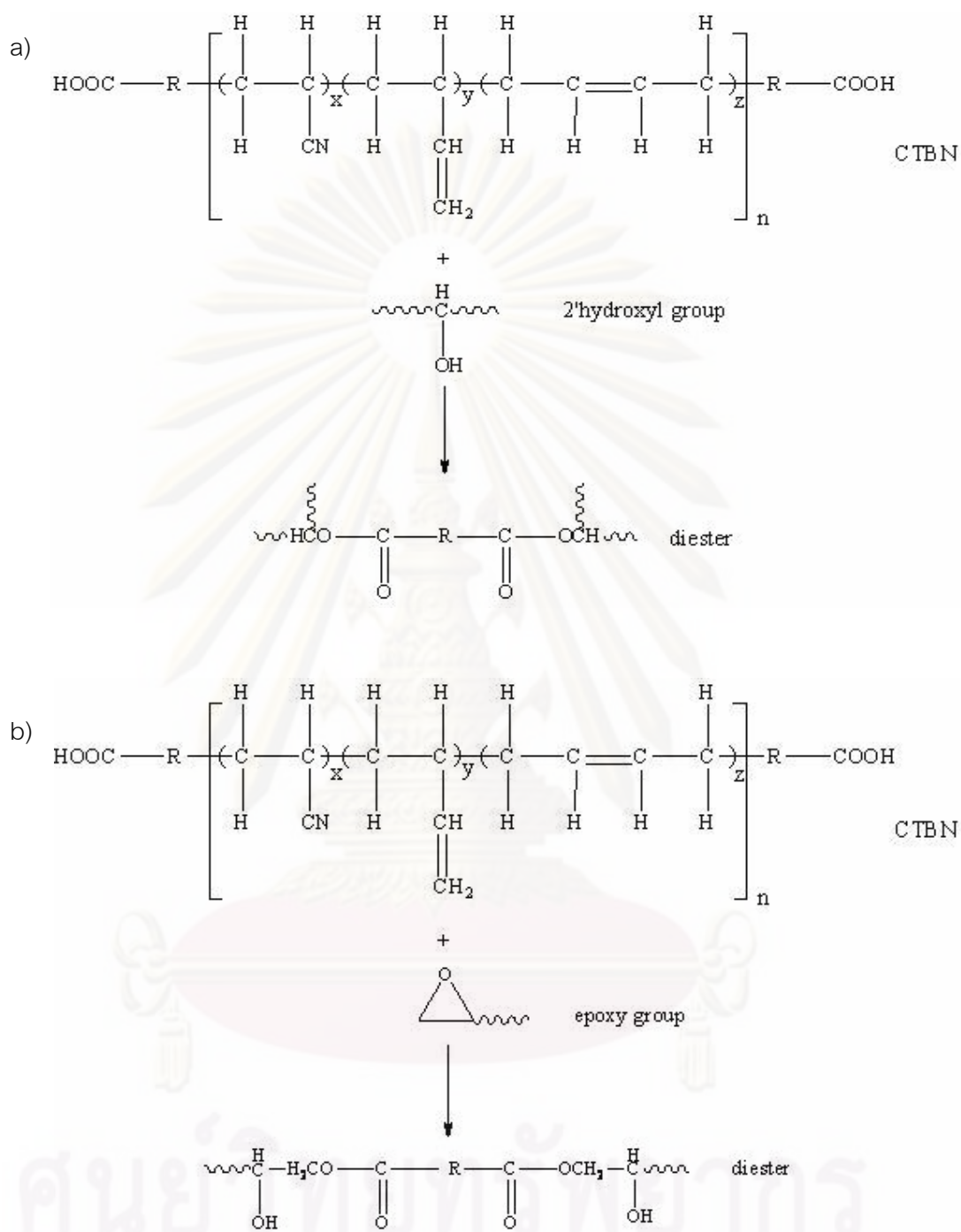


Figure 4.22 FTIR spectra of a) CTBN rubber and Epon 862 with Jeffamine T-403 (10:4) and CTBN rubber at different ratios: b) 5 phr, c) 10 phr, d) 15 phr, e) 20 phr and f) 25 phr



Scheme 4.7 Curing reaction of CTBN rubber with epoxy resin: a) CTBN reacted with

2'hydroxyl group of ring opening of epoxy resin and b) CTBN reacted with epoxy group

of epoxy resin

#### 4.7 Morphology of Epoxy Resin with CTBN Rubber

Figure 4.23 and 4.24 showed the SEM micrographs of the fractured surface of CTBN modified epoxy matrices (either Epon 828 or Epon 862) after extracting the CTBN rubber by using toluene. It is clearly seen that the increase CTBN, the increase porosity in epoxy matrices was obtained. Both epoxy matrices were not compatible with CTBN rubber, phase separation of CTBN rubber particles in epoxy matrices was observed. The size of precipitated rubber particles increased with increasing rubber content in the formulation. The increase of rubber particle size was due to the agglomeration or coalescence of dispersed rubber particles [6].

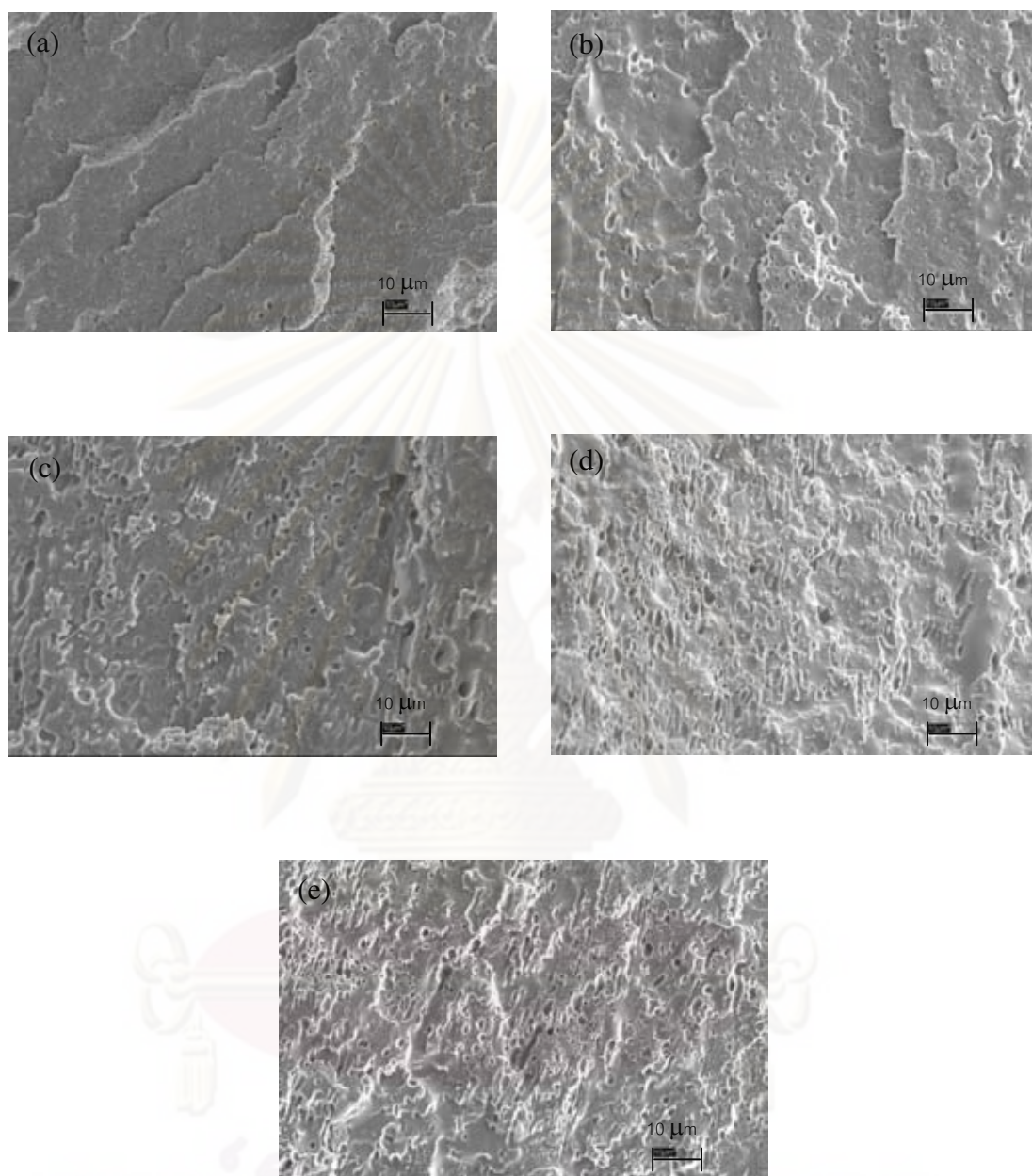


Figure 4.23 SEM micrographs of Epon 828 with Jeffamine T-403 as hardener (100:80

wt%) at (a) 5 phr of CTBN, (b) 10 phr of CTBN, (c) 15 phr of CTBN, (d) 20 phr of CTBN

and (e) 25 phr of CTBN at magnification x1000

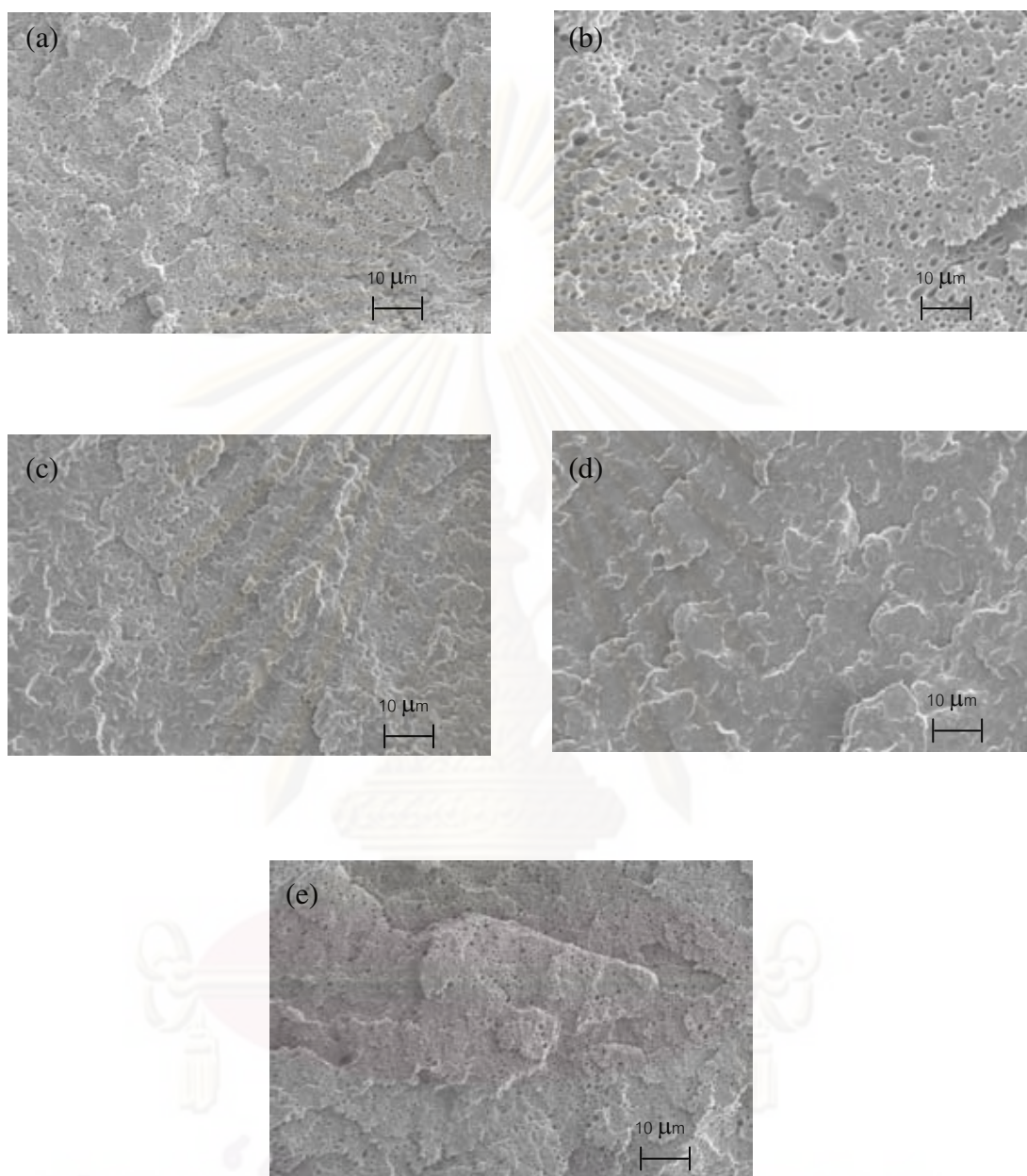


Figure 4.24 SEM micrographs of Epon 862 with Jeffamine T-403 as hardener (100:40 wt%) at (a) 5 phr of CTBN, (b) 10 phr of CTBN, (c) 15 phr of CTBN, (d) 20 phr of CTBN and (e) 25 phr of CTBN at magnification x1000



The particle size distribution at different compositions were calculated by calculation program and the results showed in Figure 4.25 and Figure 4.26 for Epon828 with Jeffamine T-403 is 100: 80 wt% with CTBN rubber and Epon 862 with Jeffamine T-403 is 100: 40wt% with CTBN rubber, respectively. From Figure 4.25, the particle size distribution of CTBN rubber in dispersed phase increased as the amount of rubber was increased, i.e., when CTBN rubber content was increased from 5 to 25 phr, the average particle size was increased two times from 1.4 to 2.8  $\mu\text{m}$ . The possibility of coalescence of CTBN at high rubber content is higher than that at low rubber content.

Figure 4.26 shows the particle size distribution of fracture surfaces of Epon 862/Jeffamine T-403/CTBN rubber by using various amounts of CTBN rubber. The average particle sizes were higher than 1 micron and comparatively higher than in case of Epon 828/ Jeffamine T-403/CTBN rubber.

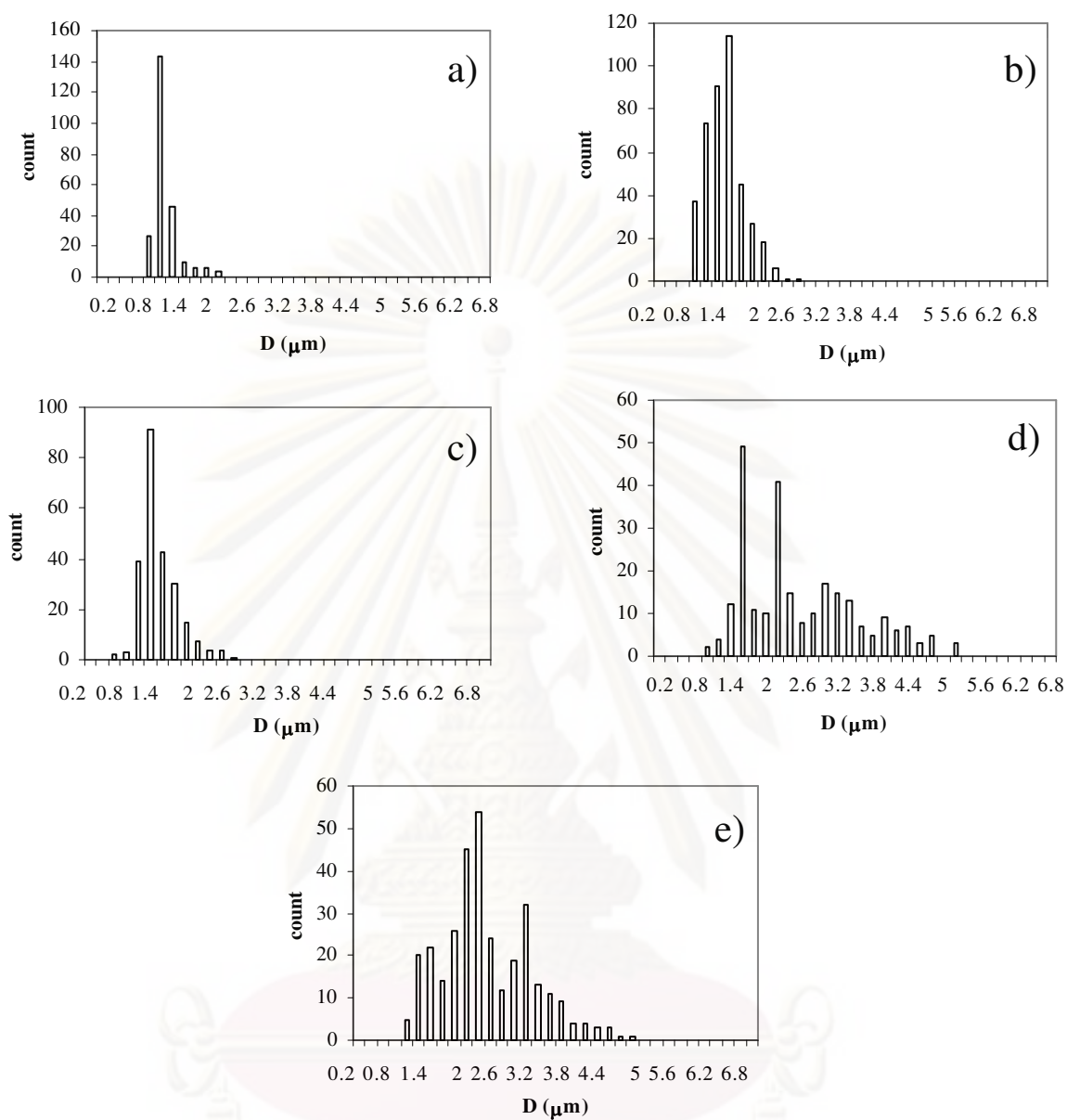


Figure 4.25 Particle size distribution of CTBN rubber in Epon 828 with Jeffamine T-403 as hardener (100:80 wt%) at (a) 5 phr of CTBN, (b) 10 phr of CTBN, (c) 15 phr of CTBN, (d) 20 phr of CTBN and (e) 25 phr of CTBN

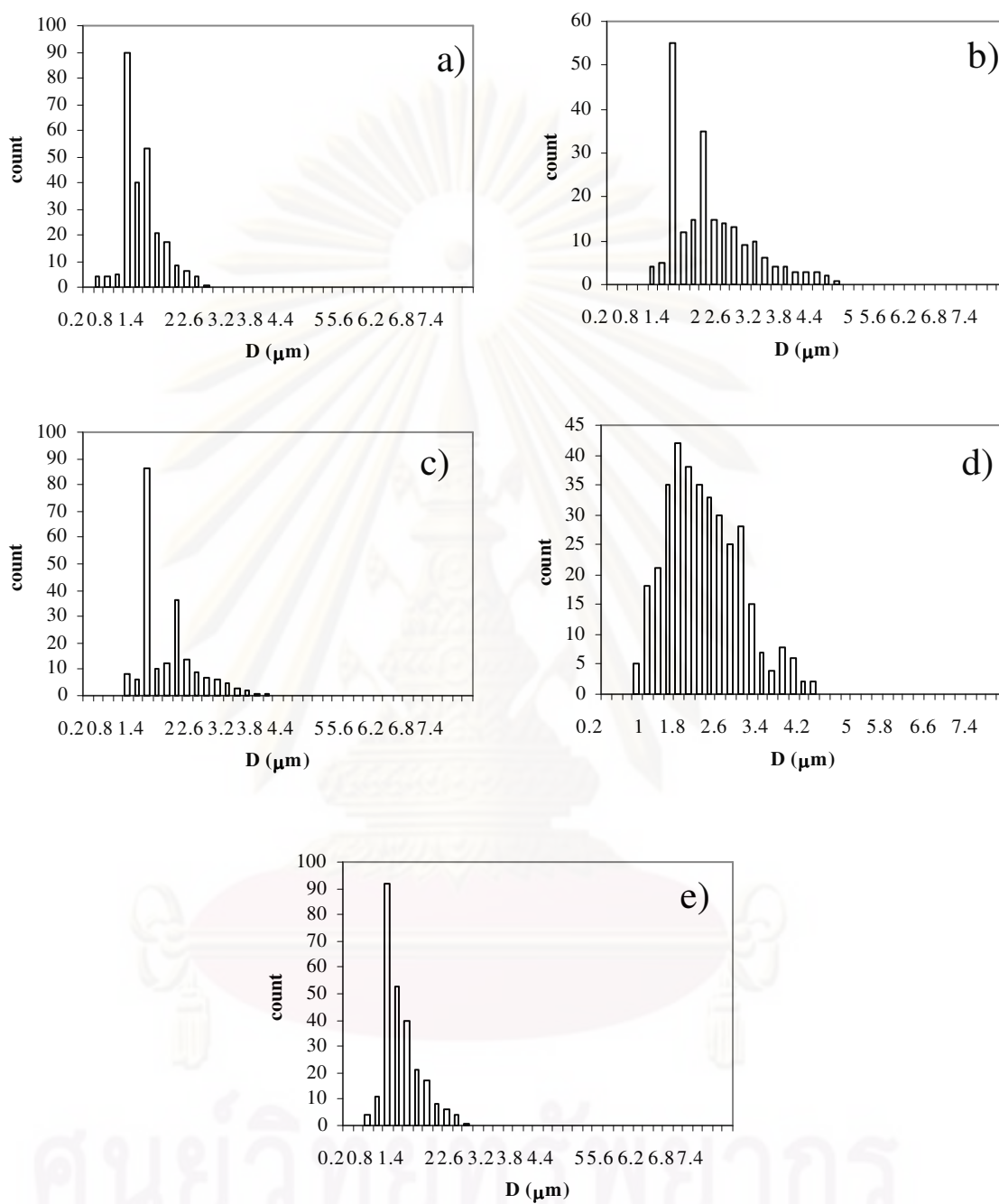


Figure 4.26 Particle size distribution of CTBN rubber in Epon 862 with Jeffamine T-403 as hardener (100:40 wt%) at (a) 5 phr of CTBN, (b) 10 phr of CTBN, (c) 15 phr of CTBN, (d) 20 phr of CTBN and (e) 25 phr of CTBN

#### 4.8 Thermal Properties

From mechanical properties results, the shear strength of Epon 862 system was higher than the shear strength of Epon 828 system. Therefore, Epon 862 was selected to study thermal properties. Table 4.5 shows the glass transition temperatures as obtained from DSC thermograms of Epon 862 based resin against CTBN content. Addition of CTBN rubber caused a slightly decrease in the glass transition temperature which is attributed to an increase in the dissolved rubber with epoxy matrix. The glass transition temperature fell from 57.88 °C for Epon 862 based epoxy resin without CTBN rubber to 54.98 °C for 25 phr CTBN rubber modified Epon 862 epoxy resin. This decrease in T<sub>g</sub> can be related to the fact that a chemical reaction occurred between the flexible CTBN rubber phase and rigid epoxy resin as other works [5, 28].

**Table 4.5** Glass transition temperatures of epoxy resin by using Epon 862 as base resin  
with different CTBN rubber contents

Composition (phr)			Tg (°C)
Epon 862	Jeffamine T-403	CTBN Rubber	
100	40	0	57.88
100	40	5	56.39
100	40	10	56.22
100	40	15	56.20
100	40	20	56.10
100	40	25	54.98

From the results in Part II, the inclusion of CTBN rubber on epoxy resins resulted in a phase separation of CTBN in epoxy matrix. The rubber particle size increased when the CTBN concentration increased. In addition, the increase of CTBN content will lead to the decreasing of both mechanical properties.

From the results of glass transition temperatures, of Epon 862 with Jeffamine T-403 and CTBN rubber as shown in Table 4.5, these adhesives can be used for low temperature application such as fiber optic application for bonding between fiber with glass.

## CHAPTER V

### CONCLUSION AND FUTURE DIRECTION

#### 5.1 Conclusion

In this study, the preparation of various types of epoxy resins by using two types of resins and three types of hardeners was carried out. Epon 828 (DGEBA) and Epon 862 (DGEBF) acted as resins. Jeffamine T-403, Imicure EMI-24 and DCA221 were used as hardeners. The effects of resin type and hardener, mixing ratio of resin to hardener on the viscosity, shear strength, tensile strength, chemical reaction and thermal properties were investigated.

Jeffamine T-403 was found to be the best hardener for both types of resins as it produced higher shear strength when compared with Imicure EMI-24 and DCA221. This may be explained by the higher functionality of Jeffamine T-403 which easily reacted with oxirane ring of epoxy resins. The optimum ratio that produced the high mechanical properties (either shear strength or tensile strength) was different for two types of resins.

The optimum ratio for Epon 828 system was 100:80 wt% of Epon 828: Jeffamine T-403. But the optimum ratio for Epon 862 system was 100:40 wt% of Epon 862: Jeffamine T-403.

Viscosities of epoxy resins for both kinds of base resins had the same trend. Due to the dilution effect, the viscosity of the fresh epoxy resin decreased when increased amount of Jeffamine T-403 and DCA221. For Imicure EMI-24 hardener, the viscosity increased when hardener concentration increased. It may be due to the hydrogen bonding that occurred between both resins with Imicure EMI-24.

From FTIR results, the absorption signal at  $3200\text{-}3400\text{ cm}^{-1}$  increased when concentration of Jeffamine T-403 increased. This may be due to the increasing of hydroxyl group from ring opening reaction of oxirane ring and remained of amine function of Jeffamine T-403. this result was similar to result of system that has DCA221 as hardener. Glass transition temperatures were decreased when hardener concentration increased. It may be due to the differences in crosslink density.

The inclusion of CTBN rubber on epoxy resins results in a phase separated network on the curing. The rubber particles size increased when concentration of CTBN rubber increased. This was due to coalescence of CTBN rubber at high rubber content. The addition of CTBN rubber into epoxy resin decreased both mechanical properties. This might be due to the increase in relative amount of dissolved rubber. The optimum condition that produced the high shear strength was the use of Epon 862 with the weight ratio of resin to Jeffamine T-403 hardener 100:40 wt% at 20 phr of CTBN rubber. At this condition, the large size of rubber particles was able to prevent the crack growing.

From the DSC result, the glass transition temperature of Epon 862 without CTBN rubber was higher than  $T_g$  of system that had higher amount of rubber. The decreasing in  $T_g$  can be due to the chemical reaction that occurred between flexible CTBN rubber phase and rigid epoxy resin.

## 5.2 Future Direction

Study in more detail on the effect of CTBN rubber on the cure kinetic of Epon 828/Jeffamine T-403 and Epon 862/Jeffamine T-403.

Explore the use of other rubber such as ATBN (amine-terminated acrylonitrile butadiene) and ENR (epoxidized natural rubber) in Epon 828 and Epon 862 system and study the relationship between chemical reaction and mechanical properties.

Investigate the effect of hardener functional groups such as mercaptan, anhydride, and amide in Epon 828 and Epon 862 system to find the best hardener that will give the high shear strength.



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APPENDICES

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## APPENDIX A

DSC heating thermogram of epoxy resin with and without CTBN rubber

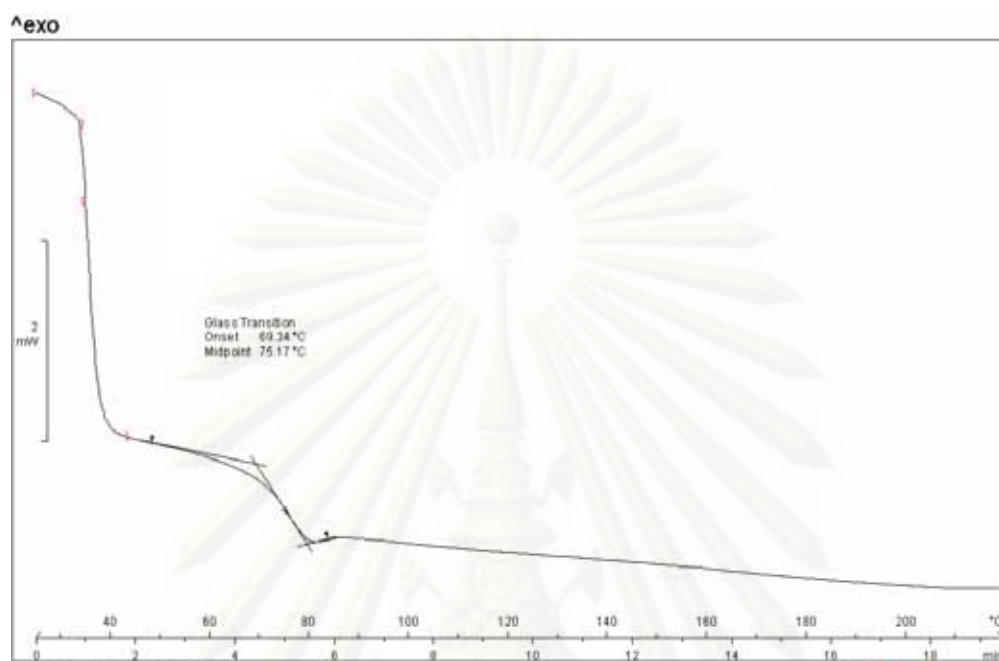


Figure A1 DSC heating thermogram of Epon 828 with Jeffamine T-403 (10:4)

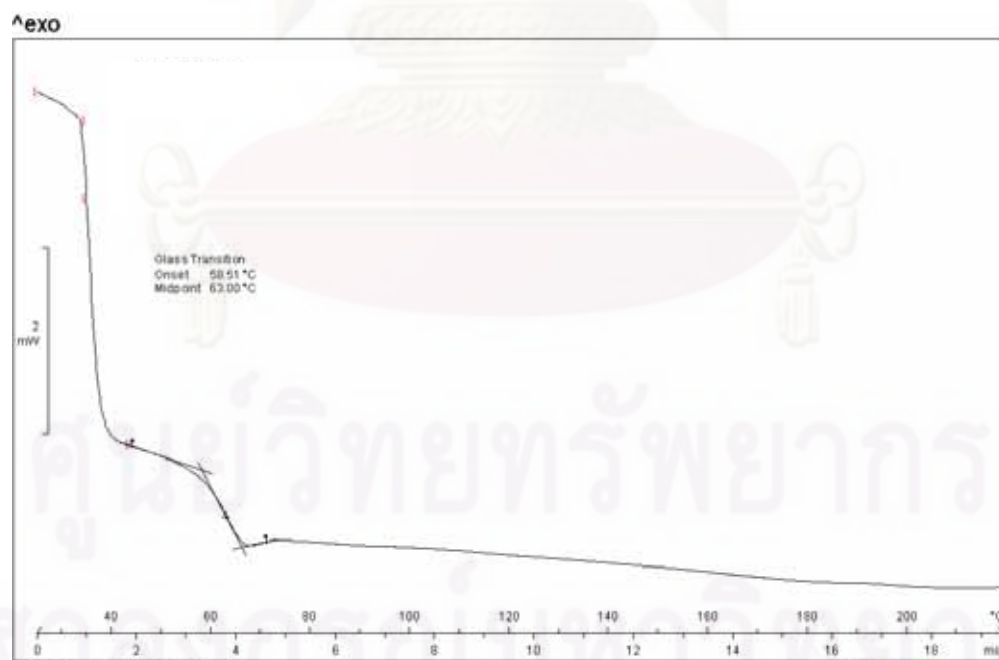


Figure A2 DSC heating thermogram of Epon 828 with Jeffamine T-403 (10:6)

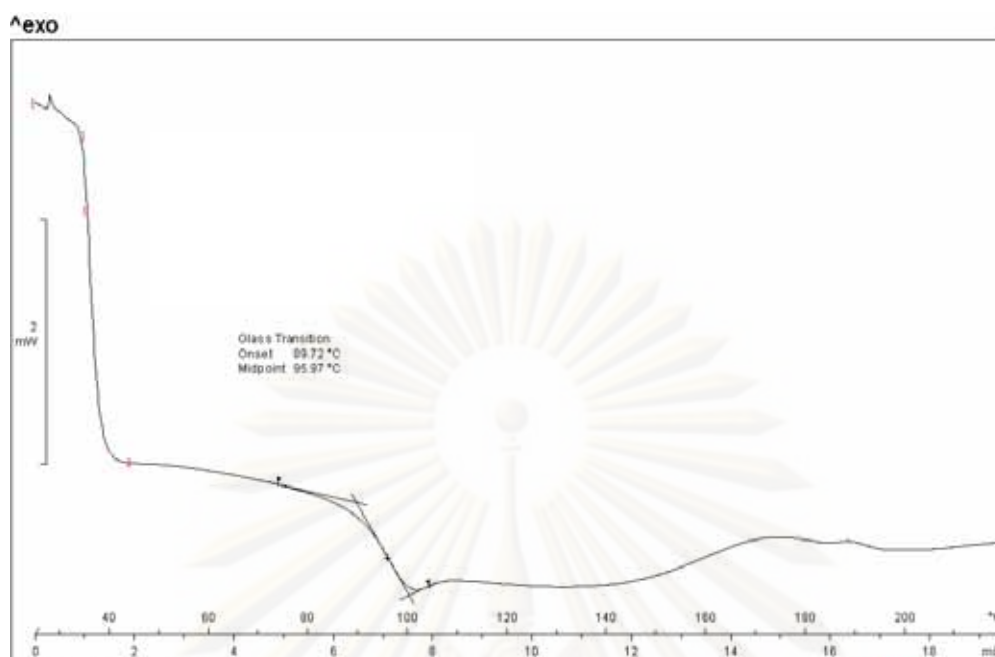


Figure A3 DSC heating thermogram of Epon 828 with Imicure EMI-24 (10:4)

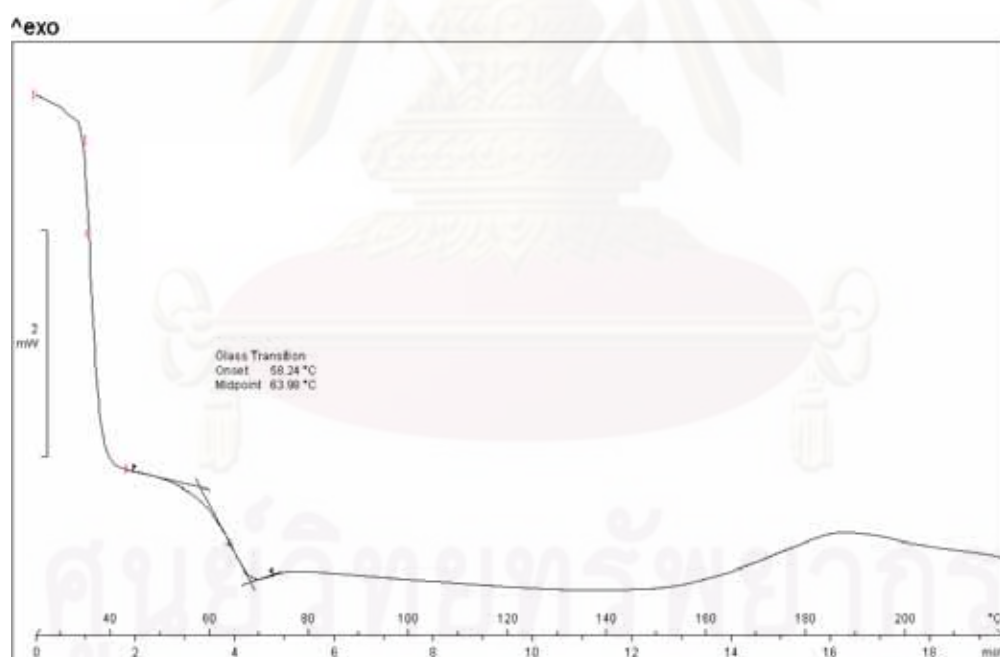


Figure A4 DSC heating thermogram of Epon 828 with Imicure EMI-24 (10:6)

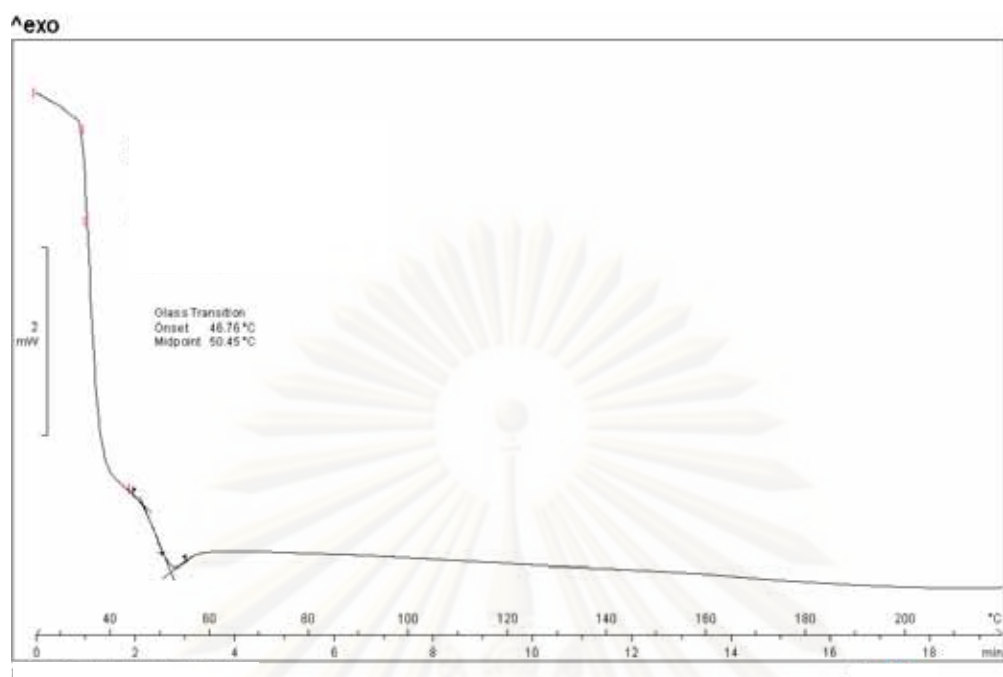


Figure A5 DSC heating thermogram of Epon 828 with DCA221 (10:4)

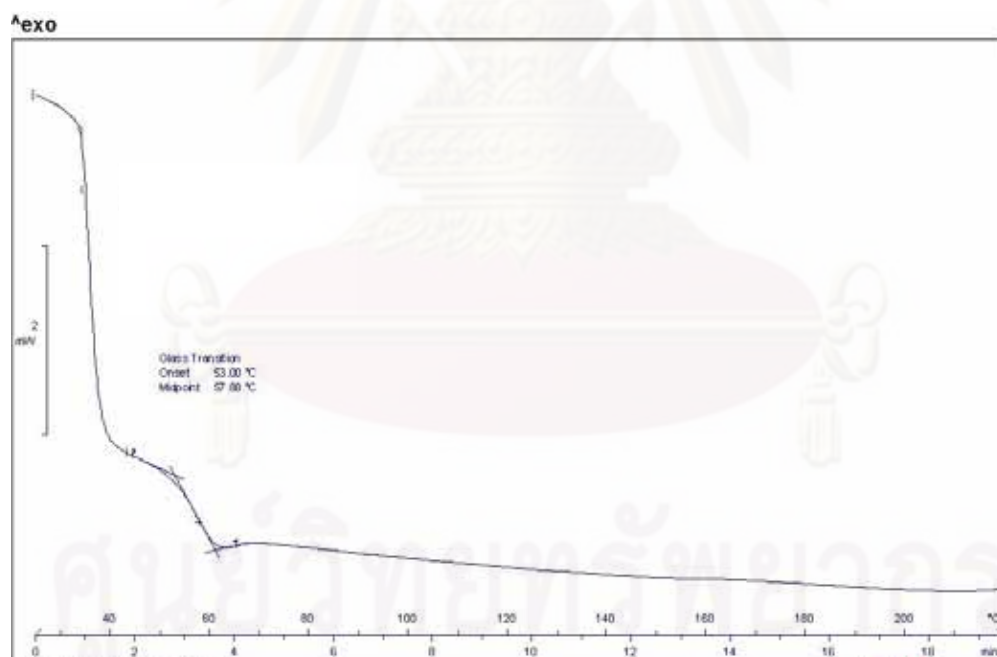


Figure A6 DSC heating thermogram of Epon 862 with Jeffamine T-403 (10:4)



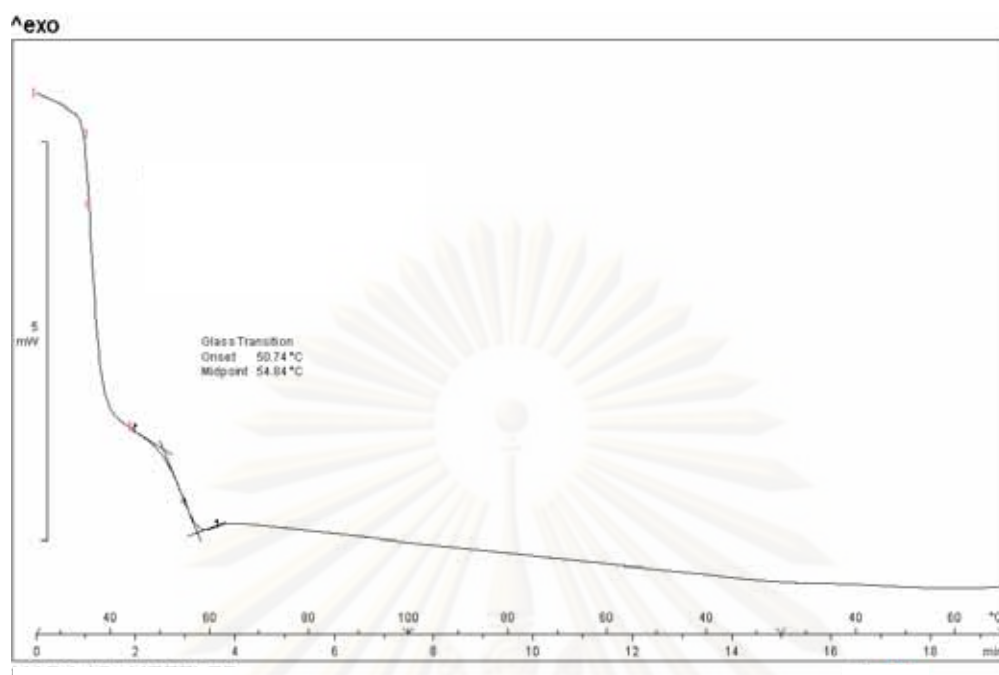


Figure A7 DSC heating thermogram of Epon 862 with Jeffamine T-403 (10:6)

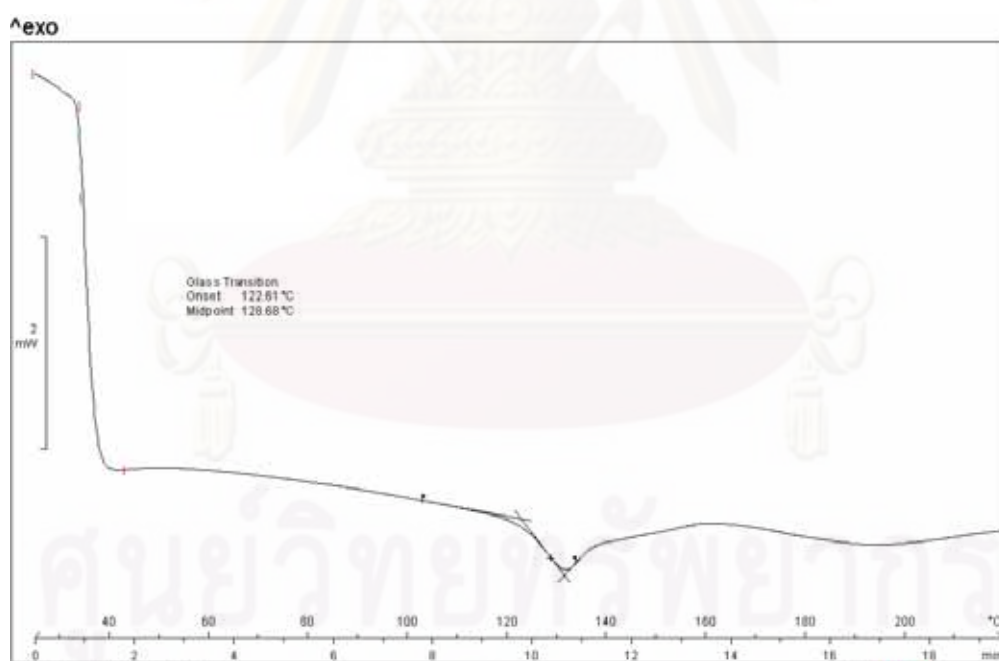


Figure A8 DSC heating thermogram of Epon 862 with Imicure EMI-24 (10:2)

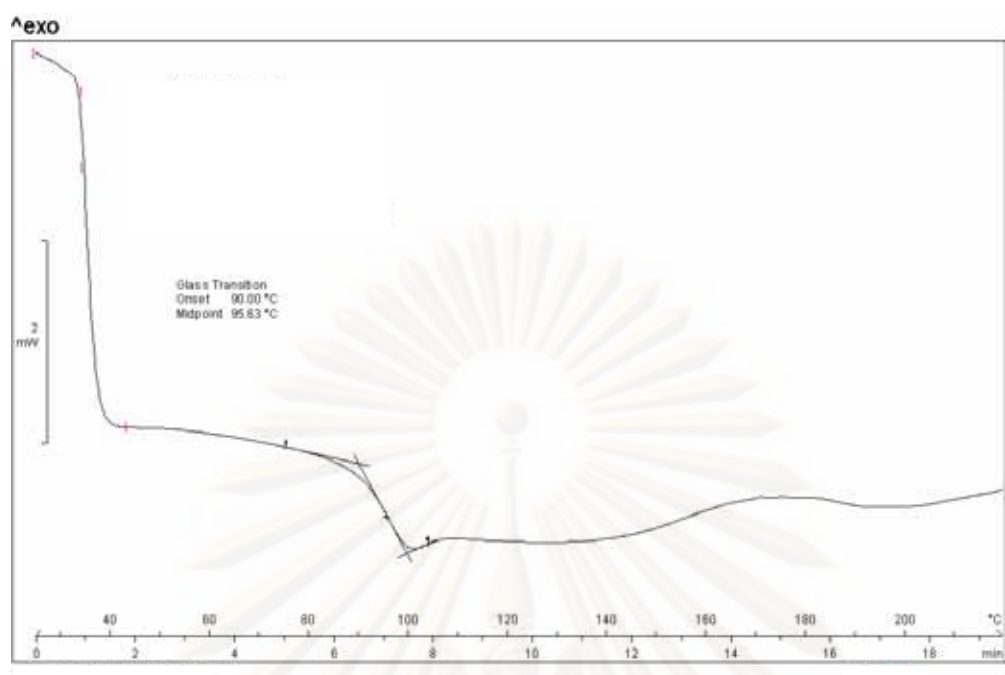


Figure A9 DSC heating thermogram of Epon 862 with Imicure EMI-24 (10:4)

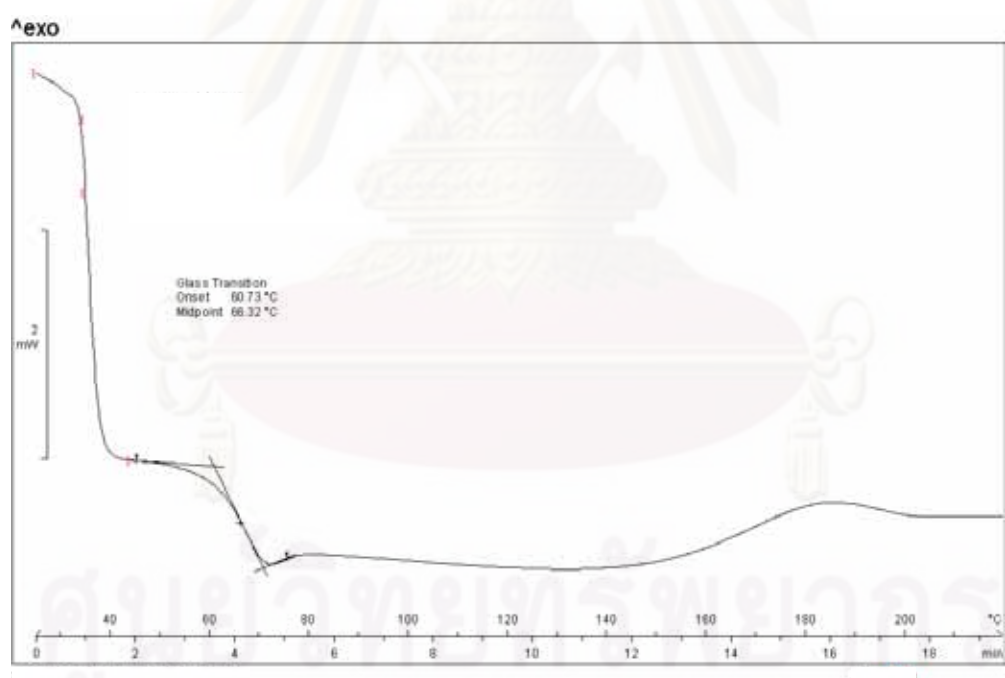


Figure A10 DSC heating thermogram of Epon 862 with Imicure EMI-24 (10:6)

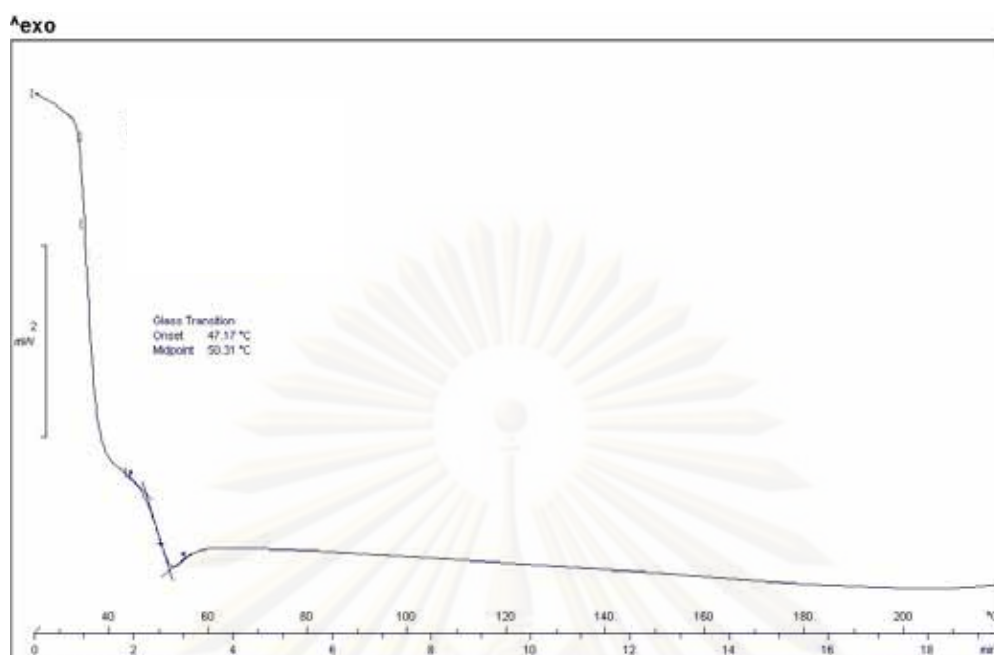


Figure A11 DSC heating thermogram of Epon 862 with DCA221 (10:2)

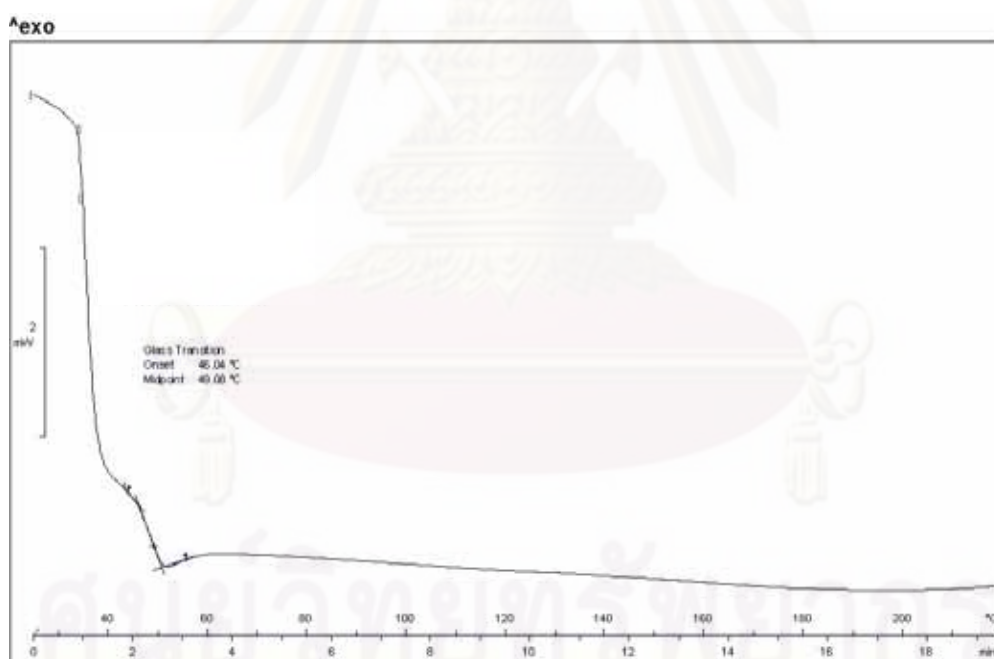


Figure A12 DSC heating thermogram of Epon 862 with DCA221 (10:4)

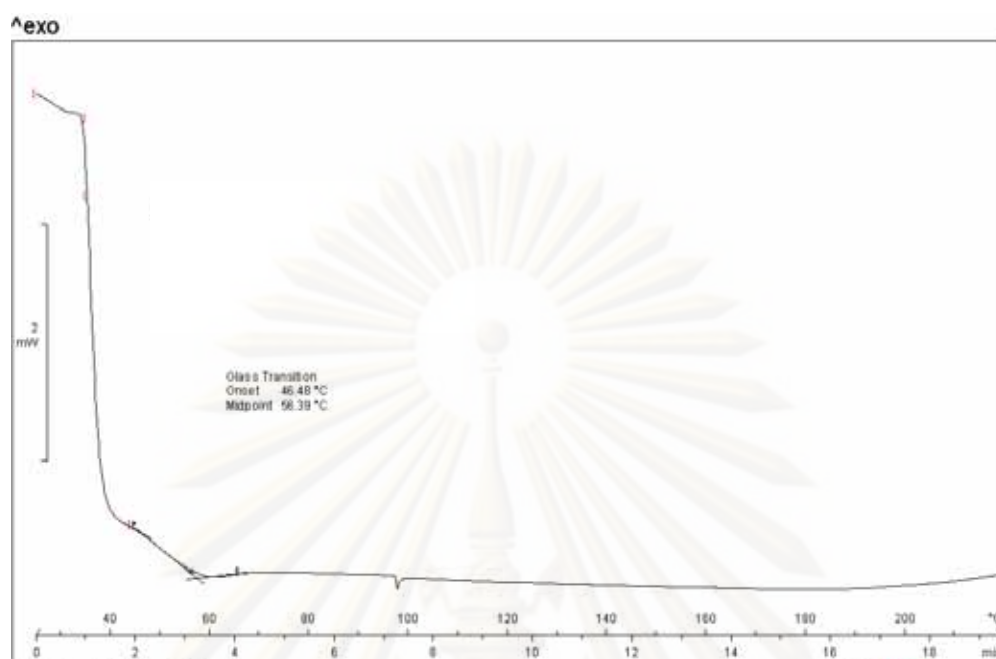


Figure A13 DSC heating thermogram of Epon 862 with Jeffamine T-403(10:4) at 5 phr of CTBN

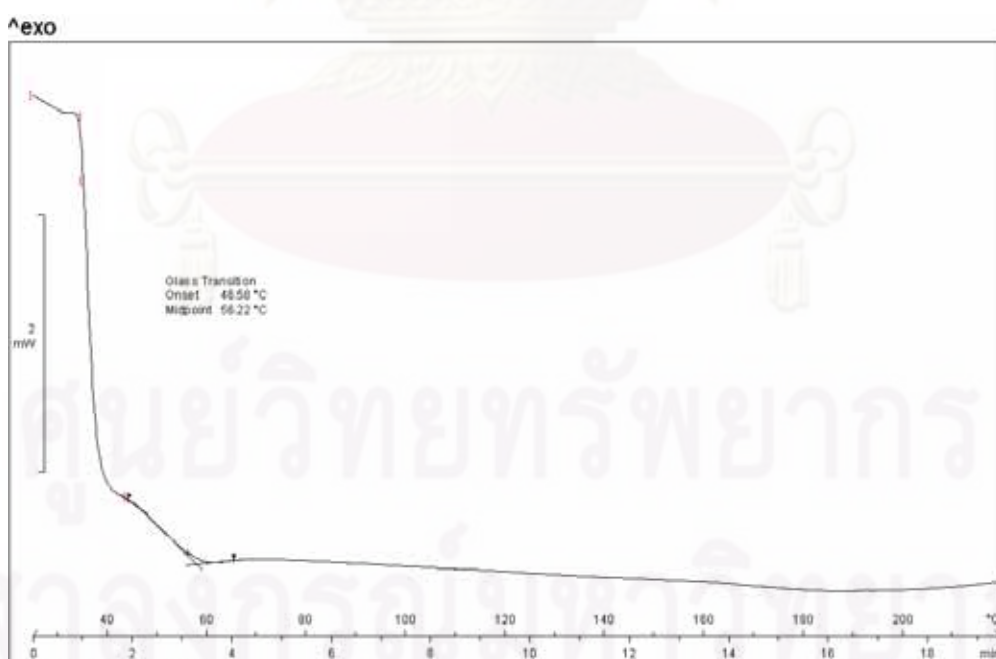


Figure A14 DSC heating thermogram of Epon 862 with Jeffamine T-403(10:4) at 10 phr of CTBN

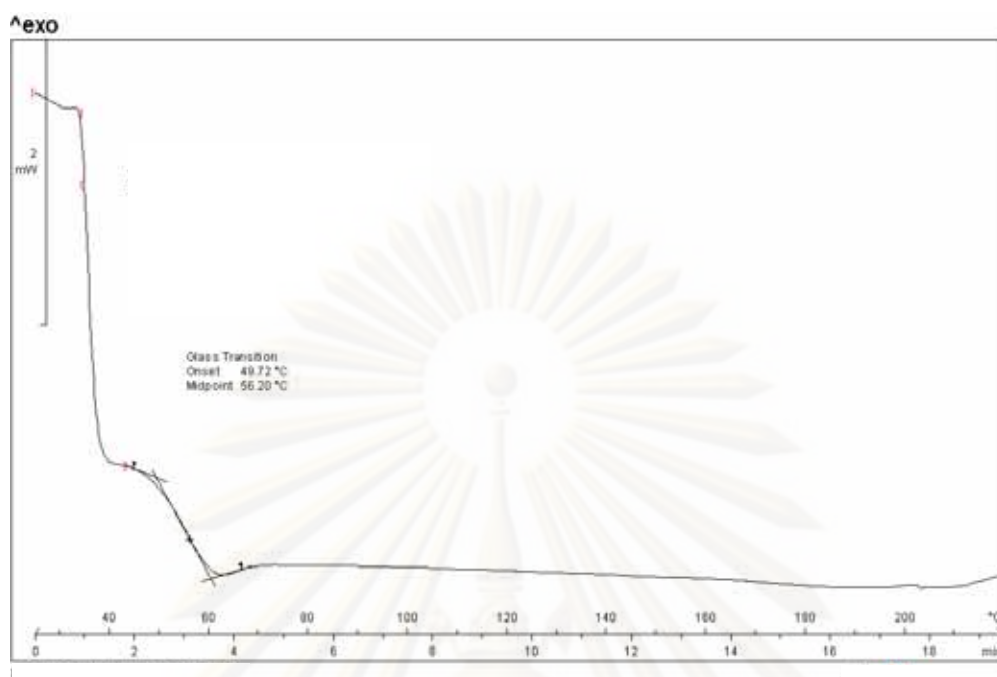


Figure A15 DSC heating thermogram of Epon 862 with Jeffamine T-403(10:4) at 15 phr of CTBN

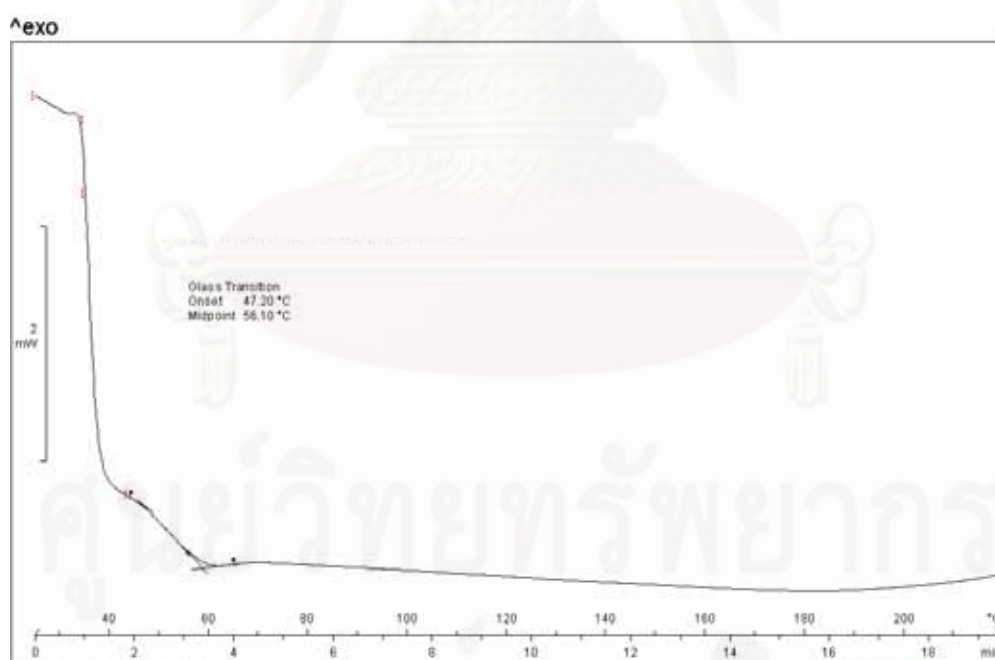


Figure A16 DSC heating thermogram of Epon 862 with Jeffamine T-403(10:4) at 20 phr of CTBN

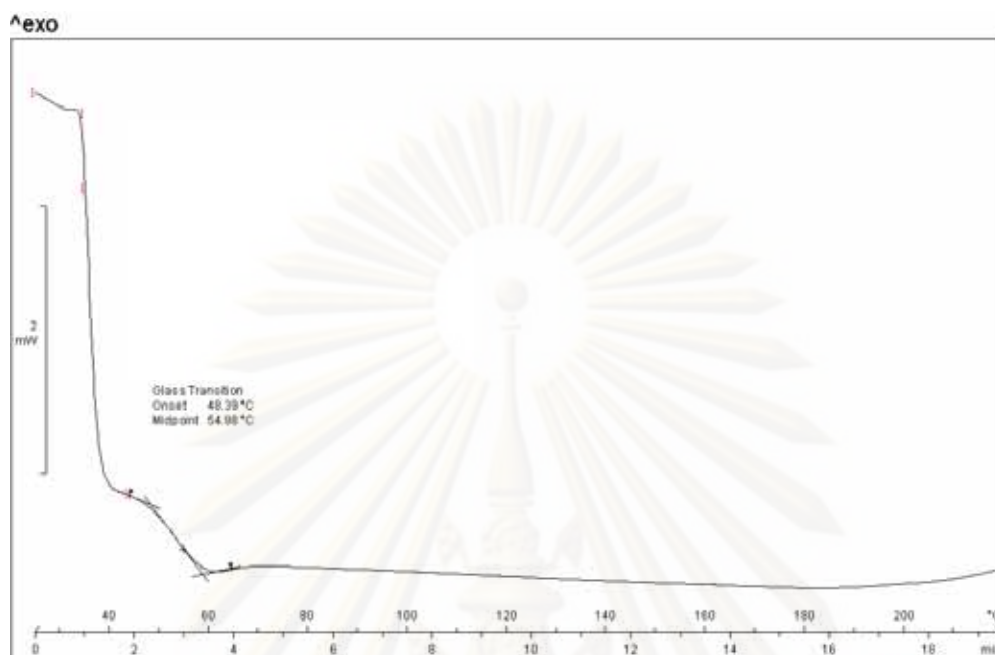


Figure A17 DSC heating thermogram of Epon 862 with Jeffamine T-403(10:4) at 25 phr of CTBN

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## VITAE

Mongkol Sirojpornpasut was born on January 11, 1982 in Ratchaburi, Thailand. He received a Bachelor's degree of Science, majoring in Chemistry from Silpakorn University in 2004. He has pursued Master's degree in Petrochemistry and Polymer, Faculty of Science, Chulalongkorn University, Bangkok, Thailand since 2007 and finished his study in 2009.

### Presentation

21-22 May 2009 Poster presentation "Effects of CTBN rubber on mechanical properties of bisphenol epoxy resin" The 2<sup>nd</sup> The Polymer Graduate Conference of Thailand at Chulalongkorn University, Bangkok, Thailand.

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย