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Development of Epoxy Adhesive for Screen Printing on Aluminum of Flexible Printed Circuit

Miss Piyarat Leeium

A Thesis Submitted in Partial Fulfillment of the Requirements
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Department of Chemical Engineering
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Thesis Title	Development of Epoxy Adhesive for Screen Printing on Aluminum of Flexible Printed Circuit
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Field of Study	Chemical Engineering
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งานวิจัยนี้ศึกษาการพัฒนากาวอิพ็อกซีสำหรับการพิมพ์บนอะลูมินัมและพอลิอิไมด์ในกระบวนการผลิตแผ่นวงจรอิเล็กทรอนิกส์ชนิดอ่อน อิพ็อกซีที่ใช้ในงานวิจัยนี้ประกอบด้วยอิพ็อกซีชนิดอะโรมาติก ได้แก่ diglycidyl ether of bisphenol-A (DGEBA) และ epoxy phenolic novolacs (EPN) ซึ่งอิพ็อกซีอะโรมาติกแต่ละชนิดถูกผสมกับอิพ็อกซีชนิดอะลิฟาติก (PPGDE) เพื่อเพิ่มความสามารถในการยึดเกาะให้สูงขึ้น อิพ็อกซีเหล่านี้สามารถทำปฏิกิริยาการบ่มได้ที่อุณหภูมิ 170 องศาเซลเซียส เป็นเวลา 15 นาที โดยใช้สารช่วยบ่มชนิด metaphenylene diamine (m-PDA) และทำการศึกษาอัตราส่วนที่เหมาะสมของอิพ็อกซีชนิดอะโรมาติกแต่ละชนิดในช่วงร้อยละ 50 ถึง 90 โดยน้ำหนัก ต่อความสามารถในการยึดเกาะ จากการทดลองเปรียบเทียบผลของอิพ็อกซีชนิดอะโรมาติกในระบบ DGEBA/PPGDE และ EPN/PPGDE พบว่าอิพ็อกซีระบบ EPN/PPGDE มีค่าความแข็งแรงในการลอก (peel strength) ซึ่งถือเป็นคุณสมบัติสำคัญของกาวสูงกว่าระบบ DGEBA/PPGDE ที่อัตราส่วนเดียวกัน โดยกาวอิพ็อกซีระบบ EPN/PPGDE ที่อัตราส่วนร้อยละ 50/50 โดยน้ำหนัก เป็นอัตราส่วนที่แสดงค่าความแข็งแรงในการลอกสูงสุดเท่ากับ 0.561 N/mm ซึ่งกาวในระบบนี้แสดงลักษณะการยึดเกาะกับอะลูมินัมได้ดี นอกจากนี้ยังพบอีกว่ากาวอิพ็อกซีระบบ EPN/PPGDE อัตราส่วนร้อยละ 50/50 โดยน้ำหนักที่เติมยาง CTBN 5 phr สามารถยึดเกาะกับพอลิอิไมด์ได้ดี โดยมีค่าความแข็งแรงในการลอกเท่ากับ 0.706 N/mm จากผลการทดลองดังกล่าวแสดงถึงกลไกการยึดเกาะที่แตกต่างกันระหว่างกาวอิพ็อกซีกับอะลูมินัมและพอลิอิไมด์ ดังนั้นกาวระบบสองชั้นจึงถูกประยุกต์นำมาใช้งาน โดยกาว EPN/PPGDE ถูกเคลือบเป็นชั้นแรกบนพื้นผิวอะลูมินัม ขณะที่กาว EPN/PPGDE ที่เติมยาง CTBN 5 phr ซึ่งยึดเกาะกับพอลิอิไมด์ได้ดี ถูกเคลือบทับด้านบนกาว EPN/PPGDE ชั้นแรก จากการทดสอบค่าความแข็งแรงในการลอกของกาวระบบสองชั้น พบว่ามีค่า 0.813 N/mm ดังนั้นกาวอิพ็อกซีระบบสองชั้นจึงเป็นระบบที่เหมาะสมที่จะนำมาใช้เป็นกาวสำหรับการพิมพ์ระหว่างอะลูมินัมและพอลิอิไมด์ของแผ่นวงจรอิเล็กทรอนิกส์ชนิดอ่อนได้

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต ....

สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

ปีการศึกษา 2559

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PIYARAT LEEIUM: Development of Epoxy Adhesive for Screen Printing on Aluminum of Flexible Printed Circuit. ADVISOR: ASSOC. PROF. SARAWUT RIMDUSIT, Ph.D., 110 pp.

The aim of this research is to develop epoxy based adhesive for screen printing on aluminum (Al) and polyimide (PI) substrates in flexible printed circuit (FPC) manufacturing. Two types of aromatic epoxy resins are evaluated in this work including diglycidyl ether of bisphenol-A (DGEBA) and epoxy phenolic novolacs (EPN). The two epoxy resins will also be blended with aliphatic epoxy (PPGDE) for adhesive property enhancement purpose. These epoxy systems can be cured at 170°C for 15 min using metaphenylene diamine (m-PDA) as a curing agent. The compositions of the aromatics epoxies were varied in a range of 50 to 90wt%. From the results, it was found that peel strength of EPN/PPGDE blends was higher than peel strength obtained from DGEBA/PPGDE systems. The maximum peel strength of EPN/PPGDE blends was measured to be 0.561 N/mm at 50/50 mass ratio. These blends were also found to show outstanding adhesive bonding with the aluminum substrate. In addition, it was also found that when the EPN/PPGDE blend at 50/50 mass ratio was modified with 5 phr of CTBN rubber, the resulting adhesive exhibited a good bonding with polyimide substrate providing maximum peel strength of about 0.706 N/mm. The above results also suggest difference in bonding mechanisms of the two adhesive layers and the Al or PI substrates. Consequently, two adhesive layers of epoxy systems with the first layer of EPN/PPGDE blend was applied on Al substrate whereas the CTBN modified EPN/PPGDE blend, a second adhesive layer, which provides a good adhesion on PI film was casted on top of the EPN/PPGDE layer. The obtained peel strength of this two-layered epoxy blends was found to be as high as 0.813 N/mm meeting the industrial requirement. These two-layered epoxy adhesive systems are a good candidate for adhesive bonding of Al and PI substrates through screening printing process.

Department:	Chemical Engineering	Student's Signature	....
Field of Study:	Chemical Engineering	Advisor's Signature	....
Academic Year:	2016		

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CHAPTER I

INTRODUCTION

1.1 General introduction

Flexible printed circuit boards are members of electronic and interconnection family. They consist of a thin insulating polymer film having conductive circuit patterns affixed thereto and typically supplied with a thin polymer coating to protect the conductor circuits. In practice, there are many different kinds of flexible circuits, including one metal layer, double sided, multilayer and rigid flex circuits [1]. Recent advances in flexible device technology have changed the paradigm of electronics from rigid objects to flexible form factors [2]. A flexible PCB has many advantages compared to a rigid PCB because of its flexibility and especially in portable electronic applications. Moreover, it can be mass-produced by the roll-type manufacturing system. Nowadays, flexible PCBs are increasingly used high density applications such as smart cards, hearing aids, liquid crystal display modules and other modules for portable electronics [3]. The most popular approaches for making flexible devices is to use flexible plastic substrates such as polyimide and aluminum stiffener [2, 4]. The substrates are typically attached with a thermosetting type adhesive [4].

In the present, flexible printed circuit is affixed to an aluminum by use of a pressure sensitive adhesive (PSA) tape. The adhesive film is then punched by a converter and manually cut into appropriately sized sheets [5]. The use of PSA film experiencing several problems. One of several problems, the punching process of adhesive films is multi-step handling which is complicated and time-consuming. The mistakes made in the handling of the adhesive and the release liner film results in product that must be scrapped. In addition, the other manufacturing process has several steps thereby resulting in susceptible contamination by dust. Therefore, how to solve such problems is to change the type of adhesive from PSA to liquid adhesive.

Currently, liquid adhesive that is commonly used as thermosetting adhesive. The properties of this thermosetting adhesive are strong, insoluble, highly inert and covalently cross-linked polymer networks [6]. As a well-known thermosets, epoxy resins such as diglycedyl ether of bisphenol A (DGEBA) have a wide range of applications in adhesives, polymer composites, high performance coatings, potting, encapsulations, and numerous other areas. They have excellent mechanical and electrical properties, very good adhesion to many substrates, low cure shrinkage, and good resistance to moisture [6-8]. One of the drawbacks of DGEBA is the brittle nature of the highly cross-linked epoxy system include their lack of toughness. Many research effort has already been put into the toughening of epoxy polymers as has been recently summarized by Mohan [9]. There are two general approaches can be taken to enhance the toughening of an epoxy polymer: first, adding filler materials as a crack arresting mechanism and second enhancing the amount of energy that can be adsorbed before a fracture occurs by addition of a more flexible aliphatic copolymer

[10]. It can be assumed that the toughness of an adhesive can affect its adhesion strength: The adhesion strength increases with increasing toughness of adhesive [11].

Downey and Drzal [10] have studied adding a more flexible aliphatic epoxy copolymer would address the issue of processability, provided that the epoxy copolymers are miscible. Having the same functional epoxy groups, the copolymers will undergo the same reaction with the diamine curing agent to form a highly cross-linked network. The higher flexible aliphatic chains should be able to absorb more impact energy prior to fracturing. The increased toughness was associated with decreases in tensile modulus and glass transition temperature. They reported that the glass transition temperature (T_g) of the mixtures decreased with decreasing of DGEBA concentration.

Moreover, Razack and Varphese [12] have studied effect of various hardeners on mechanical and thermal properties of epoxy resins. The results revealed that peel strength of DGEBA cured with m-phenylene diamine (mPDA) on aluminium substrate has greater than other types of hardener. The thermal degradation temperature at 5 wt% loss of DGEBA/mPDA is higher than DGEBA cured with other hardeners. Uddin et al. [13] have studied peel strength of anisotropic conductive adhesives film (ACF). The type of ACF used in this study was consists of an epoxy layer and filled with conductive particles. The results showed that the high temperature cured samples provided higher reaction rates and a greater curing degree as well as high adhesion strength of samples compared to those of low temperature cured samples.

In addition, Liu et al. have studied the preparation and application of CTBN modified epoxy adhesive. The adhesive was prepared with two types of epoxy resin (901 and 6128 with epoxy equivalent weight of 483 and 178 g/mol, respectively) as matrix, CTBN as toughening agent and 4,4’-diamino diphenyl sulphone (DDS) as curing agent, and the adhesive was applied to FCCL. Rubbers are generally well known to affect adhesion depending on their compatibility with epoxy matrix and content as well as the intrinsic strength of the rubber phase. The results represent the peel strength of FCCL varies with the CTBN content. The peel strength increases from 0.6 to 1.4 N/mm with increasing CTBN content at epoxy equivalent ratio of 2:1 of 901 and 6128. As obviously observed, the peel strength of FCCL gradually increases with increasing CTBN content, which might be attributed to the effect of the soft segment structure of CTBN dispersed in epoxy matrix which lead to a decrease in the stiffness and elastic modulus.

Consequently, the purpose of this study is to develop epoxy-based adhesive for interconnection between aluminum backup board and flexible printed circuit based on polyimide substrate. Those properties of modified epoxy adhesives would be investigated thermal properties including glass transition temperature and thermal stability by differential scanning calorimeter (DSC) and thermogravitric analyzer (TGA), respectively. Furthermore, the adhesion properties of epoxy adhesives such as the viscosity from rheometer and the peel strength from universal testing machine.

1.2 Objectives

1. To develop DGEBA based epoxy adhesive formulation for screen printing process in FPC fabrication.
2. To investigate effects of content of aliphatic epoxy (Polypropylene glycol diglycidyl ether) and CTBN on major properties of the obtained epoxy adhesives including curing profiles, screening printing characteristics, and peel strength.

1.3 Scopes of the study

1. Preparation of epoxy based adhesive by varying types of aromatic epoxy as DGEBA and EPN and varying aliphatic epoxy (PPGDE) content in aromatic epoxy from 0-50 wt% using mPDA as curing agent.
2. Preparation of epoxy based adhesive filled with CTBN rubber in content of 0-20 phr.
3. Determination of the fully cured condition having final curing time less than 30 minutes using DSC.
4. Characterization of viscosity of epoxy based adhesive using rheometer.
5. Characterization of thermal properties of epoxy based adhesive using
    - Differential Scanning Calorimetry (DSC)
    - Thermogravimetric analysis (TGA)

6. Characterization of adhesion property of epoxy based adhesive using universal testing machine (peeling mode).

1.4 Procedures of the study

1. Review related literature.
2. Preparation of chemicals and equipment for using in this research.
3. Preparation of adhesives from diglycidyl ether of bisphenol A (DGEBA) based epoxy/aliphatic epoxy resin mixture cured with 1,3-phenylenediamine (PDA).
4. Preparation of epoxy based adhesive filled with CTBN rubber in content of 0-20 wt%.
5. Characterization of thermal, mechanical and adhesion properties of the adhesive.
6. Analysis of the experimental results.
7. Preparation of the final report.

CHAPTER II

THEORY

2.1 Flexible Circuit Technology

The advance of electronic systems into our everyday lives is evidence of a major digital technology revolution. The success stories of the personal computer and the mobile phone serve to demonstrate that consumer and business demand for innovative products are significant. Increasingly electrical and electronic systems are entering our lives in many unanticipated ways. They can be found in our homes in the form of cordless phones and digital TVs, in our cars in the form of hands-free communications and telematics, and in business in the form of notebook computers and mobile personal data assistants (PDAs).

Importantly, and also covertly, within the above applications flexible printed circuits have also been entering our lives. Traditionally employed in the role of wire replacement, removing the need for complex wire harnesses, and replacing costly and increasingly complicated wired assemblies, flexible circuits offer a much simpler and often significantly more cost-effective interconnection method.

However, alongside increasingly innovative applications flexible-circuit technology is branching out significantly from this initial role and it is poised to be a technology that will provide enormous design freedoms for electronic engineers and product designers over the coming years. As the demands of modern electronic systems call for increasing functionality, greater circuit density, higher connectivity, better environmental performance, and all at lower cost, flexible circuitry is poised to deliver on the promise of twenty-first century electronics [14].

Figure 2.1 Flexible printed circuit [15]

2.2 Applications

There are a great many reasons for using flex circuits to make the interconnections in an electronic package. In some cases, such as dynamic flexing applications, the choice to use flexible circuits is an obvious one, driven strictly by the lack of any viable alternatives. However, there are many more subtle areas of opportunity to employ flexible circuits, and this has proven to be the real measure of their success [16].

Figure 2.2 Applications of flexible printed circuit [17]

Table 2.1 Flexible circuit applications are found in products of every type and in all of the basic electronic products markets [16].

Examples of flexible circuit applications	
Automotive	Instrument panels Under–hood controls Headliner circuits ABS systems
Consumer	Digital & video cameras Personal entertainment

	Exercise monitors Hand–held calculators
Computers & peripherals	Dot matrix print heads Disk drives Ink jet print heads Printer head cables
Industrial controls	Laser measuring Inductor coil pickups Copy machines Heater coil
Instruments	NMR analyzers X-ray equipment Particle counters Infrared analyzers
Medical	Hearing aids Heart pace-makers Defibrillators Ultrasound probe heads
Telecom	Cell phones Base stations

	High-speed cables Smart cards & RFID
Military & Aerospace	Instrumentation panels Plasma displays Radar systems Jet engine controls Night vision systems Laser gyroscopes Torpedoes Electronic shielding Radio communications Surveillance systems

2.3 Base Materials

The base material is the flexible polymer film that provides the foundation for the laminate. Under normal circumstances, the flex circuit base material provides most primary physical and electrical properties of the flexible circuit. In the case of adhesiveless circuit constructions, the base material provides all of the characteristic properties.

Although a wide range of thickness is possible, most flexible films are provided in a narrow range of relatively thin dimension, from 12 μm to 125 μm (1/2 mil to 5 mils). While it is recognizable from experience that thinner materials are more flexible, it is worth remembering the engineering principle that with most materials, stiff ness is proportional to the cube of thickness. This means that if the thickness is doubled, the material becomes eight times stiffer and will only deflect one-eighth as much under the same load [16].

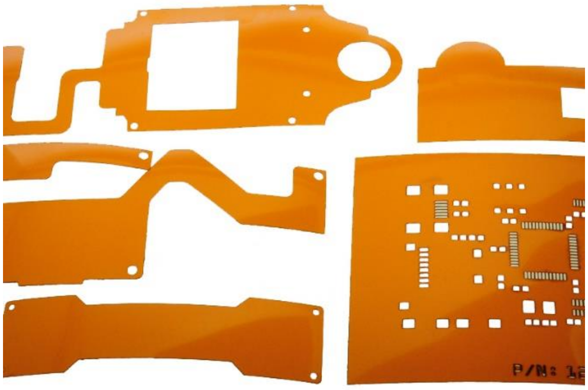


Figure 2.3 Polyimide film [18]

2.3.1 Stiffener Materials

While not an integral part of the flex circuit, stiffeners are an important element of flex circuit construction. Stiffening materials are used to reinforce flex circuits when and where required. Most commonly, stiffeners are under areas where electronic components are to be attached. There they serve to support the weight of the components both through the assembly process and in the application. Stiffeners can be made of almost any material, including metal, plastic, resin-glass laminates or even additional layers of cover layer material. The use of cover layer material to stiffen areas of a flex is actually a very common practice [16].

Figure 2.4 Aluminum stiffener [19]

2.4 Adhesives for Flex Circuits

Flexible adhesives are used either to bind the metal foil to the base material to create a laminate or to bind layers of laminate material together, such as is found in multilayer constructions. Normally, the chosen adhesive is carefully matched to achieve the best mix of desirable properties for the laminate [16].

2.4.1 Polyester Adhesive

Polyester adhesives are typically used with polyester laminates; however, they have also been used occasionally with other materials, depending on the application. Chief among the advantages of polyester adhesives are low cost and the low processing temperatures required for bonding. A drawback, however, is that polyester adhesives exhibit poor high temperature performance, limiting the number of potential applications.

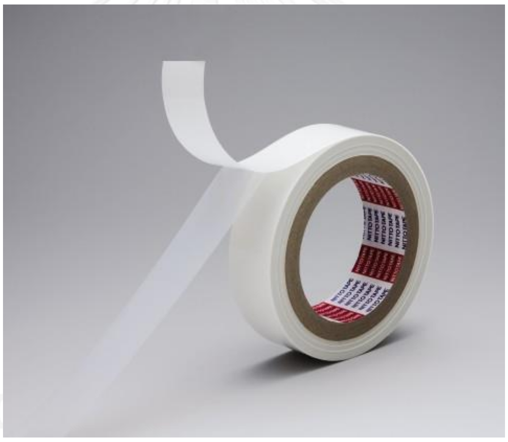


Figure 2.5 Polyester adhesive [20]

Other potential drawbacks are that the adhesive flow in lamination tends to be high, and bond strength tends to be relatively low. Still, they do work suitably in many applications where their temperature and physical limits will not be pushed [16].

2.4.2 Acrylic Adhesive

Acrylic adhesives have long been a first choice for flex circuit manufacture. They have been commonly favored for many polyimide laminates due to their excellent adhesion and ease of processing. Acrylic adhesives offer a good balance of reasonable thermal performance (withstanding soldering temperatures), process ease and natural ability to bond reasonably well too many different materials.

On the negative side of the ledger, acrylic adhesives tend to swell in the hot alkaline processing solutions common in many electroless and electrolytic circuit board plating lines. Additionally, as was referenced briefly earlier, they have a rather high coefficient of thermal expansion, which has implicated them as a prime cause of through hole plating cracks when used extensively in multilayer and rigid flex constructions due to excessive Z-axis expansion [16].

Figure 2.6 Acrylic adhesive [21]

2.4.3 Polyimide Adhesives

Polyimide adhesives are necessarily limited to use with polyimide substrates due to the higher temperature processing required. Nevertheless, use of polyimide adhesives affords better matched and thus improved laminate substrate properties. They are increasing in popularity in some product applications

Typical polyimide adhesives are thermoplastic and require relatively high lamination temperatures and pressures. The net result is that circuits made using polyimide adhesives offer the highest maximum temperature capability of any flex circuit construction. Polyimide adhesives also are seen as possibly being advantageous for multilayer and rigid flex applications due to the lower coefficient of thermal expansion (CTE).

Negative aspects of polyimide adhesives include the fact that there are a limited number of sources and experience levels which, while increasing, are not as great as they are for other adhesives. One other concern is that the bond strengths reported for polyimide adhesives are somewhat lower than alternatives. This may not prove a large problem over time, but additional experience is required [16].

Figure 2.7 Polyimide adhesives [22]

2.4.4 Butyral-Phenolic Adhesives

Another adhesive type of long-standing is butyral-phenolic adhesive. This type of adhesive was actually used to create some of the first flex circuits without benefit of a base film. Butyral-phenolic adhesives have been shown to improve flexural life in some experiments.

Butyral-phenolic adhesives offer some specific advantages. Chief among them, from the perspective of the flex manufacturer, is the low flow characteristics of the adhesive during lamination. This feature lessens the concern of having adhesive flow on to interconnection lands. Excessive flow onto lands is a rejectable condition if limits are exceeded.

Other advantages of this adhesive type are that it has reasonably low moisture absorption and one of the lowest dielectric constants among commonly used adhesives. On the negative side, circuits made with this adhesive system tend to be rather stiff in comparison to some of the alternate choices [16].

Figure 2.8 P-tert butyl phenol formaldehyde resin [23]

2.4.5 Epoxy and Modified Epoxy Adhesives

Epoxies are among the most commonly used adhesives in the world, so it is no surprise that they find some application in flex circuits. Epoxies and modified versions of epoxies are near universal adhesives, capable of bonding with many different materials, including metals, ceramics and polymers. The high temperature capabilities of epoxies are quite good, providing some of the best post solder float peel strength values. On the downside, epoxies tend by their nature to be more brittle than some of the alternative choices, however, modifications to the formula have proven successful in mitigating this issue. Epoxies are also somewhat prone to moisture uptake and thus require a bit more processing care on the part of the manufacturer [16].

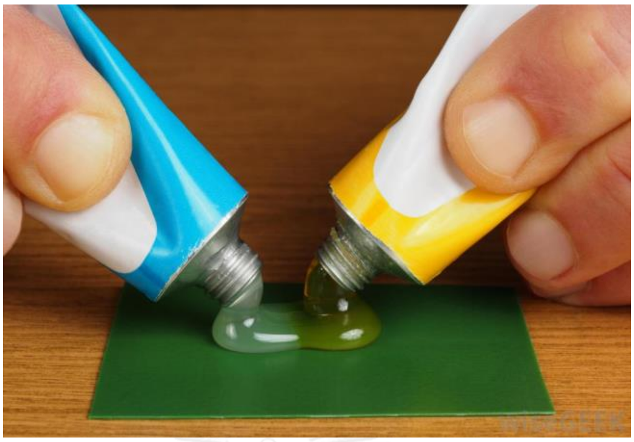


Figure 2.9 Epoxy adhesives [24]

2.4.6 Other Adhesives

In addition to all of the above-cited adhesives, a number of other thermoplastic materials have also been used in the past to fabricate flexible circuits. Included in this grouping are FEP and polyetherimide (PEI). These materials require processing much like polyimide adhesives, which must normally be bonded at very high temperatures and pressures.

FEP is sometimes used as low loss bonding film in multilayer microwave frequency boards and is often chosen because of the lower temperature for processing. FEP is a thermoplastic and can re-melt at extended periods above 550°C in assembly, which could, for example, cause delamination at some lead-free soldering temperatures. This concern over high-temperature soldering extends to PEI as well, so it is recommended that the materials be qualified for use in high temperature applications [16].

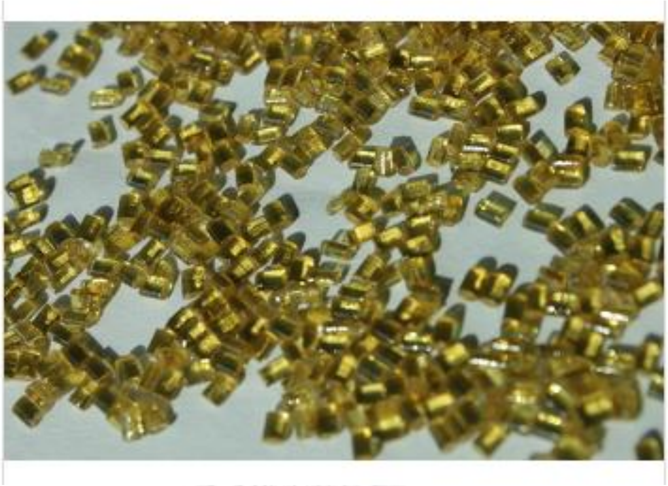


Figure 2.10 Polyetherimide resin [25]

2.5 Theories of Adhesion

Historically, mechanical interlocking, diffusion, adsorption and surface reaction, and electrostatic theories have been postulated to describe the mechanisms of adhesion. More recently, other theories have been put forward for the adhesive bonding mechanism (Table 2.2). It is often difficult to fully ascribe adhesive bonding to an individual mechanism. A combination of different mechanisms is responsible for bonding within a given adhesive system. The extent of the role of each mechanism would then vary for different systems. An understanding of these theories will be helpful to those who plan to work with most aspects of adhesion [26].

Table 2.2 Theories of Adhesion [26]

Traditional	**Recent**	**Scale of Action**
Mechanical Interlocking	Mechanical Interlocking	Microscopic
Electrostatic	Electrostatic	Macroscopic
Diffusion	Diffusion	Molecular
Adsorption/Surface Reaction	Wettability	Molecular
	Chemical Bonding	Atomic

2.5.1 Mechanical Theory

According to mechanical theory, adhesion occurs by the penetration of adhesives into pores, cavities, and other surface irregularities of the surface of the substrate or adherend. The adhesive displaces the trapped air at the interface. Therefore, it is concluded that an adhesive penetrating into the surface roughness of two adherends can bond the two. A positive contribution to the adhesive bond strength results from the “mechanical interlocking” of the adhesive and the adherends. Adhesives frequently bond better to porous abraded surfaces than to smooth surfaces. This theory is, however, not universally applicable because good adhesion also takes place between smooth surfaces. Enhanced adhesion after abrading the surface of an adherend may be due to one or more of the following: mechanical interlocking, formation of a clean surface, formation of a highly reactive surface, and an increase in contact surface area. While the surface does become rougher by mechanical of the adherend's surface increase an adhesive's strength. One can debate whether mechanical interlocking is responsible or, rather, an increase in the adhesive contact surface enhances other mechanisms. More thorough wetting and more extensive chemical bonding are expected consequences of increased contact surface area.

There is supportive data in the literature that relates joint strength and bond durability to increased surface roughness. There are also contrary observations indicating that increased roughness can lower joint strength [26].

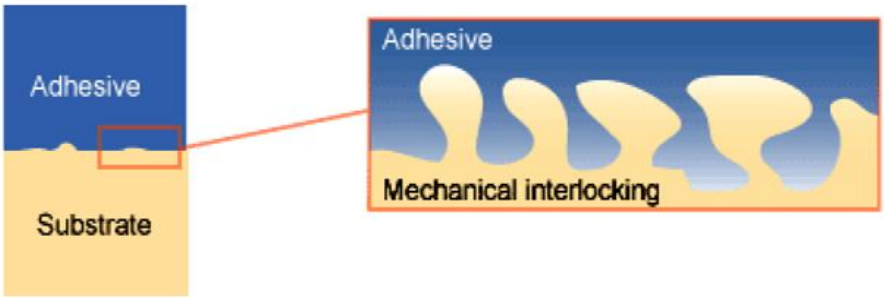


Figure 2.11 Mechanical adhesion [27]

2.5.2 Electrostatic (Electronic) Theory

This theory proposes that adhesion takes place due to electrostatic effects between adhesive and adherend. An electron transfer theoretically takes place between the adhesive and the adherend as a result of unlike electronic band structures. Electrostatic forces in the form of an electrical double layer are thus formed at the adhesive-adherend interface. These forces account for the resistance to separating. This theory gains support from the fact that electrical discharges have been observed when an adhesive is peeled from a substrate.

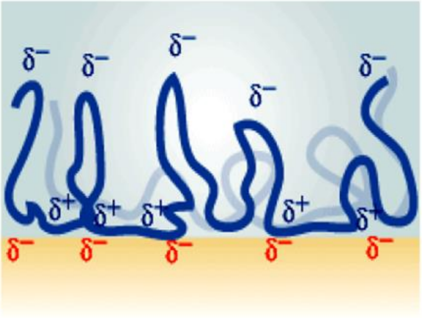


Figure 2.12 Electrostatic adhesion [28]

The electrostatic mechanism is a plausible explanation of the polymer-metal adhesion bond. In non-metallic systems, the contribution of the electronic mechanism to the work of adhesion has been calculated and been found to be dimunitive when compared to that of chemical bonding [26].

2.5.3 Diffusion Theory

This theory suggests that adhesion is developed through the interdiffusion of molecules in and between the adhesive and adherend. The diffusion theory is primarily applicable when both the adhesive and adherend are polymers with relatively long-chain molecules capable of movement. The nature of materials and bonding conditions will influence if, and to what extent, diffusion takes place. The diffuse interfacial (interphase) layer typically has a thickness in the range of 10 Å–1,000 Å. Solvent cementing or heat welding of thermoplastics is considered to be a result of diffusion of molecules [26].

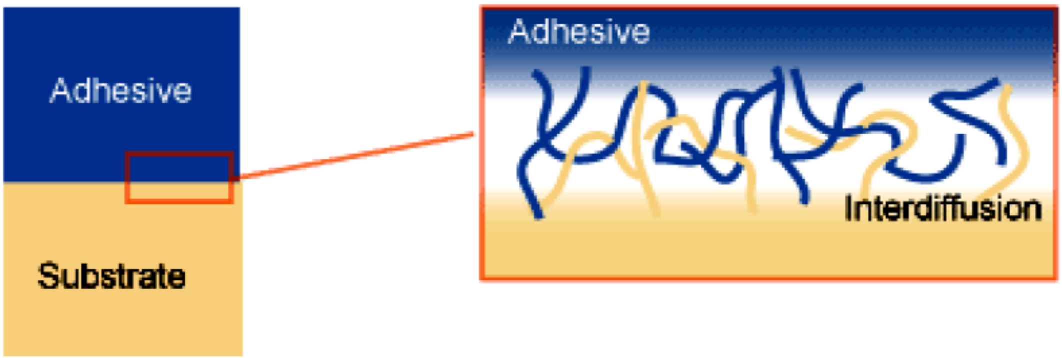


Figure 2.13 Adhesion by diffusion [29]

2.5.4 Wetting Theory

This theory proposes that adhesion results from molecular contact of two materials and the surface forces that develop between them. The first step in bond formation is to develop interfacial forces between the adhesive and the substrates. The process of establishing continuous contact between the adhesive and the adherend is called wetting. For an adhesive to wet a solid surface, the adhesive should have a lower surface tension than the critical surface tension of the solid, which is the reason for the surface treatment of plastics.

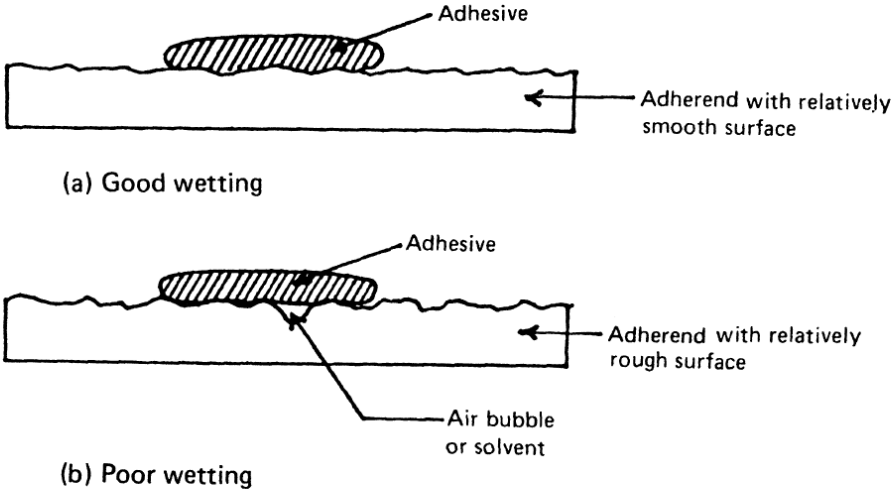


Figure 2.14 Examples of good and poor wetting by an adhesive spreading across a surface.[26]

Figure 2.11 illustrates complete and incomplete wetting of an adhesive spreading over a surface. Good wetting results when the adhesive flows into the valleys and crevices on the substrate surface. Poor wetting occurs when the adhesive bridges over the valley and results in a reduction of the actual contact area between the adhesive and adherend, and thus a lower overall joint strength. Incomplete wetting generates interfacial defects, thereby reducing the adhesive bond strength. Complete wetting achieves the highest bond strength [26].

2.5.5 Chemical Bonding

This mechanism attributes the formation of an adhesion bond to surface chemical forces. Hydrogen, covalent, and ionic bonds formed between the adhesive and adherends are stronger than the dispersion's attractive forces. In general, there are four types of interactions that take place during chemical bonding: covalent bonds, hydrogen bonds, Lifshitz-van der Waals forces, and acid-base interactions. The exact nature of the interactions for a given adhesive bond depends on the chemical composition of the interface [26].

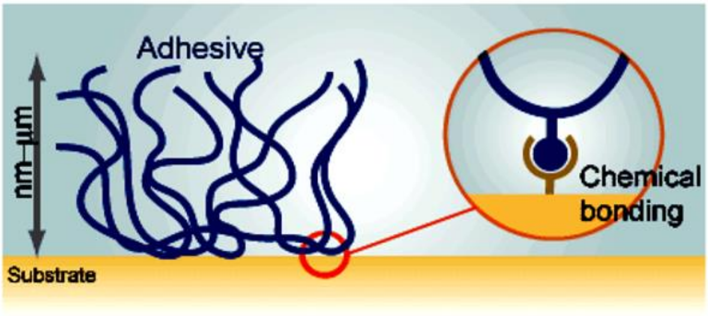


Figure 2.15 Adhesion by absorption [30]

Zalucha [31] has contributed a review article titled "Adhesives and Adhesion" in the same book. If the oxide is stable and similar in lattice spacing to the metal, it will strongly adhere to the underlying metal, which is certainly the case with aluminum adherends. Practically speaking, bonding is present in a small boundary layer which varies in composition with increasing amounts of metal toward the surface and increasingly higher in percentage of oxide toward the top of the layer exposed for bonding. Although the chemical structure of organic polymers and oxides are fundamentally different, they do have adherence potential to one another which seems to depend strongly on the nature and activity of the oxide and structure and functional groups present in the adhesive polymer. For example, polymers with hydroxyl and amino groupings can form hydrogen bonds which seem to adsorb very well on aluminum oxide. Moreover, Nakazawa [32] surmised that hydrogen bond is the basis for the adhesion of adherents to surface hydroxy groups, like wood and metals, to epoxy resins, and proposed the interfacial bond model presented in figure 2.16.

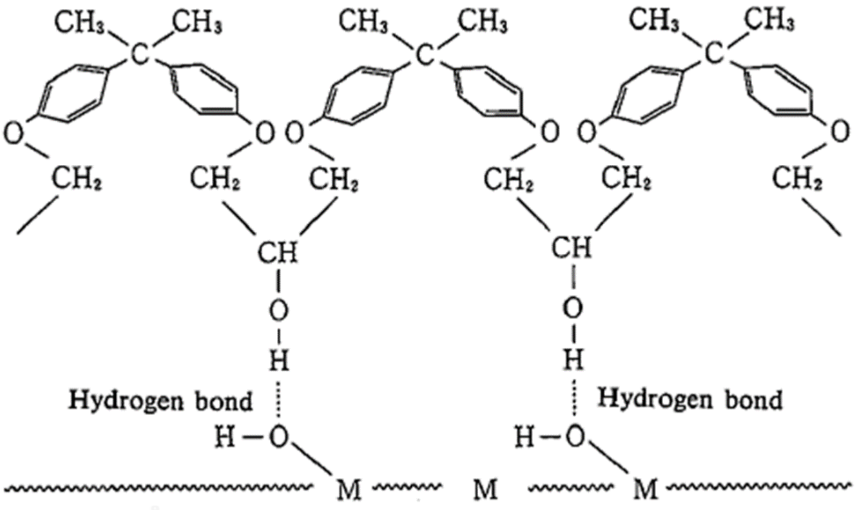


Figure 2.16 Mechanism of adhesion between epoxy resin and metal surface [32]

2.6 Screen Printing and Stencil Printing

Of the mass-transfer dispensing methods, screen printing and stencil printing are the oldest and most widely used. Screen printing has been used for over 40 years in the electronics industry to apply thick-film conductors, resistors, and dielectrics in fabricating circuits on ceramic and plasticlaminate substrates. Screen printing is also used as a batch process for depositing electrically conductive and insulative adhesives to interconnect devices on thin-film and thick-film hybrid microcircuits.

Screen printing is a simple, low-cost process for both small and large production runs. Patterns are formed on a stainless-steel mesh through a photosensitive emulsion process in which portions of the screen mesh are coated while other areas, through which the paste is to be deposited, are left open. The photolithographically formed screen patterns, however, wear out after many runs and the screens must be reprocessed or replaced. Also, separate screens are required for different circuit configurations, which presents a logistics problem in their storage, identification, and retrieval, especially where hundreds of part types are to be fabricated.

Stencils differ from screens in that the apertures are directly etched or cut into a metal sheet or foil. In both stencils and screens, the paste is squeegeed through apertures onto a substrate. Both screen printing and stencil printing can be used to deposit adhesives or solder pastes, but stencil printing produces finer dimensions and closer spacings. The key advantage of stencils over screens, especially for the laser cut and electroformed types, is the finer dimensions and smaller pitch dots that can be printed. Stencils have become essential in depositing adhesive and solder paste for small pitch devices of less than 0.5 mm. Conductive epoxies can be printed as small as 3-mil-diameter dots on 5-mil pitch. Differing from pin transfer, stencil printing can deposit small dots of various sizes and heights from a single stencil. Dots smaller than the stencil thickness can be deposited through apertures that act like tiny dispensing tips.

Stencil printing is a fast efficient process for long production runs and is widely used in surface mounting of components. In surface mounting, the solder paste is generally dispensed first by stenciling, followed by needle dispensing the adhesive; however, these processes may be reversed or both the solder and adhesive can be selectively dispensed by needle [33].

2.6.1 Adhesive material and rheology properties.

Adhesives used for screen or stencil printing in surface-mount applications are generally electrically insulative types whose functions are mechanical attachment and thermal dissipation. However, electrically conductive, silver-filled epoxies have been used for many years as ohmic contact adhesives to interconnect bare-chip devices in hybrid microcircuits and are beginning to be used as solder replacements for surface mounting of components on printed-circuit boards. Regardless of their conductivities, adhesives applied by screen or stencil printing should have the following properties:

- Low moisture absorption and workable viscosity over a 3–5 day period of exposure on the stencil.
- Viscosity suitable for dispensing (30,000–100,000 cps at 2.5 rpm).

- Thixotropic properties (ability to flow freely through the stencil/screen apertures during printing and recover quickly after printing) [33].

2.7 Epoxy Resins

Epoxy resins are high-performance thermosetting resins, which display a unique combination of properties. Epoxy resins have been commercially available for almost a half-century. Epoxy resins are arguably one of the most versatile polymers with uses across an enormously wide variety of industries. The outstanding physical properties exhibited by epoxy resins include

- Low cure shrinkage
- No volatiles given off during cure
- Compatibility with a great number of materials
- Strength and durability
- Adhesion
- Corrosion and chemical resistance
- Electrical insulation.

Furthermore, epoxy resin systems are capable of curing at either ambient or elevated temperatures and they require only minimal pressure during the cure. Thus, epoxies can be applied and cured under many adverse conditions including outdoors.

These properties provide great added value in many industries engaged in product assembly. Epoxy resins have been commercially available for almost a half-century.

Many new applications are being developed that will ensure the prominence of epoxy resins in the future. For example, epoxies are the material of choice for the reinforcement or consolidation of aging or damaged concrete structure including walls, ceiling beams, bridge columns, and anchoring mechanisms. They are the main binders for graphite-reinforced composites such as those used in manufacturing tennis rackets, fishing rods, skis, snowboards and golf club shafts. They have also been used for manufacturing high-strength, lightweight carbon fiber pultrusion as replacements for steel rebar in special concrete expansion projects.

Industries using epoxy adhesives include aerospace, civil engineering, automotive, chemical, electrical, marine, leisure, and many others. The prevailing reason for the broad acceptance of epoxy resins in these important and diverse markets is their capacity to provide a good balance of handling characteristics and ultimate physical properties. They adhere well to a very large variety of substrates, and they generate tough, environmentally resistant films or matrices.

One of the major advantages of epoxy chemistry is the wide latitude it provides the formulator for solving technical problems. Epoxies can be designed to be flexible or rigid; high or low modulus; homogeneous, filled, or foamed; conductive or insulative, fire-retardant and resistant to heat and chemicals.

The number of raw materials that the formulator has to work with is enormous. These include epoxy resins and modified epoxy resins of all types and forms, fillers and additives, modifiers, reinforcements, diluents, and solvents. The possible curing agents that can be used also provide great latitude in formulation. Often the curing agent becomes an integral part of the resulting compound. Its choice is a controlling influence on the curing properties of the mixture and on the performance properties of the cured adhesive. One of the chief advantages of epoxy resins is that they generally allow easy incorporation of additives and the resulting formulation is one that can be easily adapted to many manufacturing processes.

Epoxy resins are not the lowest-cost resins potentially available for most applications. Thus, epoxy resins must provide added value to justify their additional cost. This added value is usually realized by the incorporation of a special property or combination of properties into the final product.

The term epoxy, epoxy resin, or epoxide (Europe) refers to a broad group of reactive compounds that are characterized by the presence of an oxirane or epoxy ring, shown in Figure 2.16. This is represented by a three-member ring containing an oxygen atom that is bonded with two carbon atoms already united in some other way [34].

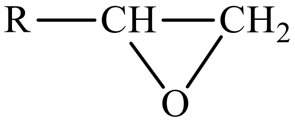


Figure 2.17 The epoxy or oxirane ring structure [34].

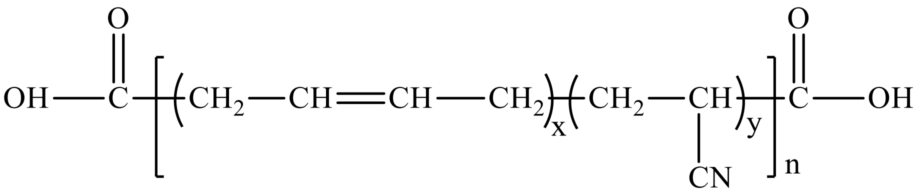
2.8 Rubbers Used for Toughening Epoxy

Liquid rubber is one of the most successful tougheners for epoxy. The attempt to toughen epoxy resins was initiated by researchers from B. F. Goodrich Company and first reported by McGarry. Since then, extensive research has been devoted to understanding the toughening mechanisms of rubber-toughened epoxies [35].

2.8.1 Carboxyl Terminated Butadiene-Acrylonitrile (CTBN)

McGarry et al. used a liquid CTBN copolymer to modify diglycidyl ether of bisphenol A (DGEBA) epoxy cured with 2,4,6-tri(dimethylaminoethyl) phenol (DMP). The results showed that the fracture toughness of modified epoxy was increased by an order of magnitude at the optimum rubber content (about 7.5 wt%). CTBN has been shown to be the most effective toughener for epoxy. In a typical process, CTBN is first dissolved in the epoxy, and after the addition of the curing agent, the rubbery phase precipitates to form the second-phase particles as the epoxy resin begins to cure and the molecular weight begins to increase. A good miscibility between rubber and epoxy is very important to achieve a satisfactory toughening effect. Bucknall and Patridge found that the miscibility between CTBN and epoxy depended largely on the type of epoxy resin used, and CTBN was more miscible with epoxy having similar solubility parameters. Verchere et al. found that the miscibility between epoxy monomers (DGEBA) and rubbers (CTBN) was very sensitive to the molecular weight of the epoxy molecule, and even a small increase in the number-average molecular weight led to a significant shift in the miscibility gap to higher temperatures. Moreover, a lower content of AN in the CTBN resulted in poorer miscibility due to the change in solubility parameter. In contrast, CTBN with a higher content of AN had a larger solubility parameter, resulting in better miscibility with epoxy.

A strong interfacial bond between the particles and the matrix is also very important to achieve improved toughness. For CTBN, the carboxyl groups react easily with the oxirane rings of the epoxy, thus resulting in a good interfacial adhesion between the two phases. The chemical structure of CTBN is shown in Figure 2.17 [35].



$$HO-\overset{O}{\overset{\|}{C}}-\left[(CH_2-CH{=}CH-CH_2)_x(CH_2-\underset{CN}{\underset{|}{CH}})_y\right]_n-\overset{O}{\overset{\|}{C}}-OH$$

Figure 2.18 The chemical structure of CTBN

2.9 Curing Agents for Epoxy Resin

Epoxy resin has excellent bonding property, and also after curing, it has excellent properties on mechanical strength, chemical resistance, and electrical insulation. In addition, epoxy resin is able to have various different properties as it is combined and cured together with various curing agents [36].

2.9.1 Amines

Amine compounds are classified into primary, secondary and tertiary amines, in which one, two and three hydrogen molecule of ammonia (NH_3) have been substituted for hydrocarbon, respectively. Amines are called monoamine, diamine, tri-amine, or polyamine according to the number of amines in one molecule. Amines are classified into aliphatic, alicyclic and aromatic amines according to the types of hydrocarbons involved and the all are important curing agents for epoxy resin.

Aliphatic amine is curing agent for epoxy resin ant able to cure at room temperature. The cured resin has excellent properties, and its heat resistance is 100°C. Aromatic amine has been developed to achieve greater heat resistance and chemical resistance than those of aliphatic amine.

The curing of epoxy resin by amine curing agents is expressed by the formula shown below; the active hydrogen in primary amine reacts with an epoxy group to form secondary amine and the secondary amine reacts with an epoxy group to cure. Then, the resultant tertiary amine polymerizes epoxy groups.

In general, curing agent must have more than three active hydrogen atoms and two amino groups in a molecule so that the cured resin becomes crosslinked polymer, according to the reaction of the above equation. The loading of the curing agent in epoxy resin becomes optimal when the number of moles in epoxy groups is equal to that of active hydrogen.

The curing speed of individual amines depends on the type and loading of amine and the type of epoxy resin. The most commonly used glycidyl-ether type resins easily cure at room temperature, but inner epoxy type such as cyclohexene oxide and epoxidized polybutadiene is hardly cured. Glycidyl-ester type cures quite faster than glycidyl-ether type. Diglycidyl ether of bisphenol A (DGEBA), which is a condensation product of bisphenol A and epichlorohydrin, is primarily cured by aliphatic amines at room temperature, but is slowly cured by aromatic amines and requires thermal curing [36].

Table 2.3 The properties and performances of representative polyamines used as curing agents for epoxy resin [36].

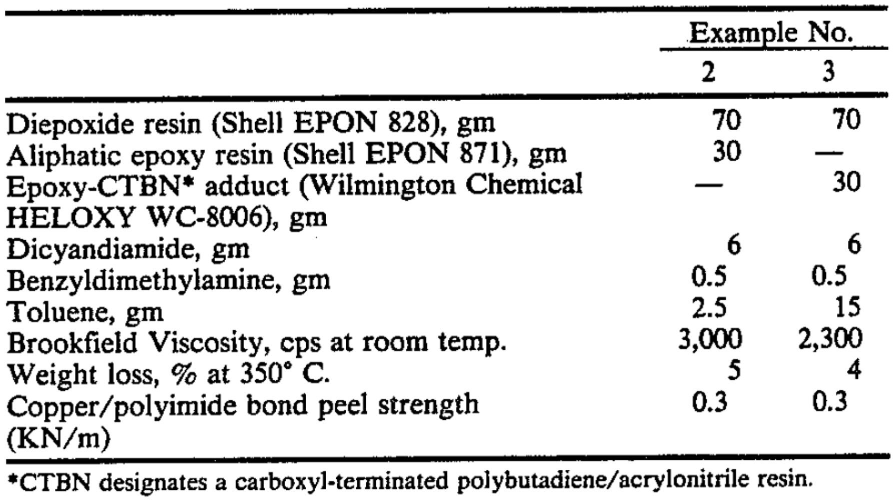
Class	Subclass	Name of curing agent	Appearance	Viscosity cps (25°C)	Active - hydrogen equivalent (amine value)	Loading amount to liquid epoxy resin (phr)	Specific gravity (g/ml) (20°C)	Pot life (100 g) (batch)	Curing conditions		Heat deformation temperature (°C)	Applicability			
									Temperature (°C)	Time (minutes)		Bonding	Lamination	Casting	Paint
Aliphatic polyamine	Chain aliphatic polyamine	Diethylenetriamine (DTA)	Transparent liquid	5.6	20.7	5 - 10 Standard value: 8	0.954	20 minutes	Normal to 100	30 minutes to 4 days	115	○	○	○	○
		Triethylenetetramine (TTA)	Transparent liquid	19.4	24.4	6 - 12 Standard value: 9	0.98	20 to 30 minutes	Normal to 100	30 minutes to 4 days	115	○	○	○	○
		Tetraethylenepentamine (TEPA)	Transparent liquid	51.9	27.1	7 - 14 Standard value: 12	1.00	30 to 40 minutes	Normal to 100	30 minutes to 7 days	115	○	○	○	○
		Diproprenediamine (DPDA)	Transparent liquid		29.0	12 - 15		20 to 30 minutes	Normal to 200	30 minutes to 7 days	110	○	○	○	○
		Diethylaminopropylamine (DEAPA)	Transparent liquid		65.0	4 - 8 Bonding = 8, Casting = 4, Lamination = 6		1 to 4 hours	65 - 115	1 - 4 hours	85	○	○	○	
		AMINE 248	Transparent liquid	1000 - 3000	42.9	35	0.83	30 minutes	Normal to 100	30 minutes to 4 days	92	○		○	
	Alicyclic polyamine	N-aminoethylpiperazine (N-AEP)	Transparent liquid		43	20 - 22	0.984	20 to 30 minutes	Normal to 200	30 minutes to 3 days	103		○	○	
		Lamiron C-260	Transparent liquid	60	31 - 33	31 - 33	0.945		80+150	2 hours + 2 hours	150		○	○	○
		Araldit HY-964	Transparent liquid	70		15 - 20	0.94	120 minutes	Normal	7 days					○
		Menthane diamine (MDA)	Transparent liquid	19.0	42.5	22		6 hours	80 - 130 130 - 200	30 minutes to 2 hours 2+3 hours	158	○	○	○	
		Isophoronediamine (IPDA)	Transparent liquid	18.2	41	24	0.924	1 hour	80+150	4+1 hours	149		○	○	
	Aliphatic aromatic amine	m-xylenediamine (m-XDA)	Crystalline liquid		34.1	16 - 18	1.05	20 minutes	Normal to 60	1 hour to 7 days	115	○			
		Sho-amine X	Liquid	68°	33 - 34	16 - 18	1.05	20 minutes	Normal to 60	1 hour to 7 days	113	○			
		Amine black	Viscous liquid	(50°C) 2000 - 6000		30 - 60	1.20	40 minutes	Normal to 60	1 hour to 7 days		○			○
		Sho-amine black	Viscous liquid	6000 - 10000		25 - 35	1.18	40 minutes	Normal to 60	1 hour to 7 days	116	○			○
		Sho-amine N	Liquid	5°	(690)	25	1.18	80 minutes	Normal to 60	1 hour to 7 days	81	○		○	
		Sho-amine 1001	Liquid	100.0		27	1.07		Normal to 60	1 hour to 7 days	73	○		○	
		Sho-amine 1010	Liquid	40.0		27			Normal to 60	1 hour to 7 days	70	○		○	
Aromatic amine		Metaphenylene diamine (MPDA)	Solid	mp62 °C	34	14 - 16	0.95	6 hours	80+150	2+4 hours	150	○	○	○	
		Diaminodiphenylmethane (DDM)	Solid	mp8 °C	49.6	25 - 30	1.05	8 hours	80+150	2+4 hours	150	○	○	○	
		Diaminodiphenylsulfone (DDS)	Solid	mp17 5°C	62.1	30 - 35	1.33	Approximately 1 year	110+200 °C	2+4 hours	180 - 190	○	○	○	

CHAPTER III

LITERATURE REVIEWS

K. S. Kim and N.Y.Katonah (Patent US1986/4626474) provide polyimide films can be laminated to metal foils by the use of an epoxy adhesive composition which consists essentially of a predominant amount of an epoxy resin and a suitable curing agent for the epoxy resin. Optional additives which can be used in lesser amount than the epoxy resin includes fexibilizers, accelerators, solvents and surfactants. The epoxy adhesive composition used in the present invention can be modified with an amount of polymeric flexibilizer, for example, which is significantly less than the amount of epoxy resin that is utilized.

Table 3.1 The results of thermal analysis of the cured compositions and peel strength [37]



	Example No.	
	2	3
Diepoxide resin (Shell EPON 828), gm	70	70
Aliphatic epoxy resin (Shell EPON 871), gm	30	—
Epoxy-CTBN* adduct (Wilmington Chemical HELOXY WC-8006), gm	—	30
Dicyandiamide, gm	6	6
Benzyldimethylamine, gm	0.5	0.5
Toluene, gm	2.5	15
Brookfield Viscosity, cps at room temp.	3,000	2,300
Weight loss, % at 350° C.	5	4
Copper/polyimide bond peel strength (KN/m)	0.3	0.3

*CTBN designates a carboxyl-terminated polybutadiene/acrylonitrile resin.

M. A. Downey and L.T. Drzal (2014) have investigated an aromatic DGEBA/mPDA epoxy system by the addition of di- and tri-functional epoxy copolymers. The DGEBA is the brittle nature of the highly cross-linked epoxy system, i.e. their lack of toughness. Once formed in an epoxy material, a crack will propagate through the material uninhibited. Unlike metals, where the crack propagation will be quickly impeded by intersection of a grain boundary, no such mechanism exists in epoxies. The approach of adding a more flexible aliphatic epoxy copolymer would address the issue of processability, provided that the epoxy copolymers are miscible. Having the same functional epoxy groups, the copolymers will undergo the same reaction with the diamine curing agent to form a highly cross-linked network.

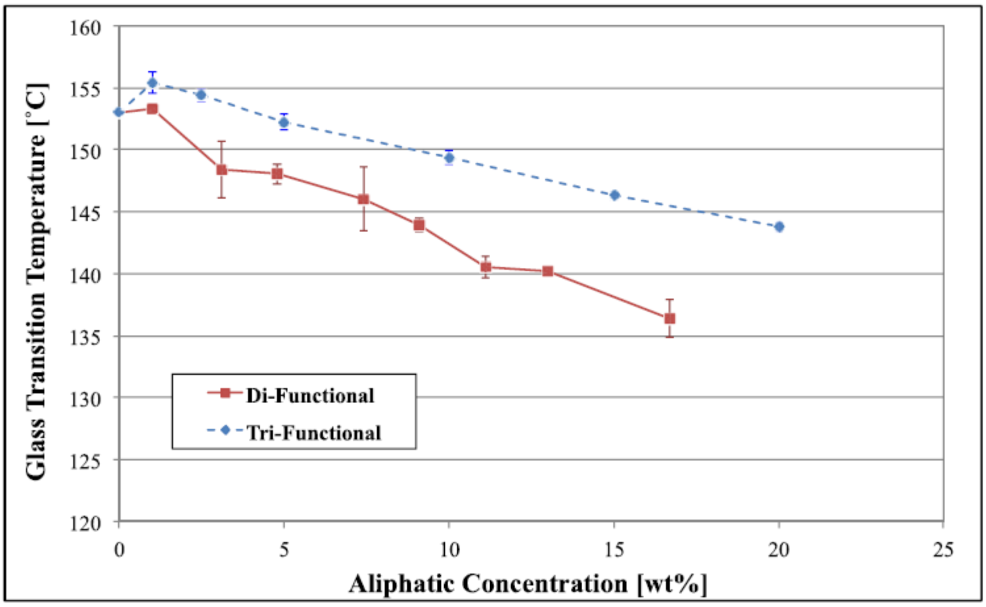
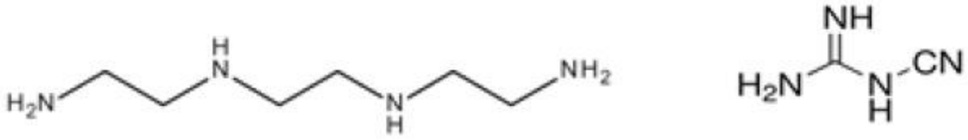


Figure 3.1 Glass transition temperature of di- and tri-functionally toughened DGEBA/mPDA determined from maxima of tan δ curve [10].

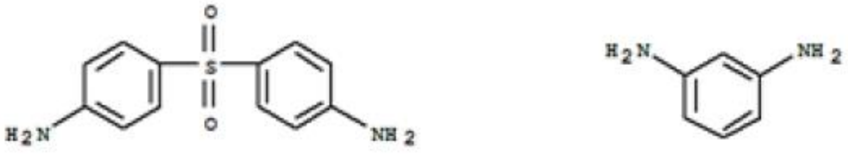
As can be seen in Figure 3.1, the results show thermal properties of DGEBA/aliphatic epoxy mixtures that the glass transition temperature (Tg) was decreased with an increasing di-functional aliphatic epoxy concentration. The maximum reduction is around 10% at ~17 wt% di-functional aliphatic. At 1 wt% tri-functional aliphatic, the Tg has an increase of about 2%. Up to a concentration of 5 wt% tri-functional aliphatic, the Tg is comparable to neat DGEBA. Above a concentration of 5 wt%, The Tg decreases with an increasing of the tri-functional aliphatic. The reduction in Tg for the tri-functional aliphatic epoxy is smaller when compared to the di-functional aliphatic epoxy. This can be attributed to the different network formation of the tri-functional epoxy. The lower epoxy equivalent weight (EEW) of the tri-functional aliphatic implies a shorter distance between cross-links and a higher cross-link density.

N.A. Razack and and L.A. Varghese (2014) studied on DGEBA is cured with both aliphatic and aromatic hardeners and a comparison was done based on mechanical characterization, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The four different hardeners (2 aliphatic and 2 aromatic) i.e. triethylene tetramine (TETA), dicyandiamide (DICY), diaminodiphenyl sulphone (DDS), and m-phenylenediamine (mPDA) were used in the stoichiometric amounts for the study. The chemical structure of epoxy hardeners are shown in Figure 3.2.



Triethylene tetramine

Dicyandiamide



Diamino diphenyl sulphone

m-phenylenediamine

Figure 3.2 Chemical structures of the various curing agents used [12].

Mechanical characterization mainly comprises of peel strength of metal-to-metal specimens. Peel strength is the average load per unit width of bond line required to part bonded materials.Peel tests involve stripping away a flexible adherend from another adherend that may be flexible or rigid. The average peel strengths of the various formulations are given in table 3.2. From the results, it is clear that aromatic amines gave better strength characteristics compared to the aliphatic amines.

A comparison of the TGA curves for the various systems are given in Figure 3.3, from which it is clearly understood that there was no loss of material upto around 250°C, which signifies the system can be used for elevated temperature applications. Eventhough aromatic amines have less electron density on nitrogen than aliphatic amines, the resin cured with aromatic amine shows higher thermal and chemical resistance property due to the presence of rigid and thermally stable aromatic rings apart from the fact that they are less reactive.

Table 3.2 Average peel strength values for various curing agents [12].

Curing agent	Average peel strength (N/mm)
Triethylene tetramine (TETA)	0.272
Dicyandiamide (DICY)	0.333
Diamino diphenylsulphone (DDS)	0.706
m-Phenylene diamine (mPDA)	1.240

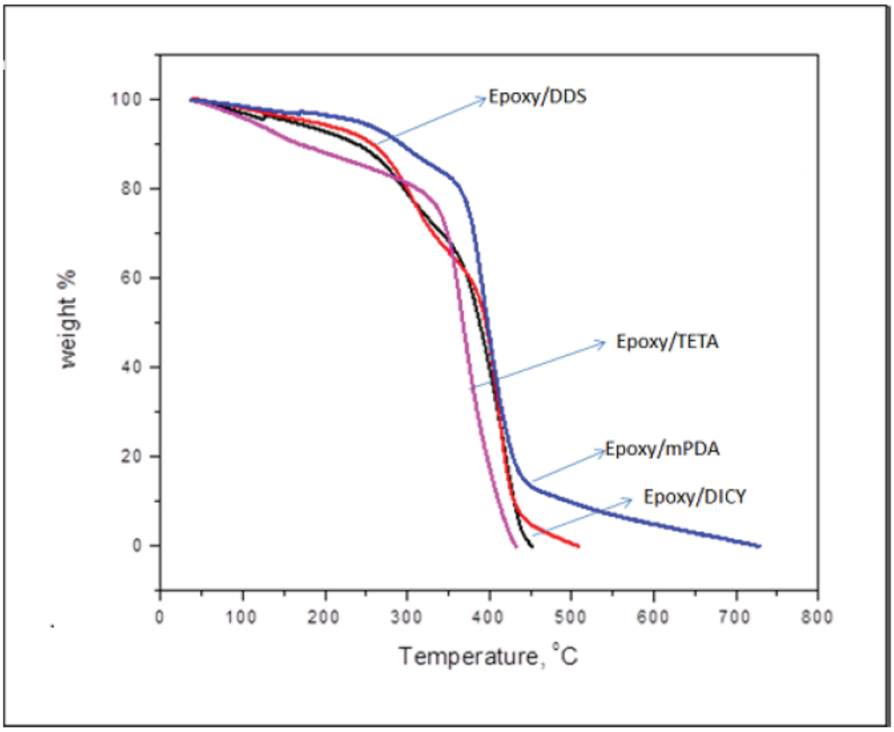


Figure 3.3 Thermogravimetric analysis curves for various epoxy/hardener systems [12].

M.A. Uddin *et al.* (2003) have investigated the optimum curing conditions to achieve the best performance of anisotropic conductive adhesives film (ACF) joints. The ACF is a thermosetting epoxy matrix impregnated with small amount of electrically conductive particles. Differential scanning calorimeter was used to measure the curing degree. In parts of, adhesion strength of the ACF and flexible substrate were evaluated by 90° peeling test. As can be seen in the Figure 3.4, the dependence of the 90° peel strength of the joints on the curing degree of ACF was observed that peel strength increases at first slowly with curing degree and after 75% curing, it starts to increase quickly. This is a very common phenomenon reported elsewhere that partially cured polymer shows weaker strength and later it increases with the degree of curing. However, in this experiment, after 87% curing of ACF (i.e. bonded at 210°C), peel strength increases at an unusual manner than the typical polymer. It implies that other mechanism is also contributing to increase the strength. Fracture mode for these higher cured samples is also different than that of the expectation.

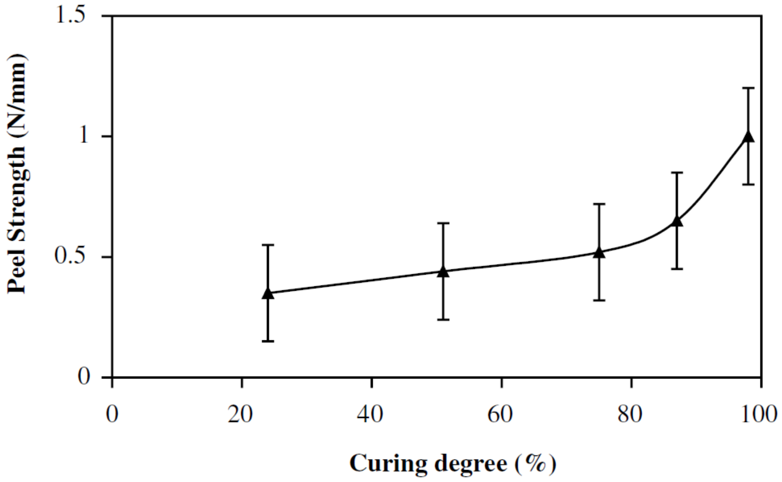


Figure 3.4 Dependence of the peel strength of the joints on the curing degree [13].

L. Liu *et al.* (2015) studied on the peel strength of the modified epoxy adhesive as a function of the CTBN content and epoxy equivalent ratio of 901 and 6128. Figure 3.5 also shows that the peel strength of FCCL varies with the CTBN content. Rubbers are generally well known to affect adhesion depending on their compatibility with epoxy matrix and content as well as the intrinsic strength of the rubber phase.

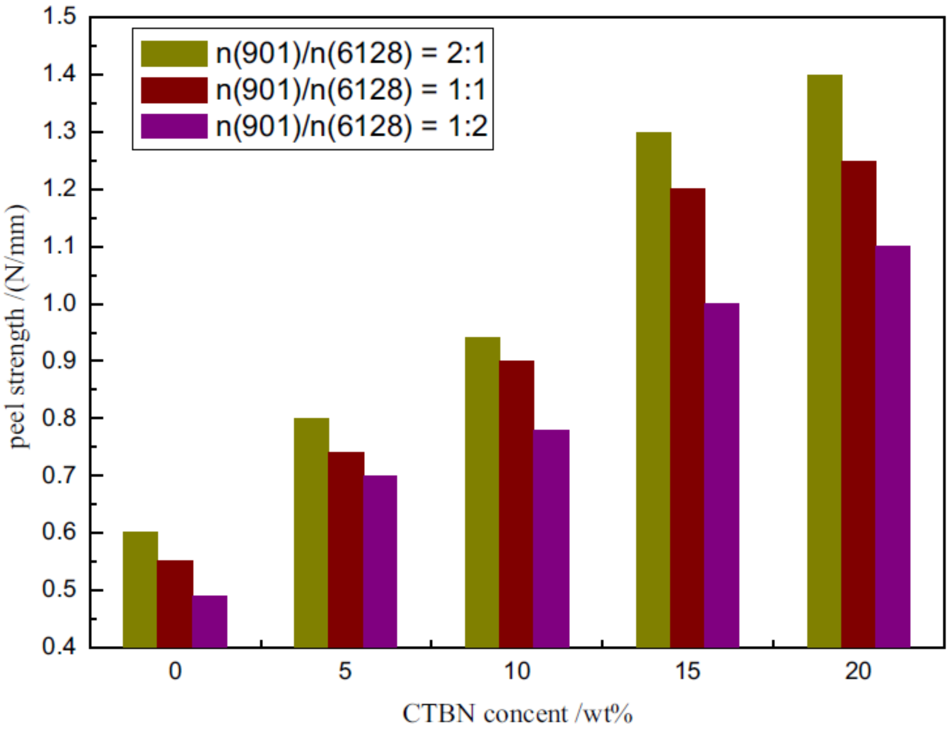


Figure 3.5 Effect of CTBN content and epoxy ratio (901/6128) on the peel strength of FCCL [38].

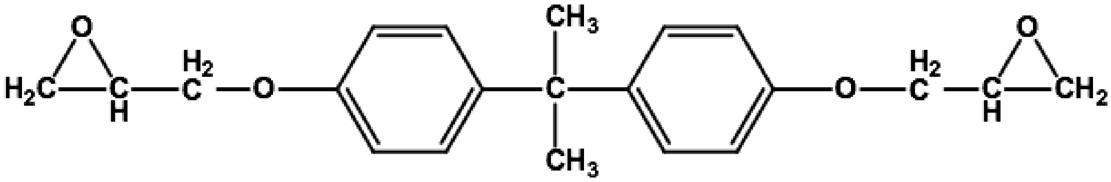
As observed, the peel strength of FCCL gradually increases with increasing CTBN content, which might be attributed to the effect of the soft segment structure of CTBN dispersed in epoxy matrix which lead to a decrease in the stiffness and elastic modulus, hence reducing stress concentration at the interface of PI film and copper foil. Generally, there is one way to toughen an epoxy resin with a polymer. That is to add some rubber-like materials into the polymer to form a rubbery second phase, and this rubbery second phase should be bonded to the matrix through the functional groups of the polymer. In Figure 3.5, the peel strength increases from 0.6 to 1.4 N/mm with increasing CTBN content at epoxy equivalent ratio of 2:1 of 901 and 6128.

CHAPTER IV

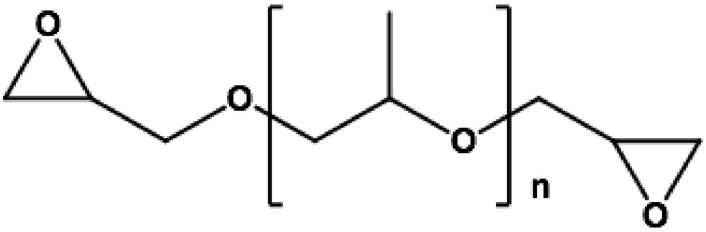
EXPERIMENTS

4.1 Raw Materials

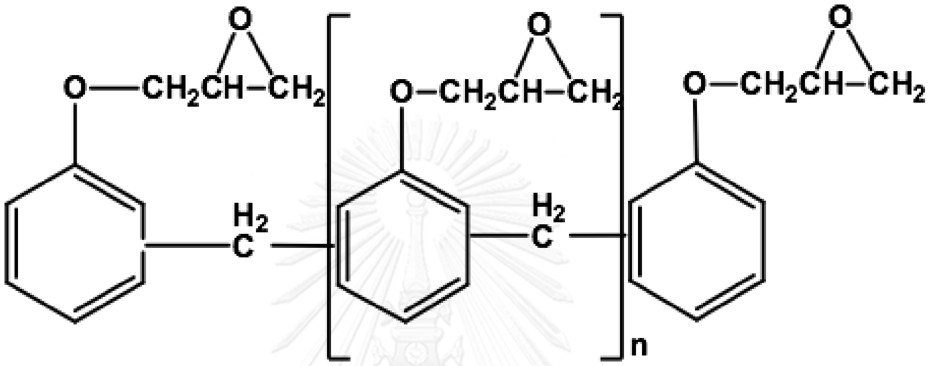
The chemical resins used in this research are epoxy resins and carboxyl terminated butadiene-acrylonitrile rubber (CTBN). Epoxy resins were kindly supplied by Aditya Birla Chemicals (Thailand) Ltd. The epoxy system based on the commercial grade rigid diglycedyl ether of bisphenol A (DGEBA) (YD-128) with an average epoxy equivalent of 186.3 g/eq. Polypropylene glycol diglycidyl ether (PPGDE) was used to impart flexibility having an average epoxy equivalent of 335.8 g/eq. Epoxy phenol novolac resin (EPN) (YDPN-661) as multifunctional having an average epoxy equivalent of 172.7 g/eq. 1,3-Phenylenediamine (mPDA) as an aromatic diamine curing agent and CTBN was purchased from Sigma–Aldrich chemical company. The chemical structures of epoxy resins, curing agent, and CTBN are shown in Figure 4.1.



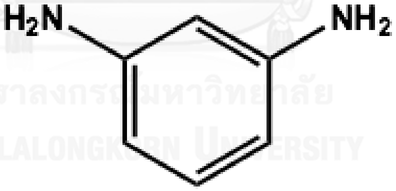
Diglycedyl ether of bisphenol A (DGEBA)



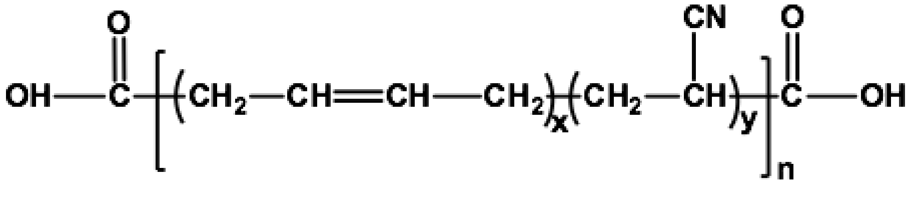
Polypropylene glycol diglycidyl ether (PPGDE)



Epoxy phenol novolac resin (EPN)



1,3-Phenylenediamine (mPDA)



Carboxyl terminated butadiene-acrylonitrile rubber (CTBN)

Figure 4.1 Chemical structures of materials used in this research.

4.2 Adhesive preparation

Diglycedyl ether of bisphenol A (DGEBA) or epoxy phenol novolac resin (EPN) as rigid epoxy were blended with polypropylene glycol diglycidyl ether (PPGDE) to provide epoxy mixtures. Then, the mixtures were mixed with curing agent in a small bottle at a stoichiometric molar balance of hydrogen of amine to epoxide ring of 1:1 and stirred to yield a homogeneous mixture for 30 min at room temperature. The mixture was laminated between aluminum backup board and polyimide films. After that, the sample was placed in an oven at 170^{o}C for 15 min to cure the adhesives film. The sample was finally left to cool down to room temperature and was then ready for material characterizations.

Subsequently, epoxy-CTBN adhesive system was further prepared by an addition of carboxyl terminated butadiene-acrylonitrile rubber (CTBN) into the selected epoxy system from the previous experimental part. The CTBN were added at various amounts of 0 - 20 parts per hundred resins (phr). After that, epoxy-CTBN adhesive was also prepared with the same steps of the previous preparation part.

4.3 Characterization Methods

4.3.1 Differential Scanning Calorimetry (DSC)

The curing characteristic of the epoxy adhesives were evaluated by using a differential scanning calorimeter (DSC) model DSC1 from Mettler-Toledo (Thailand) Ltd. The samples were sealed with a mass in range of 5 - 10 mg in an aluminum pan. They were systematically scanned with a heating rate of 10°C/min from 0°C up to 250°C under a nitrogen flow rate of 50 ml/min. The glass transition temperature (T_g) and curing temperature (Tcure) were obtained from the thermograms while the degree of conversion was calculated from the DSC thermograms.

The degree of conversion of a sample was determined according to the relationship in Equation (4.1):

$$\text{Conversion (\%)} = \left(\frac{H_{rxn}}{H_0}\right) \times 100 \qquad (4.1)$$

Where: H_{rxn} = heat of reaction of partially cured samples

H_0 = heat of reaction of uncured resin mixture

4.3.2 Fourier transform infrared spectroscopy (FTIR)

The curing reaction was further confirmed by fourier transform infrared spectroscopy (FTIR). FTIR spectra of the uncured epoxy samples, CTBN rubber and epoxy-CTBN blend were measured with a Nicolet 6700 FTIR spectrometer from

PerkinElmer Co., Ltd. in a spectral range of 4000 - 400 cm^{-1} with 128 scans at a resolution of 4 cm^{-1}.

4.3.3 Thermogravimetric Analysis (TGA)

Thermal stability of epoxy adhesives were performed on a thermogravimetric analyzer (model TGA1 Module) from Mettler-Toledo (Thailand). The testing temperature program was ramped at a heating rate of 20°C/min from 25°C up to 850°C under nitrogen atmosphere with a constant N_2 purge gas flow rate of 50 ml/min. The sample mass used was approximately 5 - 10 mg. The degradation temperature (T_d) and char yield of the samples were reported at their 5% weight loss and at 800°C, respectively.

4.3.4 Mechanical Property Test (Peel test)

The 90° peel strength was measured by a universal testing machine (Instron, model 5567) based on IPC-TM-650-249 from Instron(Thailand)Co.,Ltd. The specimens (5 mm width of a peel test specimen) of the adhesive joints between an aluminum backup board and polyimide film was evaluated with a peel rate of 50 mm/min. Figure 4.2 shows the schematic arrangement for measuring the peel strength. The peel strength is calculated during a peel test at a constant speed rate by divided the average force required during the test by the unit width of the bonded samples.

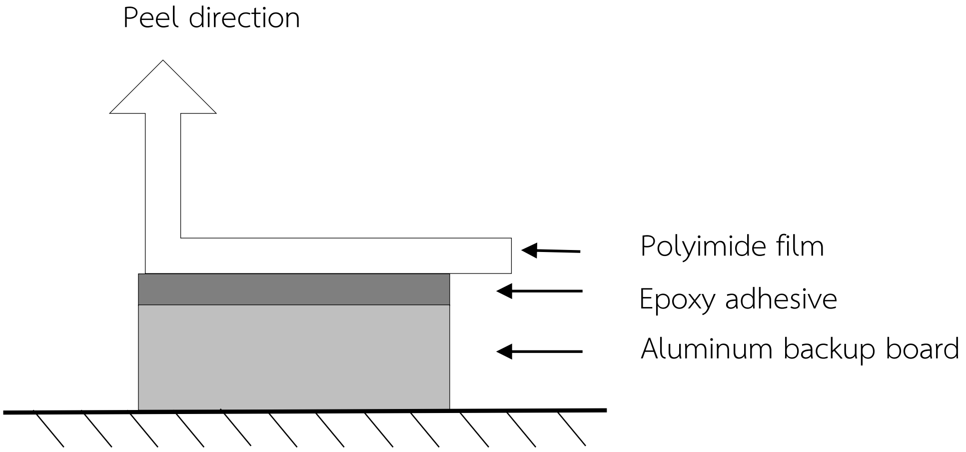


Figure 4.2 Schematic arrangement for measuring the peel strength

4.3.5 Viscosity and pot life

Viscosity was obtained by using a parallel plate rheometer, TA instrument model AR G2, varying shear rate of 0.1 - 100 s^{-1}. Pot life time was studied by monitoring the time-dependent viscosity under a constant shear rate of 1 s^{-1}. All experiments were carried out at room temperature.

CHAPTER V

RESULTS AND DISCUSSION

5.1 Curing Behaviors of DGEBA/PPGDE Blends

The curing reaction of neat DGEBA, neat PPGDE and DGEBA/PPGDE binary mixtures at mass ratios of 90/10, 80/20, 70/30, 60/40 and 50/50 were examined by a differential scanning calorimeter that was shown in Figure 5.1. From these thermograms, a single exothermic peak of the curing behaviors of each resin mass ratios were observed. The exothermic peak of neat DGEBA and neat PPGDE were 155°C and 205°C, respectively. The exothermic peak of each binary polymeric mass ratio was slightly shifted to higher temperature when increasing of PPGDE mass fraction in the mixtures. As shown in this figure, the exothermic peak positions at 90/10, 80/20, 70/30, 60/40 and 50/50 mass ratios were found to be 157°C, 164°C, 165°C, 168°C, and 170°C, respectively. This phenomenon was possibly because the less reactive in epoxide rings of PPGDE when compared with DGEBA resin in ring-opening polymerization reaction, as similarly reported by Ratna *et al*. [39]. In addition, the area under the exothermic curve of various mass ratios were evaluated about the heat of reaction of the resin mixtures. From this figure, heat of reaction of neat DGEBA and neat PPGDE were 342 J/g and 66J /g, respectively. Whereas, heat of reaction values of the mixtures decreased with increasing PPGDE mass fraction. The heat of reaction values of the DGEBA/PPGDE resin mixtures, which were determined to be 338 J/g, 296 J/g, 271 J/g, 230 J/g, and 196 J/g at DGEBA/PPGDE mass ratios of 90/10, 80/20, 70/30, 60/40, and 50/50, respectively. From the principle, a decreasing of heat of reaction was due to the DGEBA/DGEBA ring-opening interaction by using m-PDA for help harden that possessed a higher heat of reaction per mole of the reactant when compared with DGEBA/PPGDE ring-opening interaction. Consequently, this behavior is ascribed to the change from the DGEBA/DGEBA ring-opening interaction to a more DGEBA/PPGDE ring-opening interaction with increasing the PPGDE mass fraction in the binary mixture.

Furthermore, the DSC thermogram was also reported glass transition temperature (T_g) of neat DGEBA, neat PPGDE and DGEBA/PPGDE blends after curing process at various mass ratios, as shown in Figure 5.2. From this figure, glass transition temperature of neat DGEBA and neat PPGDE were 139°C and 31°C, respectively. The T_gs of DGEBA/PPGDE blends that used in this research increased with increasing DGEBA mass fraction. The values were determined to be 130°C, 81°C, 77°C, 68°C and 54°C at DGEBA/PPGDE mass ratio of 90/10, 80/20, 70/30, 60/40 and 50/50, respectively. The enhancement of T_g of this copolymers can be attributed to the more rigid molecular structure and possibly much higher intramolecular and intermolecular forces in DGEBA polymer compared to the PPGDE, the results were similarly reported by Downey and Drzal [10]. From their results, glass transition temperature of the DGEBA/di-functional aliphatic epoxy mixtures was decreased with increasing of aliphatic epoxy mass fraction from 1 to 17 wt%. Whereas, the T_g of DGEBA with tri-functional aliphatic epoxy also has a same trend. Whereas, heat of reaction of the all samples that cured with a temperature of 170°C for 15 min were decreased to be zero. The results demonstrate this temperature used for cure the samples resulting in fully-cured reaction in this binary system. The heat of reaction can be calculated by Equation 4.1.

5.2 Thermal Degradation and Thermal Stability of DGEBA/PPGDE Blends

The thermal degradation temperature (T_d) at 5wt% loss and residual weight at 800°C are important parameters used to determine the temperature stability of polymeric materials that investigated by a thermogravimetric analyzer. Figure 5.3 exhibits TGA thermograms of the DGEBA/PPDGE blends at various mass ratios. The polymeric blends were scanned under nitrogen purging from room temperature to 850°C with heating rate of 20°C/min. From the figure, degradation temperature at 5wt% loss of various samples were found to slightly decrease with increasing of PPGDE. The TGA curves of this binary system at various mass fractions of DGEBA at 90wt%, 80wt%, 70wt%, 60wt% and 50wt% introduced that the addition of PPGDE into the DGEBA resin gradually decreased the thermal degradation temperature of the obtained mixtures. The degradation temperatures of DGEBA/PPGDE blends at the DGEBA mass ratio of 90wt%, 80wt%, 70wt%, 60wt% and 50wt% were determined to be 373°C, 365°C, 356°C, 349°C and 343°C, respectively. Therefore, one advantage of the blending DGEBA resin with

PPGDE resin is the potential improvement of thermal stability of PPGDE due to higher thermal stability of DGEBA. In addition, the residual weight at 800°C of the DGEBA/PPGDE blends was found to increase with increasing of the PPGDE mass fraction in the binary polymeric system. As can be seen in this figure, the residual weight of DGEBA/PPGDE blends at mass ratios of 90/10, 80/20, 70/30, 60/40, and 50/50 were determined to be 12.5%, 12.3%, 11.9%, 11.6%, and 11.3%, respectively. The increase of thermal stability of the DGEBA/PPGDE blends with the increasing of DGEBA mass ratio is attributed to the fact that the structure that composed of aromatics ring of DGEBA provide higher thermal properties than the aliphatic structure of PPGDE as similarly reported in previous research by Park *et al*. [40].

5.3 Mechanical Properties of DGEBA/PPGDE Blends

Mechanical properties of DGEBA/PPGDE blends such as 90° peel strength was investigated by a universal testing machine (UTM) with 90° peeling mode. Peel strength is the measure of the average force of the two parts bonded materials. The strength is calculated by the average force required during the test with a constant speed rate divided by the width of the bonded samples [41, 42]. Figure 5.4 shows the 90° peel strength of DGEBA/PPGDE blends at various mass ratios from 50/50, 60/40, 70/30, 80/20 and 90/10, respectively. From these plots, the results were tended to increase to the maximum value at 70/30 mass ratio of DGEBA/PPGDE blends. The 90° peel strength of various mass ratios were determined to be 0.099 N/mm, 0.110 N/mm, 0.121 N/mm, 0.117 N/mm and 0.061 N/mm, respectively. In this experimentation, we can observe that the adherence of this epoxy system was failure on the polyimide films.

5.4 Effects of CTBN Rubber for Curing Behaviors of DGEBA/PPGDE/CTBN Blends

From previous experimentation, DGEBA/PPGDE blends at mass ratio of 70/30 illustrates the maximum value of 90° peel strength. But this value was not high enough for applied on the industry scale Therefore, this experimental part was studied the effect of mass content of CTBN rubber filled in DGEBA/PPGDE blends to find the appropriate mass ratio that affects to an increasing of the peel strength. Figure 5.5 shows DSC thermogram of CTBN rubber at various mass ratios of 5 phr, 10 phr, 15 phr and 20 phr that filled in 70/30 mass ratio of DGEBA/PPGDE mixtures. As shown in this figure, curing temperature of DGEBA/PPGDE resin at mass ratio of 70/30 was $165^{\circ}C$. Whereas, curing temperature of 70/30 mass ratio of DGEBA/PPGDE mixtures at various CTBN mass contents were measured to be $158^{\circ}C$, $160^{\circ}C$, $158^{\circ}C$ and $158^{\circ}C$, respectively. These results indicate that the effect of CTBN rubber were not affect to the curing temperature in this tertiary system.

Moreover, heat of reaction of this polymeric system was also evaluated from this figure. The DSC plots present a decreasing of heat of reaction with increasing CTBN mass content. The heat of reaction of DGEBA/PPGDE blends at mass ratio of 70/30 was 271 J/g and the values at various mass contents of CTBN rubber at 5 phr, 10 phr, 15 phr and 20 phr were determined to be 232 J/g, 229 J/g, 223 J/g and 213 J/g, respectively. The reason of this behavior was possibly due to the less polymerization enthalpy of CTBN rubber in crosslinking reaction between DGEBA/PPGDE resin mixtures. This behavior was similar reported in previous work by Szeluga *et al*. [43].

Furthermore, the T_gs of various CTBN mass contents filled DGEBA/PPGDE blends were also evaluated. Figure 5.6 exhibits T_g of DGEBA/PPGDE blends at mass ratio of 70/30 and T_gs of DGEBA/PPGDE/CTBN blends at various CTBN mass content of 5 phr, 10 phr, 15 phr and 20 phr. The T_gs of DGEBA/PPGDE/CTBN blends were evaluated to be 77°C, 69°C, 67°C, 64°C and 63°C at mass ratio of 70/30/0, 70/30/5, 70/30/10, 70/30/15 and 70/30/20, respectively. As can be seen from this thermogram, the slight reduction in T_g of the CTBN modified DGEBA/PPGDE networks can be attributed to the more flexible chain of CTBN rubber affects to the easy chain movement due to the linear structure of CTBN. Therefore, an increasing of CTBN mass content in the polymer matrix affected to the T_g reduction [44].

5.5 Characterization of DGEBA/PPGDE/CTBN Blends

FTIR spectroscopy was used to verify the molecular structures and interactions of epoxy networks and CTBN rubber. FTIR spectra of DGEBA/PPGDE blends at mass ratio of 70/30, CTBN rubber, and cured blend sample containing 10 phr CTBN rubber in DGEBA/PPGDE blends at mass ratio of 70/30 cured with mPDA have been shown in Figure 5.7. The DGEBA/PPGDE blends showed peaks at 912 and 831 cm^{-1} due to the oxirane group of epoxy resin. Absorption bands at 1740 and 1712 cm^{-1}, which can be ascribed to the carboxylic group of CTBN rubber, was observed in the FTIR spectra of CTBN rubber. On the other hand, the absorption band at 1742 cm^{-1} was observed, in the DGEBA/PPGDE/CTBN blends that might indicate the formation of function group ester. The presence of an absorption band near 3390 cm^{-1} in the DGEBA/PPGDE/CTBN blends that might be ascribed to the -OH group of epoxy resin. A sharp -C ≡ N peak at 2237 cm^{-1} was also observed in the spectrum of CTBN rubber. However, the addition of CTBN rubber in to epoxy cause chemical interaction between the oxirane ring of epoxy and carboxyl functional group of the CTBN rubber. These spectra were also previously reported by Tripathi and Srivastava [45].

5.6 Effect of CTBN Rubber on Thermal Degradation and Thermal Stability of DGEBA/PPGDE/CTBN Blends

Degradation temperature at 5wt% loss and char yield at 800^{o}C of DGEBA/PPGDE/CTBN blends were also investigated by a thermogravimetric analyzer. Figure 5.8 exhibits degradation temperature at 5wt% loss and char yield at 800^{o}C of DGEBA/PPGDE blends at 70/30 mass ratio and CTBN filled DGEBA/PPGDE blends at CTBN mass content of 5 phr, 10 phr, 15 phr and 20 phr. From these results, it was observed that DGEBA/PPGDE blends at 70/30 mass ratio possesses the T_d at 356^{o}C and char yield at 800^{o}C was measured to be 11.9%. Whereas, The T_d and char yield of

DGEBA/PPGDE/CTBN blends were tended to slightly decrease with increasing CTBN mass content. As seen from this figure, The T_ds of DGEBA/PPGDE/CTBN blends at CTBN mass content of 5 phr, 10 phr, 15 phr and 20 phr were determined to be 344°C, 340°C, 338°C and 335°C. On the other hand, the values of char yield were 10.6%, 10.4%, 8.1% and 6.9%, respectively. This phenomenon was due to the fact that the addition of CTBN rubber to epoxy system could weak the thermal stability of the resin system [46, 47].

5.7 Effect of CTBN Rubber on Mechanical Properties of DGEBA/PPGDE/CTBN Blends

The 90° peel strength of DGEBA/PPGDE/CTBN Blends was also evaluated by a universal testing machine (UTM) with 90° peeling mode. From the experimental part in title 5.3, we can conclude that DGEBA/PPGDE blends at 70/30 mass ratio shows the maximum 90° peel strength. In this part, CTBN rubber was varied in a range of 5 phr to 20 phr to fill in DGEBA/PPGDE blends for improve the 90° peel strength of this polymeric blends. Figure 5.9 exhibits peel strength of DGEBA/PPGDE blends at 70/30 mass ratio and CTBN filled DGEBA/PPGDE blends at CTBN mass content of 5 phr, 10 phr, 15 phr and 20 phr. From the results, it was observed that DGEBA/PPGDE blends at 70/30 mass ratio possesses the 90° peel strength that was measured to be 0.121 N/mm. Moreover, the 90° peel strength of DGEBA/PPGDE/CTBN blends at CTBN mass content of 5 phr, 10 phr, 15 phr and 20 phr were determined to be 0.182 N/mm, 0.246

N/mm, 0.183 N/mm and 0.161 N/mm, respectively. As the observed, the addition of CTBN rubber in DGEBA/PPGDE blends at 70/30 mass ratio enhances the 90^{o} peel strength and DGEBA/PPGDE/CTBN blends shows the maximum 90^{o} peel strength at the mass ratio of 70/30/10. This phenomenon might be attributed to the effect of the soft segment structure of CTBN rubber dispersed in epoxy system which lead to a decrease in the stiffness and elastic modulus, hence reducing stress concentration at the interface of PI film and aluminum substrate. This behavior was reported in the previous research by Liu *et al*. [38]. Furthermore, The substantial increase in the adhesive strength observed for the CTBN-modified system can be attributed to the increased toughness of the cured epoxy matrix brought about by the inclusion of the elastomer [48].

However, CTBN filled DGEBA/PPGDE blends indicates that the aluminum substrate adhesive failure. Whereas, the adhesion characteristic of DGEBA/PPGDE blends exhibits PI film adhesive failure. It can be explained that the difference of adhesive mechanism on each substrate. Therefore, these failures were modified by the two layers adhesive with DGEBA/PPGDE blends at 70/30 mass ratio that laminated on aluminum substrate and then the 70/30/10 mass ratio of DGEBA/PPGDE/CTBN blends was also laminated over DGEBA/PPGDE layer. After, the PI film was covered on the top. The 90^{o} peel strength of the two layers adhesive was increased from the maximum value in the above experiment that was determined to be 0.401 N/mm.

5.8 Curing Behaviors of EPN/PPGDE Blends

From the previous researches that studied by Zalucha [31] and Nakazawa [32]. They have explained the adhesive mechanism between epoxy and metal substrates that an improvement of –OH group in polymer chain affects to an increasing of adhesion ability of the epoxy on the metal substrate. From these researches, epoxy phenol novolac resin (EPN) was interested due to the chemical structure of this epoxy resin composes of oxirane rings more than DGEBA. In the mechanism, the –OH groups in the polymer chain were obtained by the ring-opening polymerization of oxirane rings in epoxy molecular structure. These –OH groups enhance the opportunity to occur hydrogen bonding with oxygen atoms on the metal surface.

In this experimental part, the curing reaction of the EPN/PPGDE binary system at mass ratios of 90/10, 80/20, 70/30, 60/40 and 50/50 were also determined to know the curing behavior of this polymeric blends by a differential scanning calorimeter that were scanned by using a heating rate of 10°C/min with a temperature range of 0 to 250°C, as shown in Figure 5.10. From this thermogram, a single exothermic peak of each resin mass ratios was observed. The exothermic peak of each mass ratio was slightly shifted to higher temperature with an increasing of PPGDE mass fraction. As shown in this figure, the exothermic peak positions of neat EPN, 90/10, 80/20, 70/30, 60/40, 50/50 and neat PPGDE mass ratios were found to be 148°C, 150°C, 156°C, 160°C, 162°C, 168°C and 205°C, respectively. The reason of this phenomenon was also similarly reported in the above session by Ratna *et al*. [39].

Furthermore, the heat of reaction of various the resin mixtures that can evaluate by the area under the exothermic curve. In this figure, the values of heat of reaction increased with decreasing PPGDE mass content. The heat of reaction values of the EPN/PPGDE resin mixtures, which were determined to be 418 J/g, 363 J/g, 356 J/g, 281 J/g, 277 J/g, 265 J/g and 66 J/g at EPN/PPGDE mass ratios of 100/0, 90/10, 80/20, 70/30, 60/40, 50/50 and 0/100, respectively. From the principle, the systematic decrease of the area with an increasing of PPGDE suggested that interaction of EPN and PPGDE possessed a lower heat of reaction per mole of the reactant than interaction of both EPNs.

In addition, the thermogram also reported glass transition temperature (T_g) of EPN/PPGDE blends at various mass ratios after curing process, as shown in Figure 5.11. From this figure, glass transition temperature of EPN/PPGDE blends increased with increasing EPN mass fraction. The values were determined to be 130°C, 104°C, 92°C, 65°C, 56°C, 46°C and 31°C at EPN/PPGDE mass ratio of 100/0, 90/10, 80/20, 70/30, 60/40, 50/50 and 0/100, respectively. An increasing of the T_g of this copolymers can be attributed to the more rigid molecular structure and possibly much higher intramolecular and intermolecular forces in EPN polymer compared to the PPGDE, the results can be described with similar research by Downey and Drzal [10]. Moreover, the T_g of EPN/PPGDE blends was lower than DGEBA/PPGDE system at the same ratio. This behavior was due to the branched chain structure of EPN/PPGDE blends resulting in the higher free volume between the structures than the linear DGEBA/PPGDE epoxy system.

5.9 Thermal Degradation and Thermal Stability of EPN/PPGDE Blends

The thermal degradation temperature (T_d) at 5wt% loss and residual weight at 800°C in this part were also investigated by thermogravimetric analyzer. Figure 5.12 exhibits TGA thermograms of the EPN/PPDGE blends at various mass ratios. Degradation temperature at 5wt% loss of various samples were found to slightly decrease with increasing of PPGDE. The TGA curves of this binary system at various mass ratios of EPN at 90wt%, 80wt%, 70wt%, 60wt% and 50wt% introduced that the addition of PPGDE into the EPN resin gradually decreased the thermal degradation temperature of the obtained mixtures. The degradation temperatures of EPN/PPGDE blends at the EPN mass ratio of 90wt%, 80wt%, 70wt%, 60wt% and 50wt% were determined to be 365°C, 356°C, 352°C, 341°C and 331°C, respectively. Therefore, the obviously feature of the blending EPN resin with PPGDE resin is the significant enhancement of thermal stability of the binary system due to higher thermal properties of EPN aromatic structure. In addition, the residual weight at 800°C of the EPN/PPGDE blends was found to increase with increasing of the PPGDE mass fraction in the binary polymeric system. As can be seen in this figure, the residual weight of EPN/PPGDE blends at mass ratios of 90/10, 80/20, 70/30, 60/40, and 50/50 were determined to be 21.8%, 19.0%, 16.7%, 16.3%, and 16.1%, respectively. The improvement of thermal stability of the EPN/PPGDE blends with the increasing of EPN mass content was attributed to the fact that the structure that comprised of the aromatics rings of EPN provide greater thermal properties than the aliphatic structure of PPGDE as similarly reported in previous research by Park *et al*. [40].

5.10 Mechanical Properties of EPN/PPGDE Blends

The 90° peel strength of EPN/PPGDE blends was also measured as shown in Figure 5.13. The 90° peel strength of EPN/PPGDE blends at various mass ratios from 50/50, 60/40, 70/30, 80/20 and 90/10, respectively. From these plots, it was found that the maximum value of 90° peel strength at 50/50 mass ratio of EPN/PPGDE blends. The trend of 90° peel strength was increased with decreasing EPN mass content. The values of 90° peel strength of various mass ratios were determined to be 0.561 N/mm, 0.429 N/mm, 0.411 N/mm, 0.359 N/mm, and 0.345 N/mm at various mass ratios from 50/50, 60/40, 70/30, 80/20 and 90/10, respectively.

The 90° peel strength showed an increasing trend with decreasing EPN mass content due to the enhanced toughness and flexibility of aliphatic structure of PPGDE as similar reported by Gouri [49]. From the results, the excess EPN mass content in the binary resin mixtures could be result in a decreasing of adhesive ability. From this description, it was possible that the crosslinking of EPN resin with each other affects to the more brittle structure of EPN network. In addition, EPN/PPGDE system shows higher the values of 90° peel strength than DGEBA/PPGDE blends. Due to the multifunctional novolac epoxy resin can produce a more tightly crosslinked by three-dimensional network compared to two-dimensional DGEBA and can give better adhesive strength retention at elevated temperatures [48]. Alternatively, the mechanical properties of the PPGDE modified EPN in the polymer formulation leads to an increase in peel strength and flexibility of the system. This could be the result of reduced brittleness and crosslink density of the polymeric blends. For one thing, the adhesion characteristic of EPN/PPGDE system also illustrates adhesive failure on PI films.

5.11 Effects of CTBN Rubber for Curing Behaviors of EPN/PPGDE/CTBN Blends

From previous experimentation, EPN/PPGDE blends demonstrates the maximum value of 90° peel strength at mass ratio of 50/50. In this part, the CTBN rubber was used to fill in EPN/PPGDE blends to enhance the adhesion ability between PI films and Aluminum substrates.

Figure 5.14 shows DSC thermogram of CTBN rubber at various mass ratios of 5 phr, 10 phr, 15 phr and 20 phr that filled in 50/50 mass ratio of EPN/PPGDE mixtures. As shown in this figure, curing temperature of EPN/PPGDE resin at mass ratio of 50/50 was 168°C. Whereas, curing temperature of 50/50 mass ratio of EPN/PPGDE mixtures at various CTBN mass contents were measured to be 162°C, 165°C, 162°C and 164°C, respectively. These results indicate that the effect of CTBN rubber were not affect to the curing temperature in this tertiary system.

Moreover, heat of reaction of this polymeric system was also evaluated from this figure. The DSC plots present a decreasing of heat of reaction with increasing CTBN mass content. The heat of reaction of EPN/PPGDE blends at mass ratio of 50/50 was 265 J/g and the values at various mass contents of CTBN rubber at 5 phr, 10 phr, 15 phr and 20 phr were determined to be 255 J/g, 247 J/g, 240 J/g and 234 J/g, respectively. The reason of this behavior was possibly due to the less polymerization enthalpy of CTBN rubber in crosslinking reaction between EPN/PPGDE resin mixtures. This behavior was similar reported in previous work by Szeluga *et al*. [43].

Furthermore, the T_gs of various CTBN mass contents filled EPN/PPGDE blends were also evaluated. Figure 5.15 exhibits T_g of EPN/PPGDE blends at mass ratio of 50/50 and T_gs of EPN/PPGDE/CTBN blends at various CTBN mass content of 5 phr, 10 phr, 15 phr and 20 phr. The T_gs of EPN/PPGDE/CTBN blends were evaluated to be 46°C, 38°C, 35°C, 33°C and 31°C at mass ratio of 50/50/0, 50/50/5, 50/50/10, 50/50/15 and 50/50/20, respectively. As can be seen from this thermogram, the T_g values for all CTBN rubber modified EPN/PPGDE samples are lower than the unmodified epoxy. The decrease in T_g values with increase CTBN mass content can be related to the chemical interaction between CTBN and epoxy matrix, which induces compatibility of

EPN/PPGDE/CTBN as previously reported by Saleh *et al.* [50]. Moreover, Verchere *et al*. [51] have explained in the similar system about the effect of terminated butadiene/acrylonitrile rubber filled in an aliphatic amine cured DGEBA on T_g of epoxy system. From their research, the lowering of T_g of the CTBN rubber may be due to heterogeneous composition of acrylonitrile rubber in the copolymer chains, which causes fractional composition of the acrylonitrile butadiene copolymer during the phase precipitation process.

5.12 Characterization of EPN/PPGDE/CTBN Blends

Figure 5.16 shows the IR spectrum of pure epoxy sample, EPN/PPGDE. The peaks related to oxirane functionality appeared near 915 and 841 cm^{-1}. The disappearance of carboxyl absorption peak at 1,712 and 1,740 cm^{-1} in CTBN rubber [45] and the appearance of ester absorption peak at 1,723 cm^{-1} in EPN/PPGDE/CTBN blends indicated the reaction between carboxyl of CTBN and epoxy group of the epoxy resin. The presence of an absorption band near 3400 cm^{-1} in the EPN/PPGDE/CTBN blends that might be ascribed to the hydroxyl group absorption peak of epoxy resin. A sharp $-C \equiv N$ peak at 2237 cm^{-1} was also observed in the spectrum of CTBN rubber [52]. The $-C \equiv N$ group was not observed in the EPN/PPGDE/CTBN blends. This was perhaps due to lower mass fraction of CTBN in the blend system [52]. However, the addition of CTBN rubber in to epoxy cause chemical interaction between the oxirane ring of epoxy and carboxyl functional group of the CTBN rubber.

5.13 Effect of CTBN Rubber on Thermal Degradation and Thermal Stability of EPN/PPGDE/CTBN Blends

Degradation temperature at 5wt% loss and char yield at 800°C of EPN/PPGDE/CTBN blends were also evaluated by a thermogravimetric analyzer. Figure 5.17 exhibits degradation temperature at 5wt% loss and char yield at 800°C of EPN/PPGDE blends at 50/50 mass ratio and CTBN filled EPN/PPGDE blends at CTBN mass content of 5 phr, 10 phr, 15 phr and 20 phr. From these results, it was observed that EPN/PPGDE blends at 50/50 mass ratio possesses the T_d at 331°C and char yield at 800°C was measured to be 16.1%. Whereas, The T_d and char yield of EPN/PPGDE/CTBN blends were tended to slightly decrease with increasing CTBN mass content. As seen from this figure, The T_dS of EPN/PPGDE/CTBN blends at CTBN mass content of 5 phr, 10 phr, 15 phr and 20 phr were determined to be 314°C, 300°C, 282°C and 279°C. On the other hand, the values of char yield were 15.7%, 13.0%, 11.3% and 6.9%, respectively. This behavior can be explained in the same manner as the title 5.6.

5.14 Effect of CTBN Rubber on mechanical properties of EPN/PPGDE/CTBN Blends

The mechanical properties that represents the ability of adhesion was peel strength. Figure 5.18 shows peel strength in 90° peeling mode of EPN/PPGDE blends at 50/50 mass ratio and CTBN filled EPN/PPGDE blends at CTBN mass content of 5 phr, 10 phr, 15 phr and 20 phr. From this figure, it was observed that EPN/PPGDE blends at 50/50 mass ratio possesses the 90° peel strength was measured to be 0.561 N/mm. Whereas, the 90° peel strength of EPN/PPGDE/CTBN blends at CTBN mass content of 5 phr, 10 phr, 15 phr and 20 phr were determined to be 0.706 N/mm, 0.454 N/mm, 0.026 N/mm and 0.020 N/mm, respectively. From the results, the adhesive strength of this epoxy system decreased with increasing CTBN mass content. It can be clarified that the EPN/PPGDE compositions that containing higher concentrations of CTBN rubber initiated to the adhesive strength was found to continuously decrease with increasing CTBN mass content. At higher loadings of CTBN, the rubber behaved gather that resulting in the loss of adhesive strength of the epoxy system [48, 53].

However, EPN/PPGDE/CTBN blends presents the adhesive failure on aluminum substrate. Whereas, the adhesion characteristic of EPN/PPGDE blends exhibits PI film adhesive failure. It can be explained that the difference of adhesive mechanism on each substrate. Accordingly, this failure has been amended by the two layers laminating adhesive with EPN/PPGDE blends at 50/50 mass ratio that laminated on aluminum substrate and then the 50/50/5 mass ratio of EPN/PPGDE/CTBN blends was also laminated over the first layer of EPN/PPGDE blends. The 90° peel strength of the two layers adhesive was increased from the maximum value in the above experiment that was determined to be 0.813 N/mm. Furthermore, the 90° peel strength of 50/50 mass ratio of EPN/PPGDE blend that adhere between both of aluminum substrates was measured to be 3.577 N/mm. The result represents the excellent adherence of EPN/PPGDE blend on each other aluminum surfaces.

5.15 Viscosity and Pot Life Time of EPN/PPGDE/CTBN Blends

Viscosity is an important parameter for selecting an adhesive to use. A parallel plate rheometer was employed to study the viscosity by varying shear rate, and pot life time with a constant shear rate. In this experiment, the EPN/PPGDE/CTBN blends at 5 phr of CTBN rubber was chosen as a representative for all epoxy adhesive samples. Figure 5.19 shows the viscosity of EPN/PPGDE/CTBN blends at 5 phr of CTBN rubber remained constant as varying the shear rate. The viscosity value of this sample was 1,159 cPs at shear rate of 1 s^{-1}. For one thing, the appropriate viscosity that used for screen printing on FPC was 30,000 cPs. The solution guidelines may be achieved by using B-staging process or increasing PPGDE viscosity.

Pot life time is an index used to define time duration that an adhesive can be handled before its viscosity changes substantially. In general, the pot life time of adhesive was evaluated when the initial viscosity changes to be double. In this research, the viscosity profile of EPN/PPGDE/CTBN blends at 5 phr of CTBN rubber was measured at room temperature under a constant shear rate of 1 s^{-1}. It was found that the viscosity of EPN/PPGDE/CTBN blends at 5 phr of CTBN rubber significantly increased when the time changed. The initial viscosity converted to more viscous which indicates that the crosslinking reaction between carboxyl groups of CTBN rubber and epoxide rings of the epoxies gradually proceeded at surrounding condition. This reason probably affects to increase the crosslink density of the adhesive. The EPN/PPGDE/CTBN blends at 5 phr of CTBN rubber had pot life of 228 minutes at room temperature.

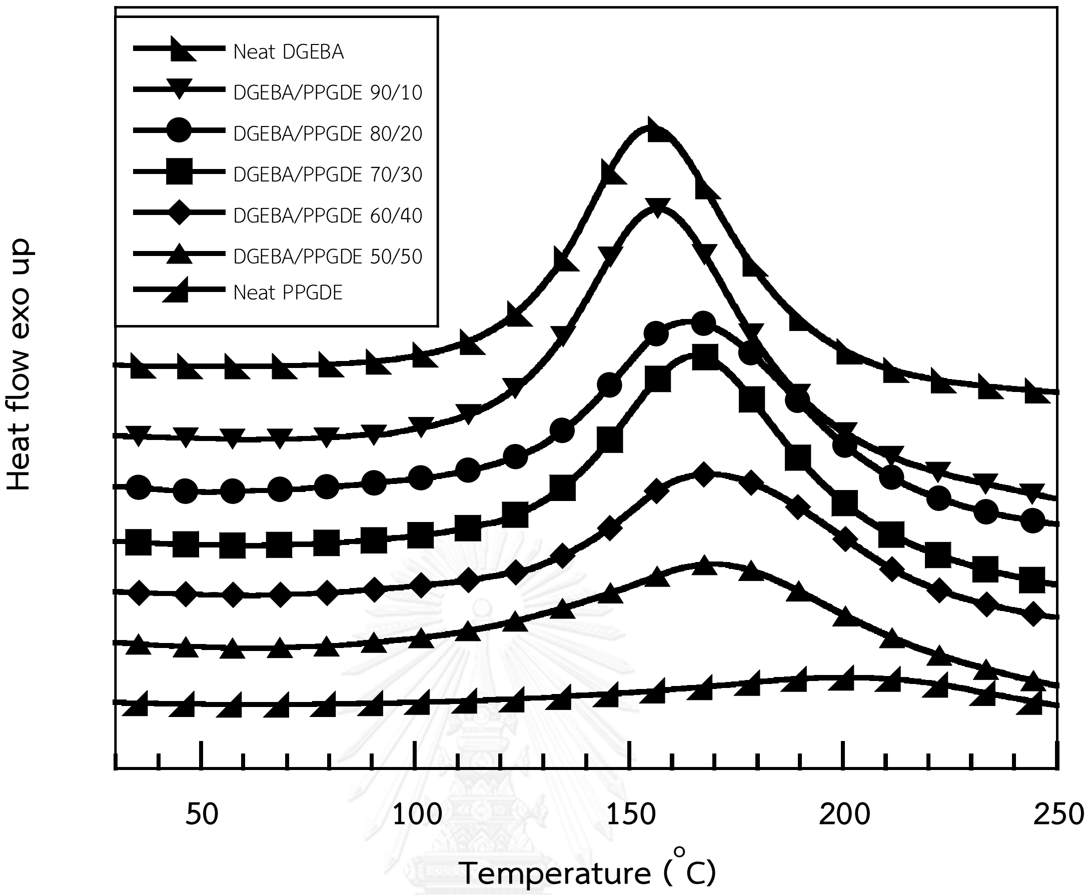


Figure 5.1 DSC thermogram of DGEBA/PPGDE resin mixtures at various mass ratios: (◣) Neat DGEBA, (▼) 90/10, (●) 80/20, (■) 70/30, (◆) 60/40, (▲) 50/50, and (◢) Neat PPGDE.

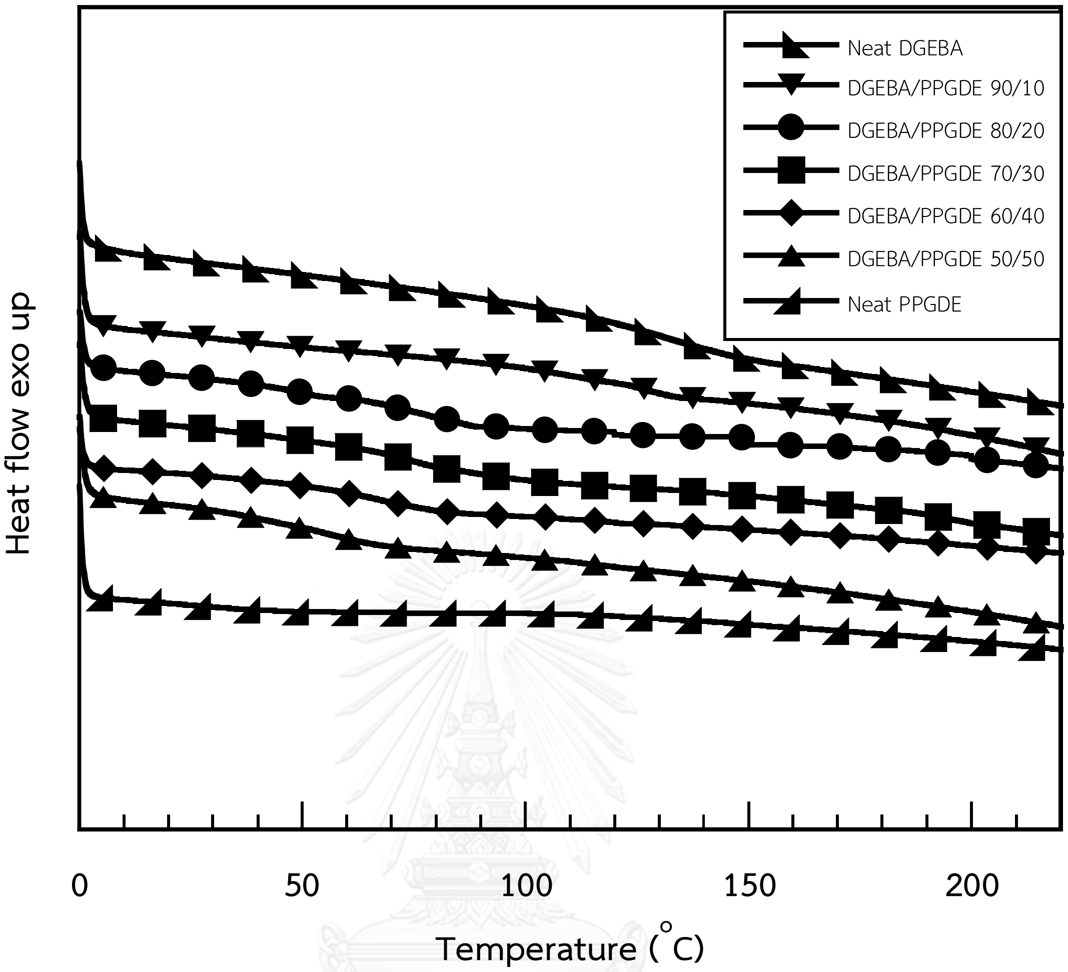


Figure 5.2 DSC thermogram of DGEBA/PPGDE blends after curing at 170°C for 15 min at various mass ratios: (◣) Neat DGEBA, (▼) 90/10, (●) 80/20, (■) 70/30, (◆) 60/40, (▲) 50/50, and (◢) Neat PPGDE.

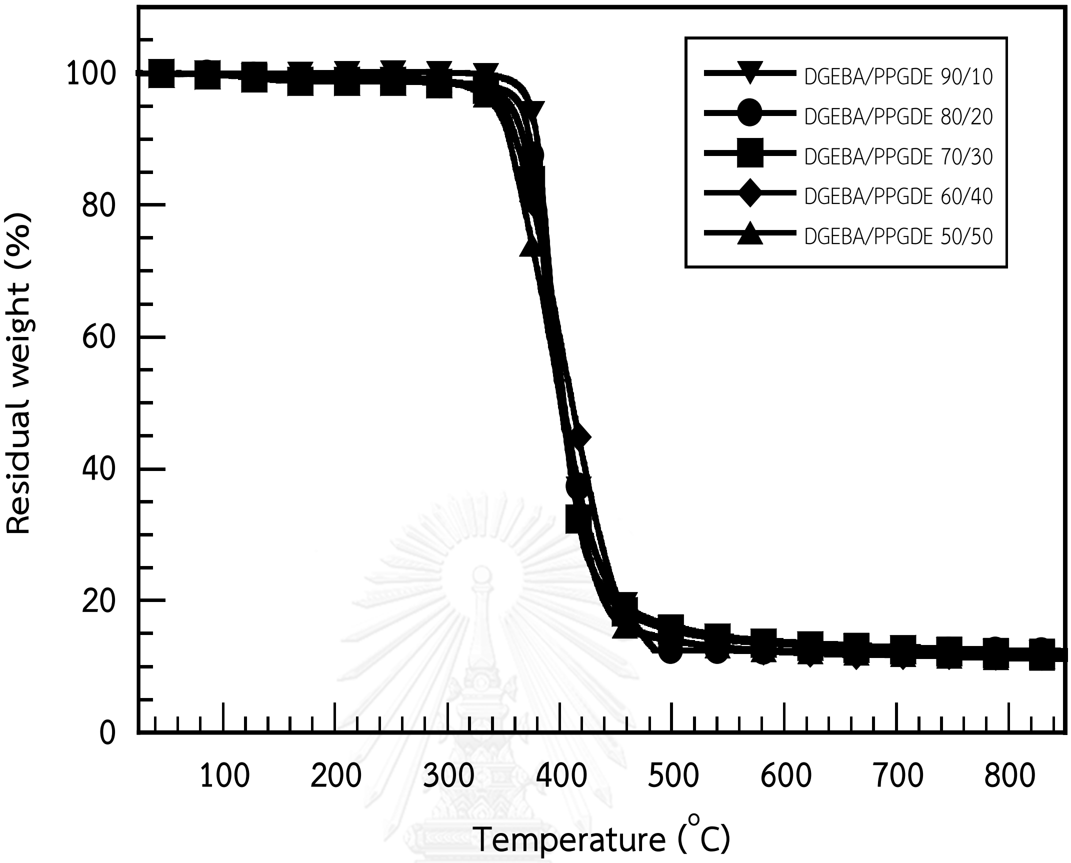


Figure 5.3 TGA thermogram of DGEBA/PPGDE blends at various mass ratios: (▼) 90/10, (●) 80/20, (■) 70/30, (◆) 60/40, and (▲) 50/50.

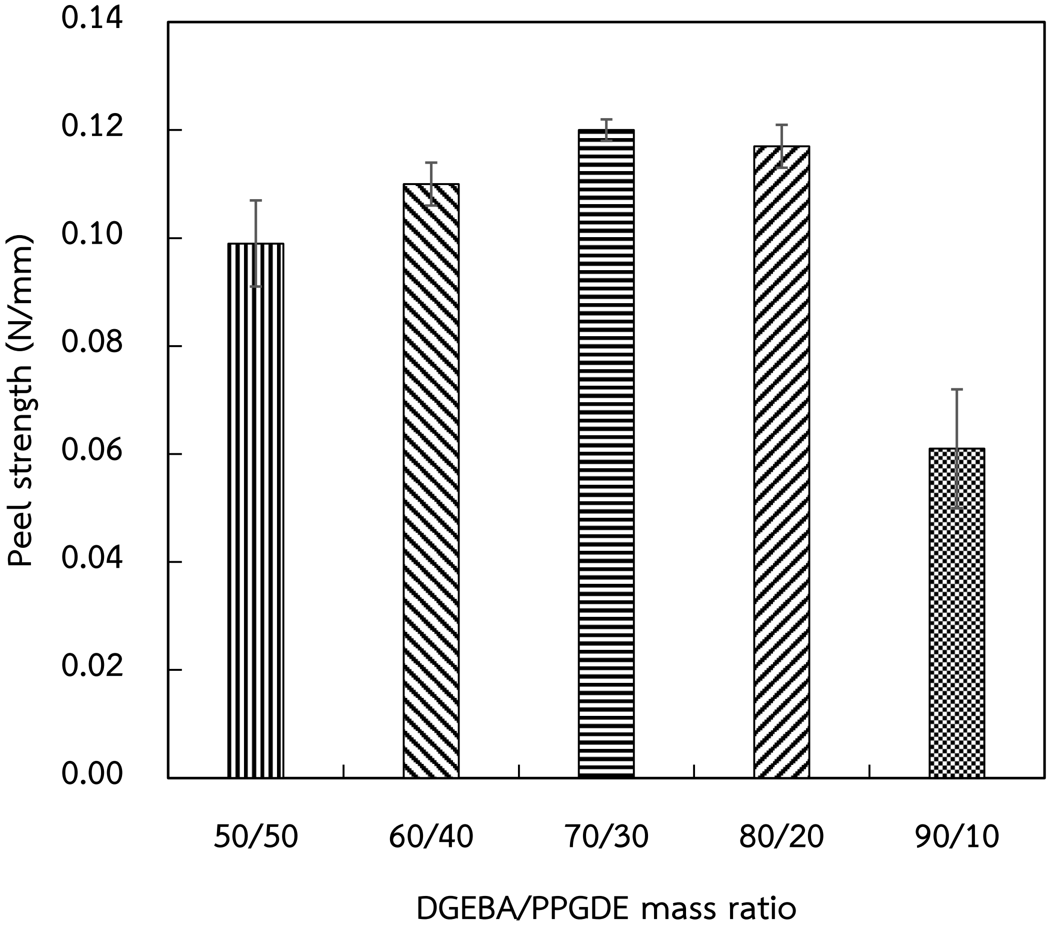


Figure 5.4 90° peel strength of DGEBA/PPGDE blends at various mass ratios.

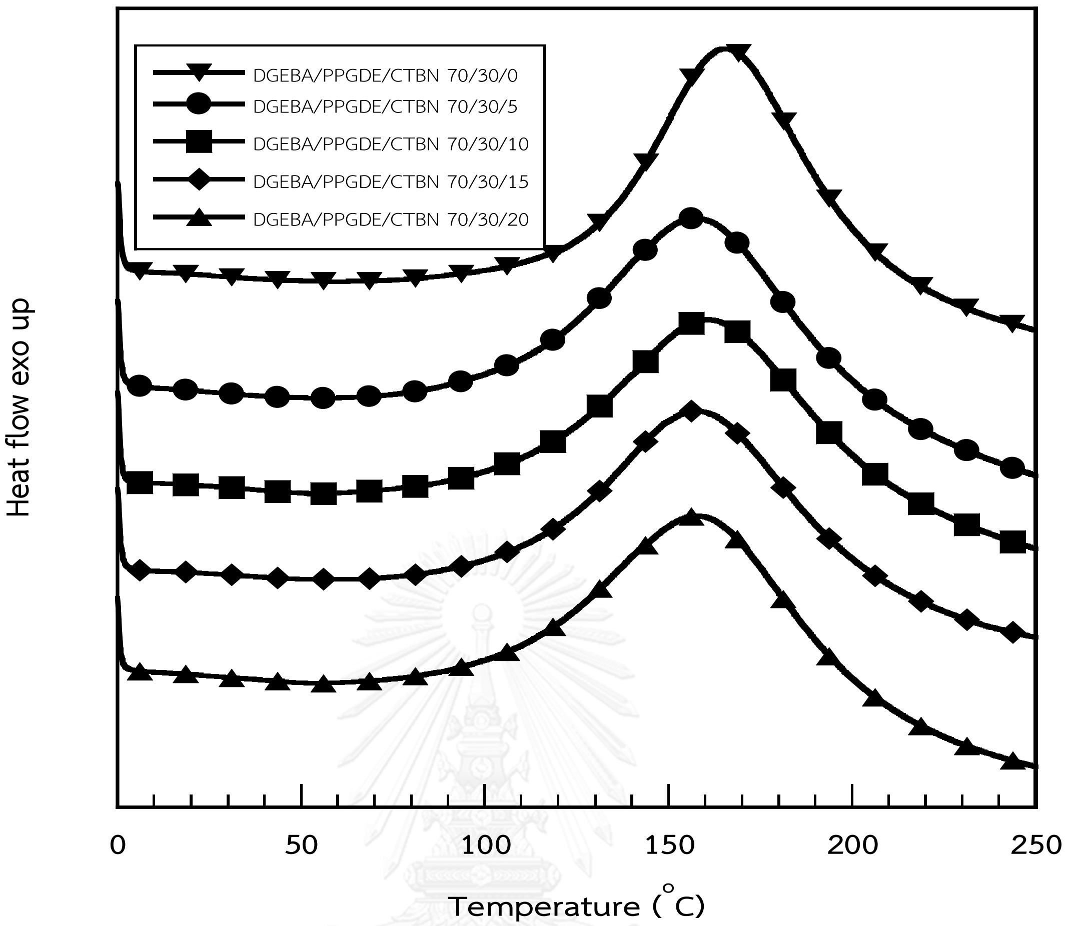


Figure 5.5 DSC thermogram of DGEBA/PPGDE resin mixtures with CTBN rubber contents of 5, 10, 15, and 20 phr: (▼) 70/30/0, (●) 70/30/5, (■) 70/30/10, (◆) 70/30/15, and (▲) 70/30/20.

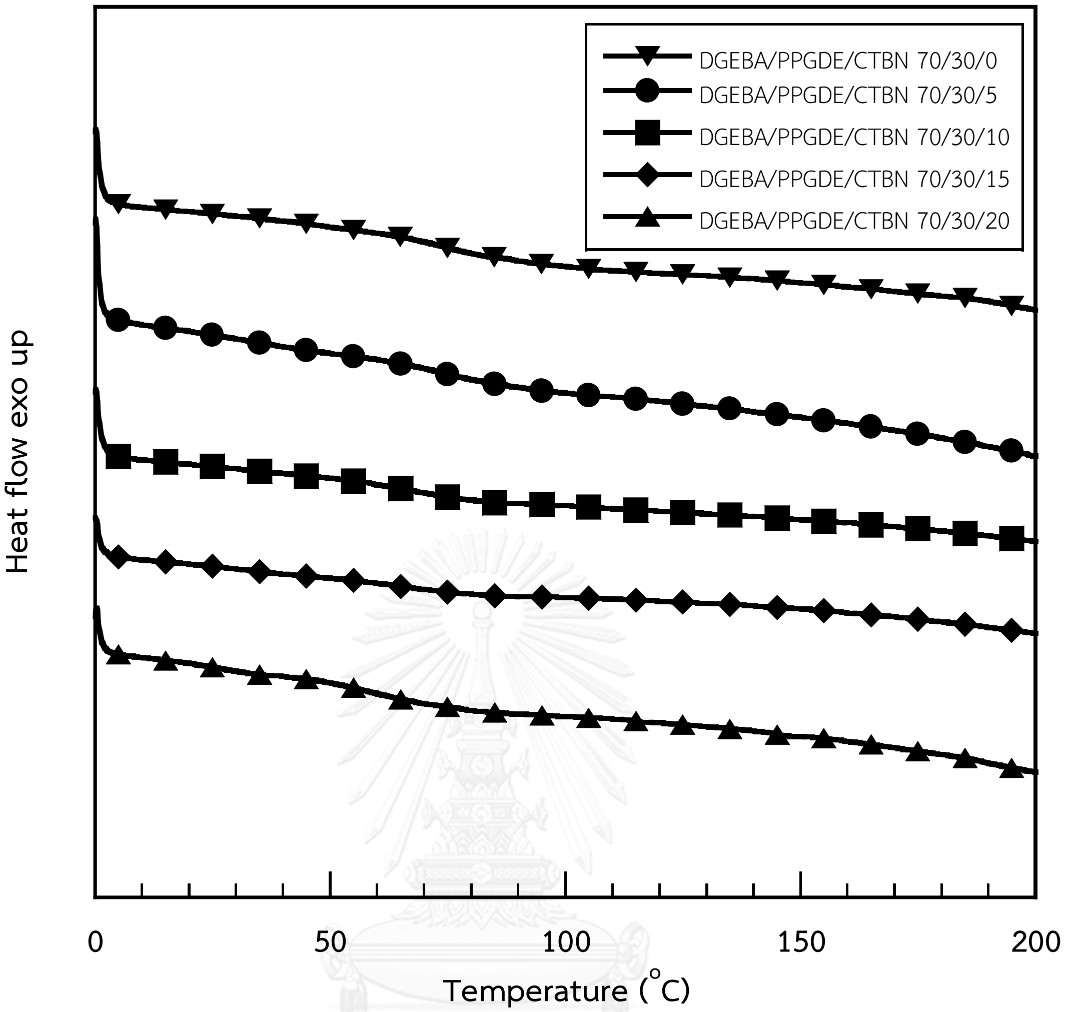


Figure 5.6 DSC thermogram of DGEBA/PPGDE blends with CTBN rubber content of 5, 10, 15, and 20 phr after curing at 170°C for 15 min: (▼) 70/30/0, (●) 70/30/5, (■) 70/30/10, (◆) 70/30/15, and (▲) 70/30/20.

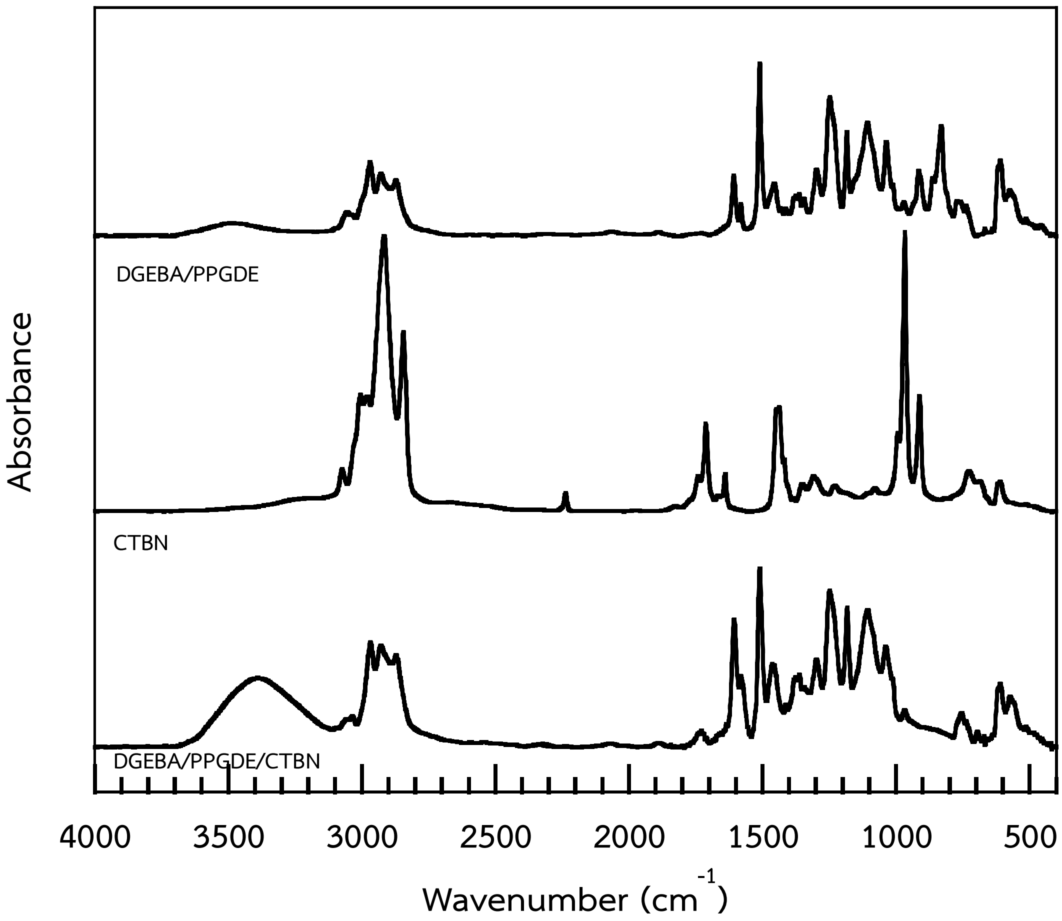


Figure 5.7 FTIR spectra of DGEBA/PPGDE resin mixtures, CTBN rubber, and DGEBA/PPGDE/CTBN blends.

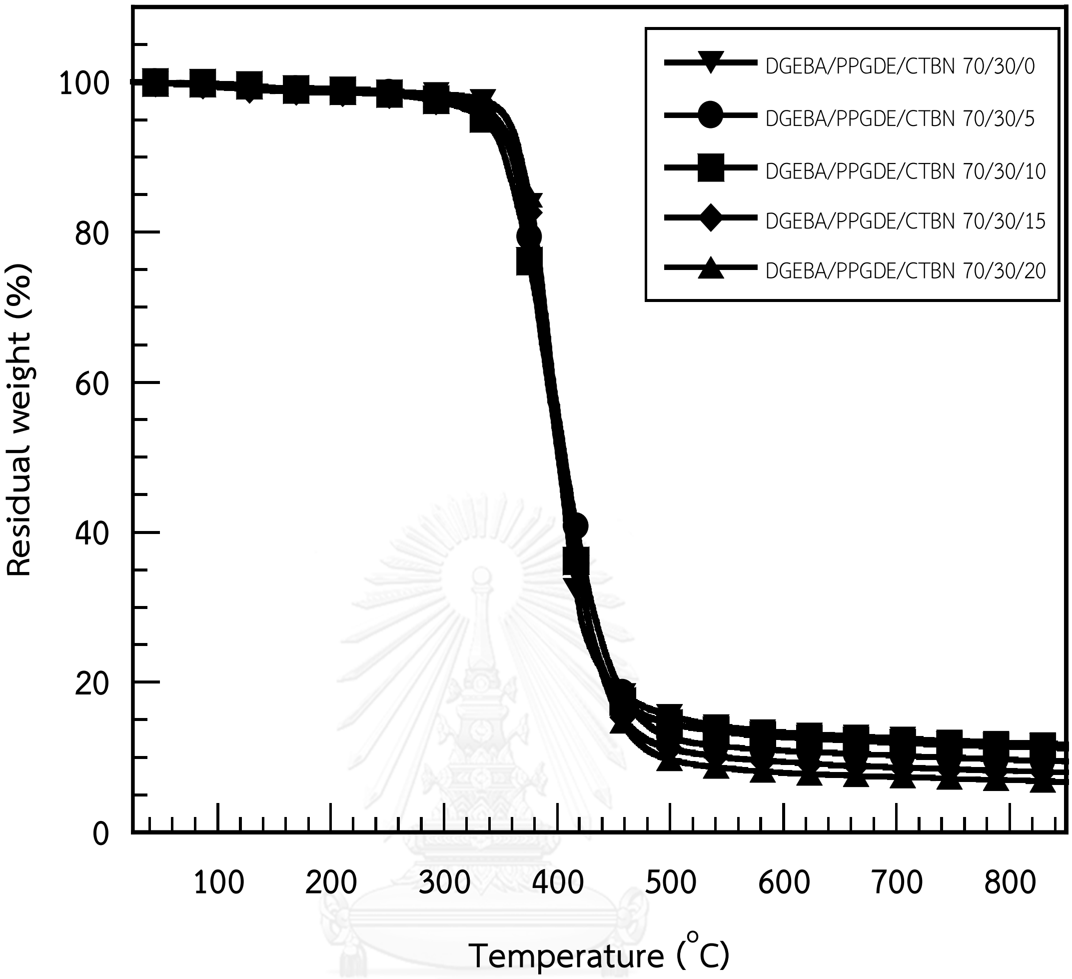


Figure 5.8 TGA thermogram of DGEBA/PPGDE blends with CTBN rubber content of 5, 10, 15, and 20 phr: (▼) 70/30/0, (●) 70/30/5, (■) 70/30/10, (◆) 70/30/15, and (▲) 70/30/20.

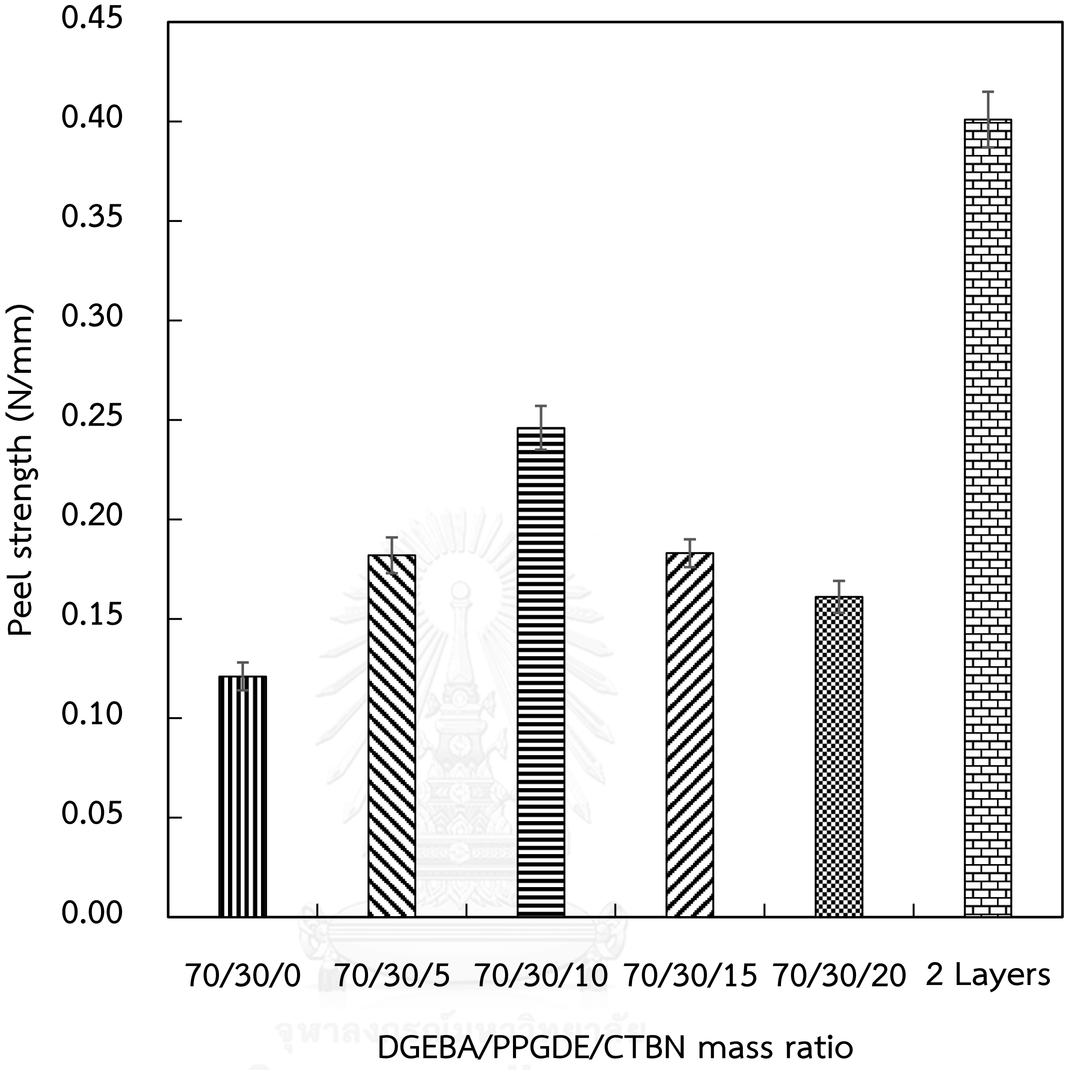


Figure 5.9 90° peel strength of DGEBA/PPGDE blends with CTBN rubber content of 5, 10, 15, and 20 phr and two layers adhesive of DGEBA/PPGDE and DGEBA/PPGDE/CTBN blends.

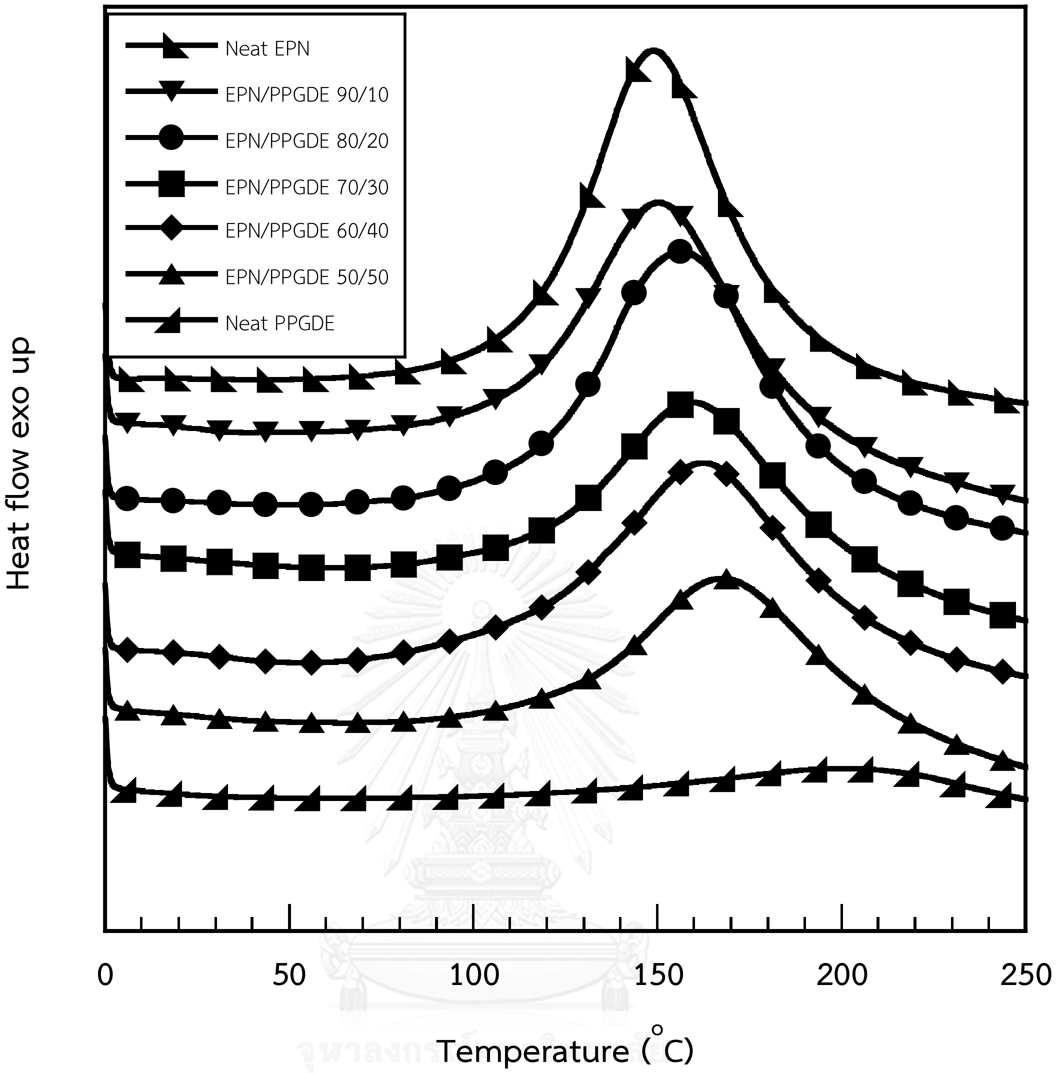


Figure 5.10 DSC thermogram of EPN/PPGDE resin mixtures at various mass ratios: (◣) Neat EPN, (▼) 90/10, (●) 80/20, (■) 70/30, (◆) 60/40, (▲) 50/50, and (◢) Neat PPGDE.

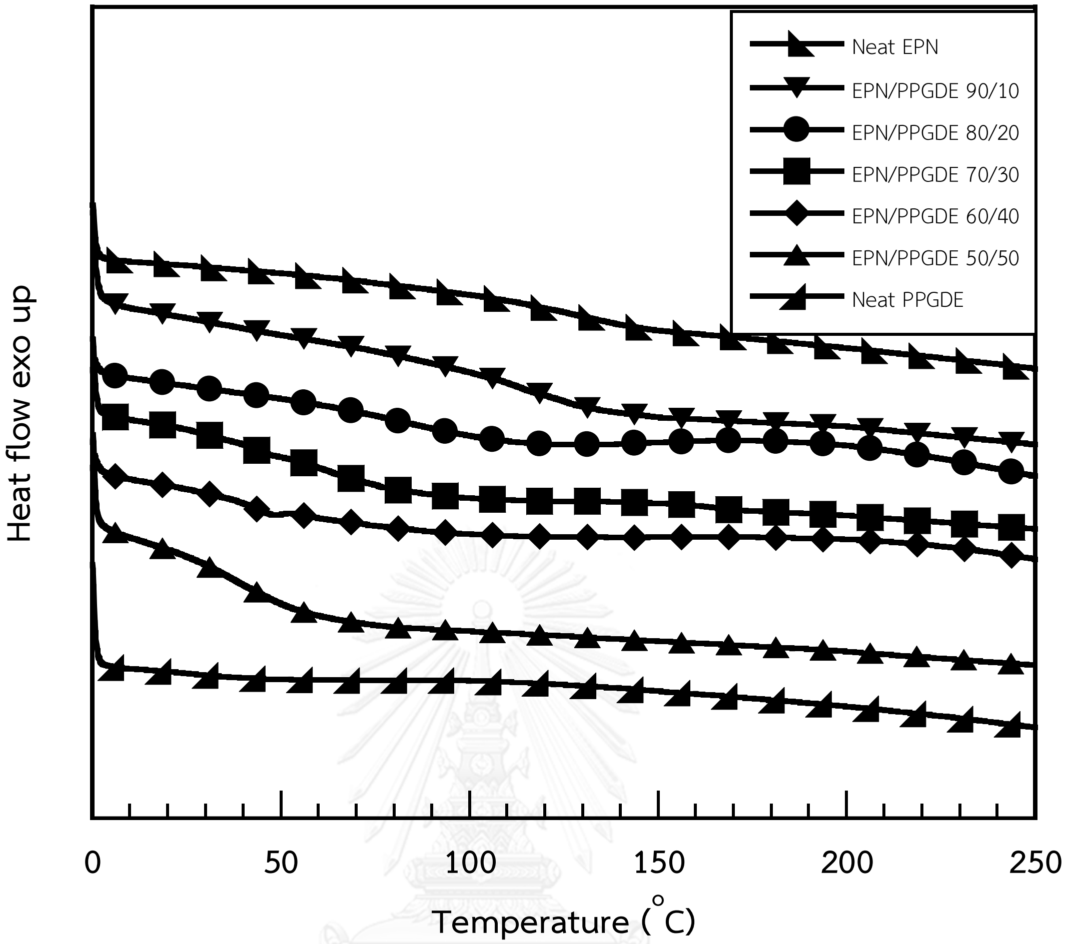


Figure 5.11 DSC thermogram of EPN/PPGDE blends after curing at 170°C for 15 min at various mass ratios: (◣) Neat EPN, (▼) 90/10, (●) 80/20, (■) 70/30, (◆) 60/40, (▲) 50/50, and (◢) Neat PPGDE.

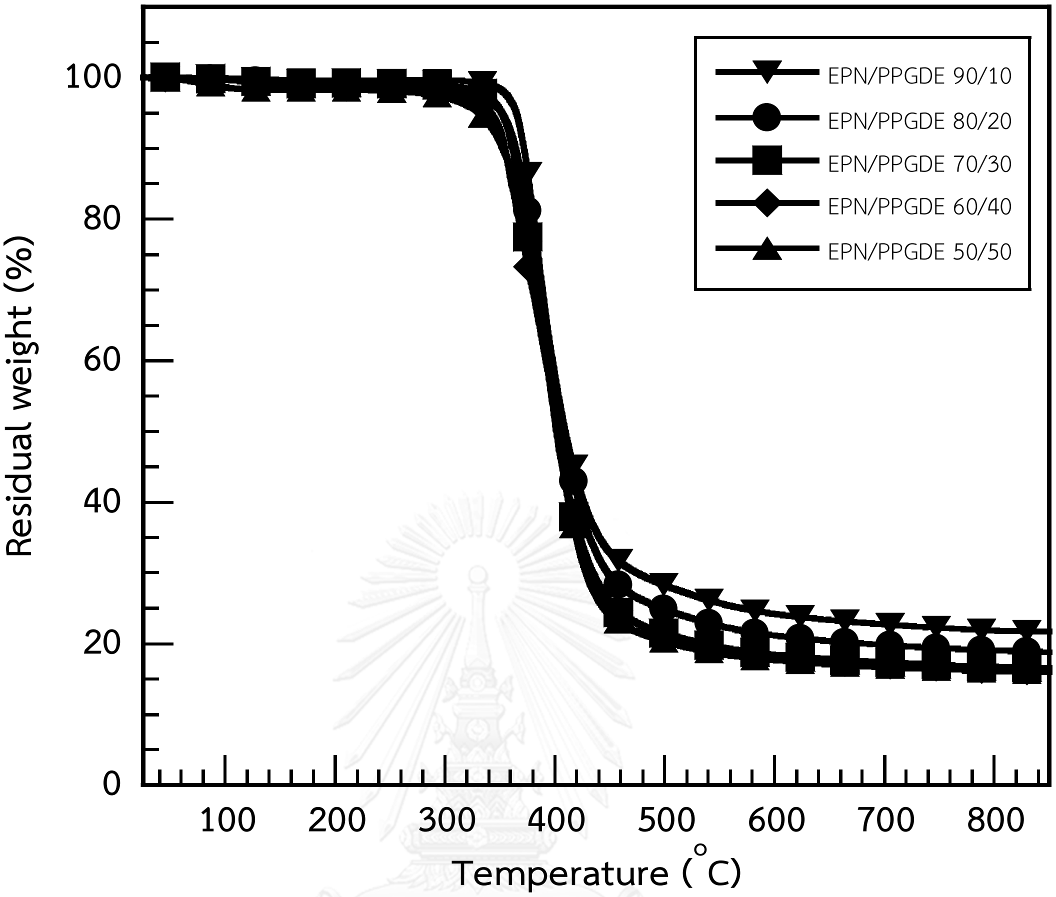


Figure 5.12 TGA thermogram of EPN/PPGDE blends at various mass ratios: (▼) 90/10, (●) 80/20, (■) 70/30, (◆) 60/40, and (▲) 50/50.

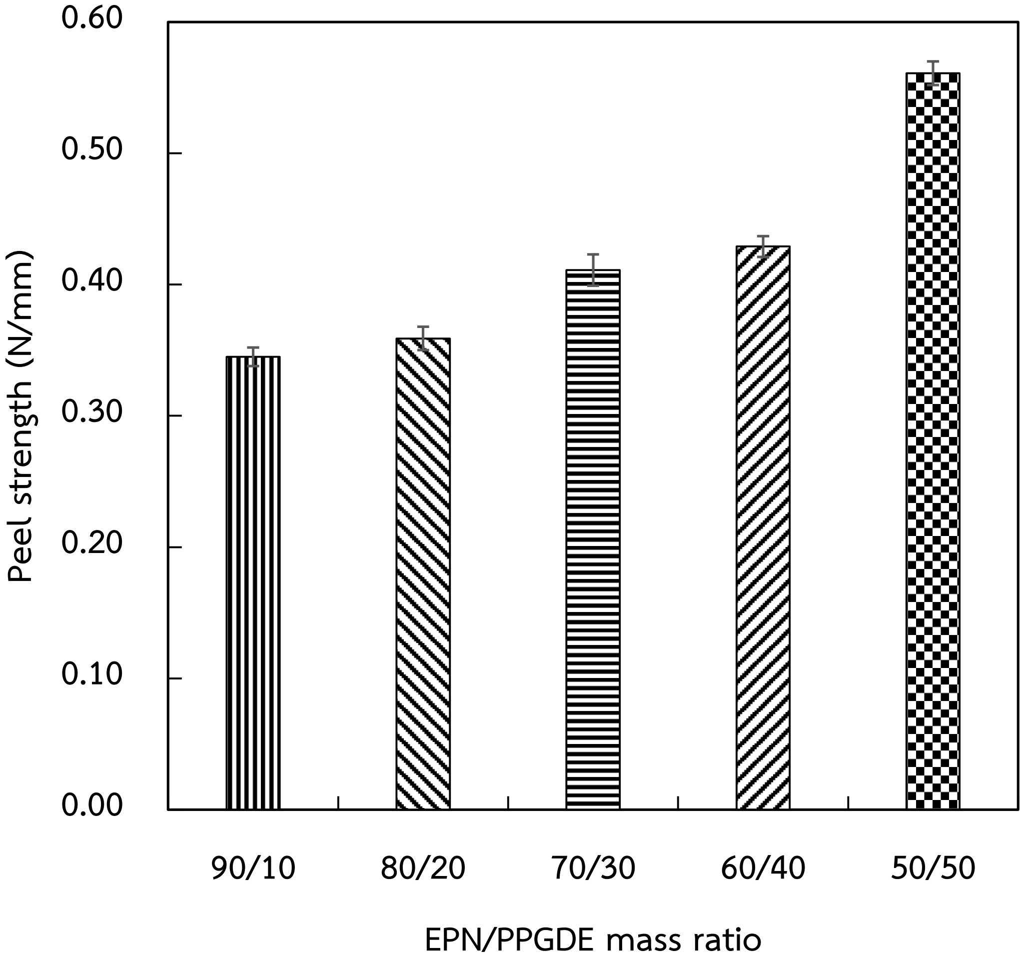


Figure 5.13 90° peel strength of EPN/PPGDE blends at various mass ratios.

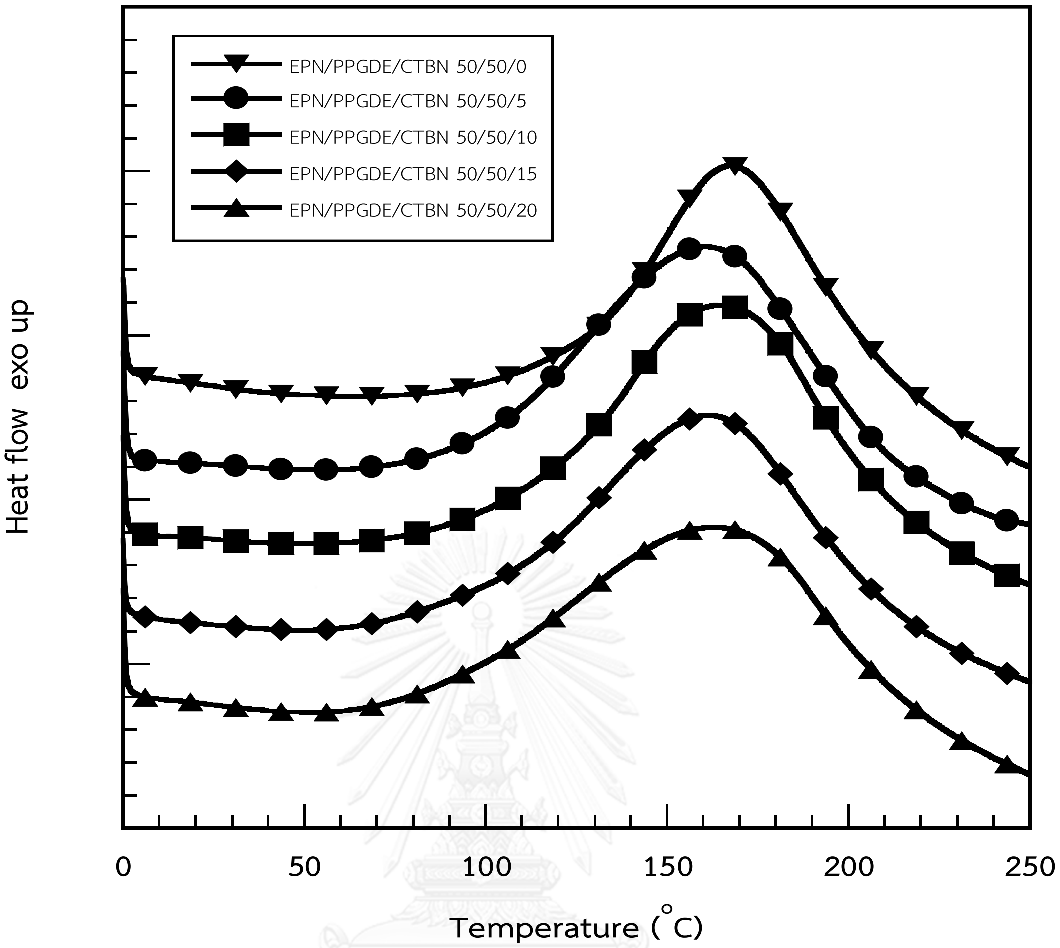


Figure 5.14 DSC thermogram of EPN/PPGDE blends with CTBN rubber content of 5, 10, 15, and 20 phr: (▼) 50/50/0, (●) 50/50/5, (■) 50/50/10, (◆) 50/50/15, and (▲) 50/50/20.

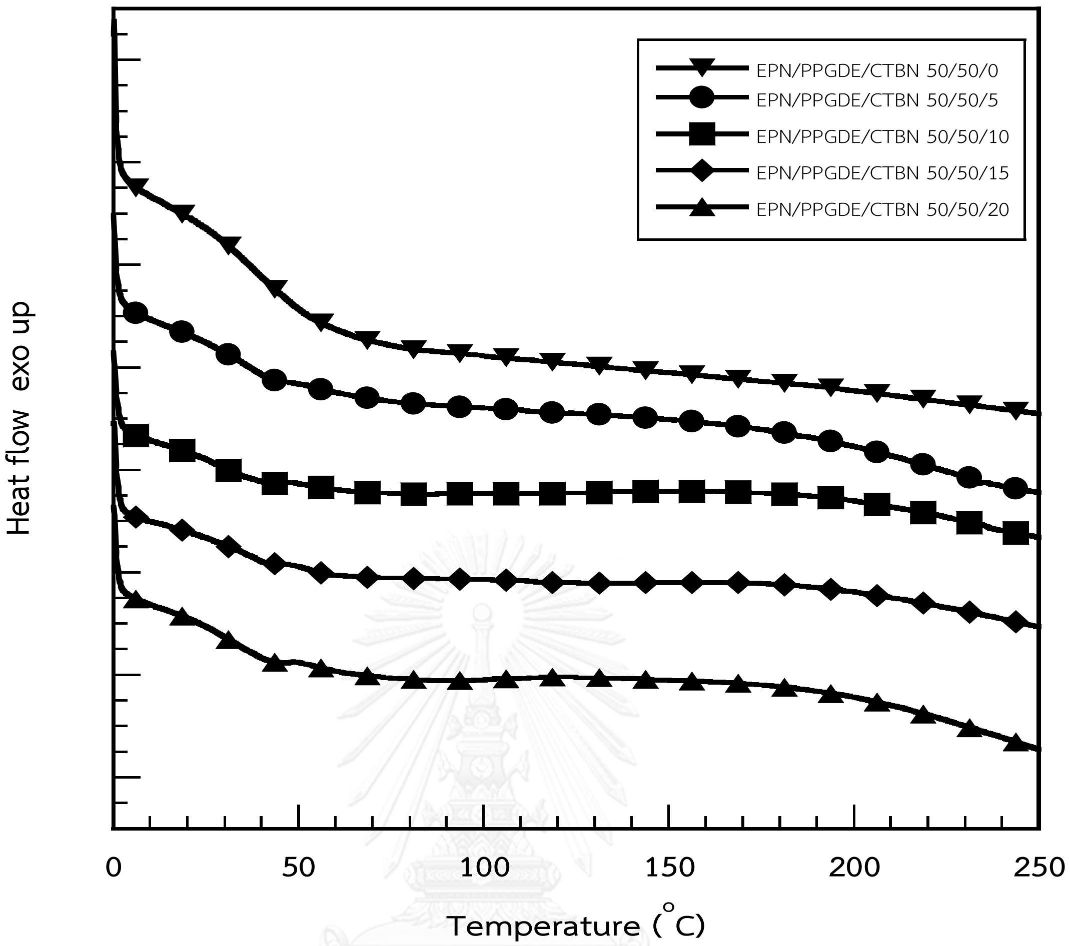


Figure 5.15 DSC thermogram of EPN/PPGDE blends with CTBN rubber content of 5, 10, 15, and 20 phr after curing at 170°C for 15 min: (▼) 50/50/0, (●) 50/50/5, (■) 50/50/10, (◆) 50/50/15, and (▲) 50/50/20.

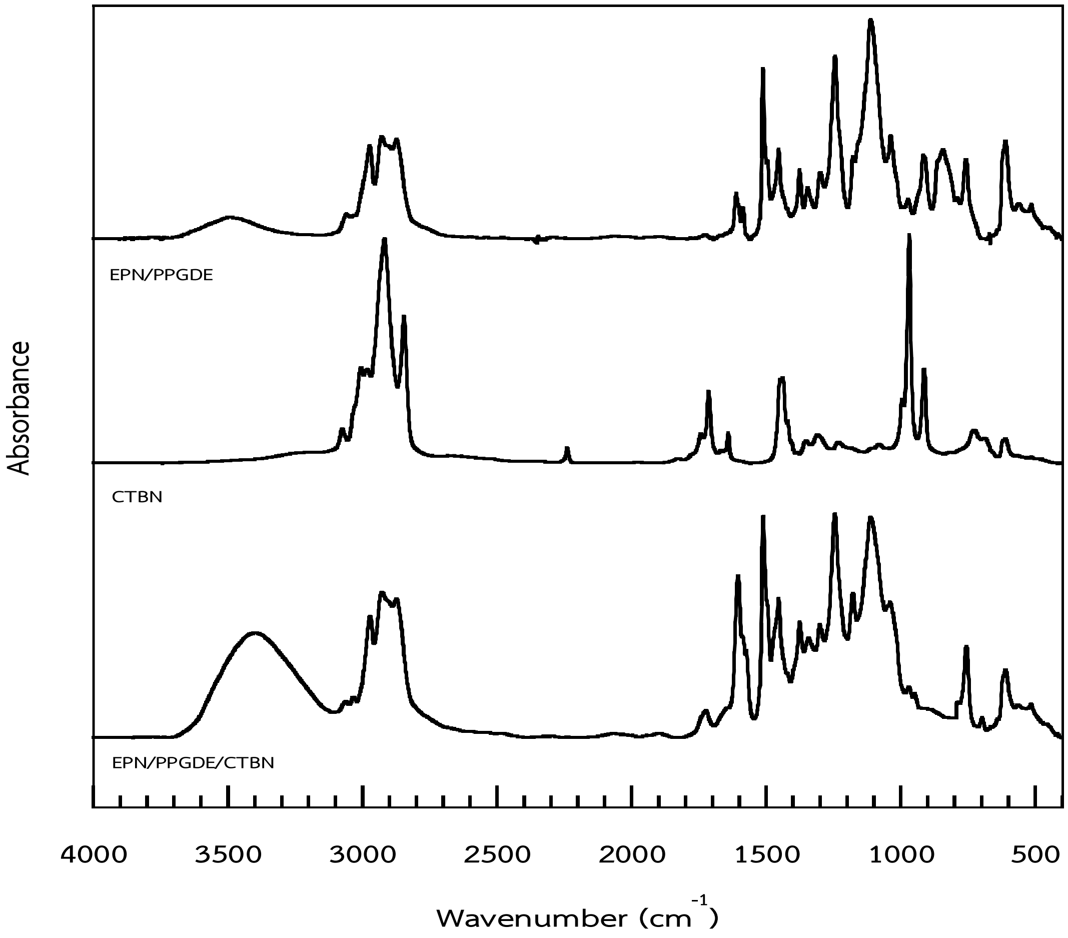


Figure 5.16 FTIR spectra of EPN/PPGDE resin mixtures, CTBN rubber, and EPN/PPGDE/CTBN blends.

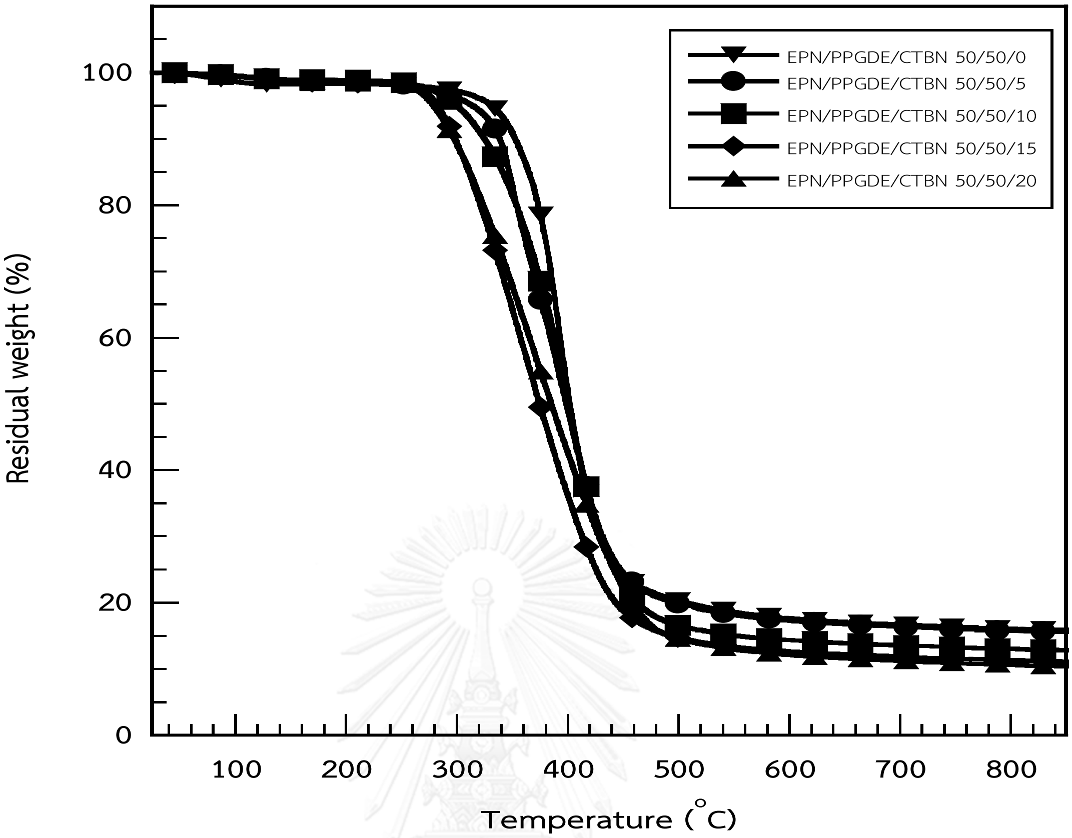


Figure 5.17 TGA thermogram of EPN/PPGDE blends with CTBN rubber content of 5, 10, 15, and 20 phr: (▼) 50/50/0, (●) 50/50/5, (■) 50/50/10, (◆) 50/50/15, and (▲) 50/50/20.

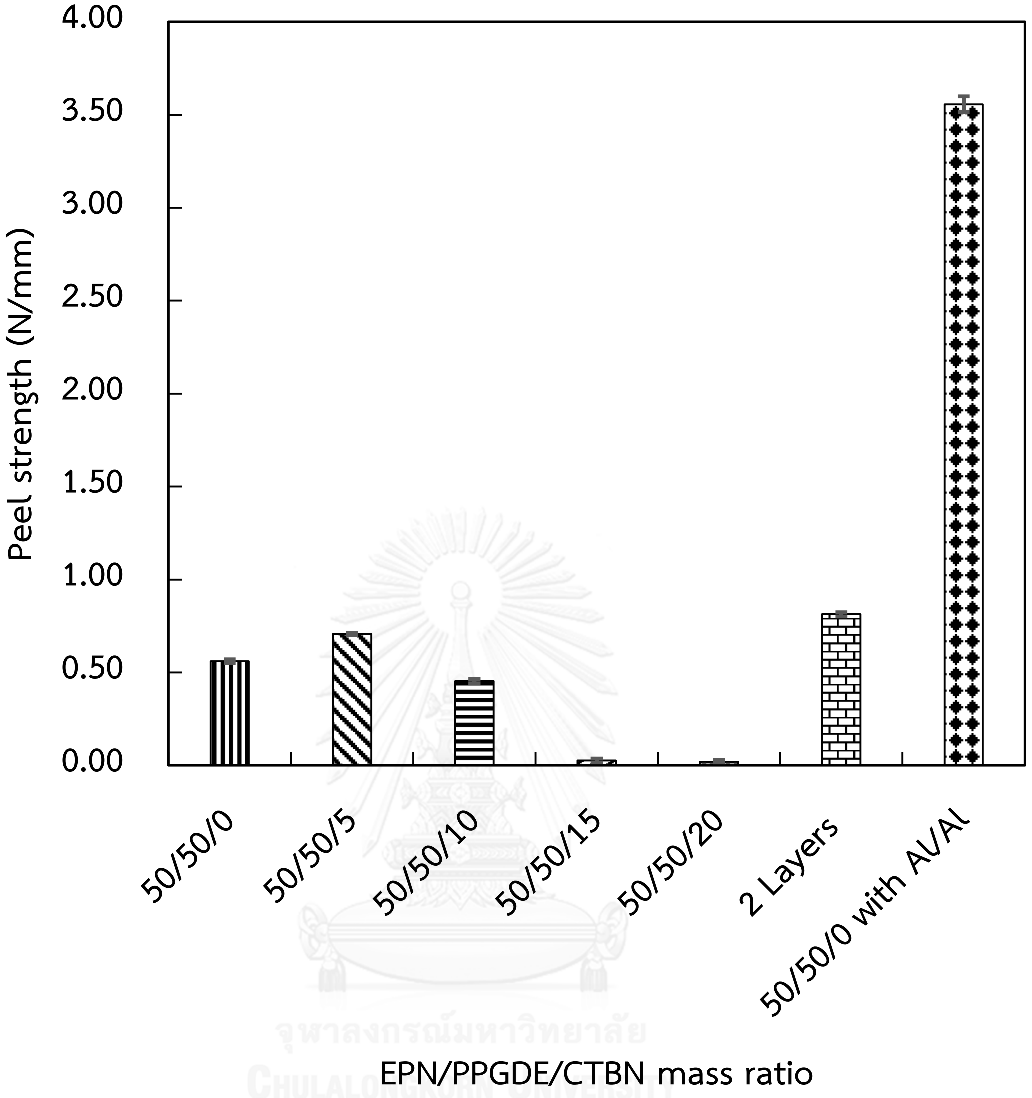


Figure 5.18 90° peel strength of EPN/PPGDE blends with CTBN rubber content of 5, 10, 15, and 20 phr and two layers adhesive of EPN/PPGDE and EPN/PPGDE/CTBN blends.

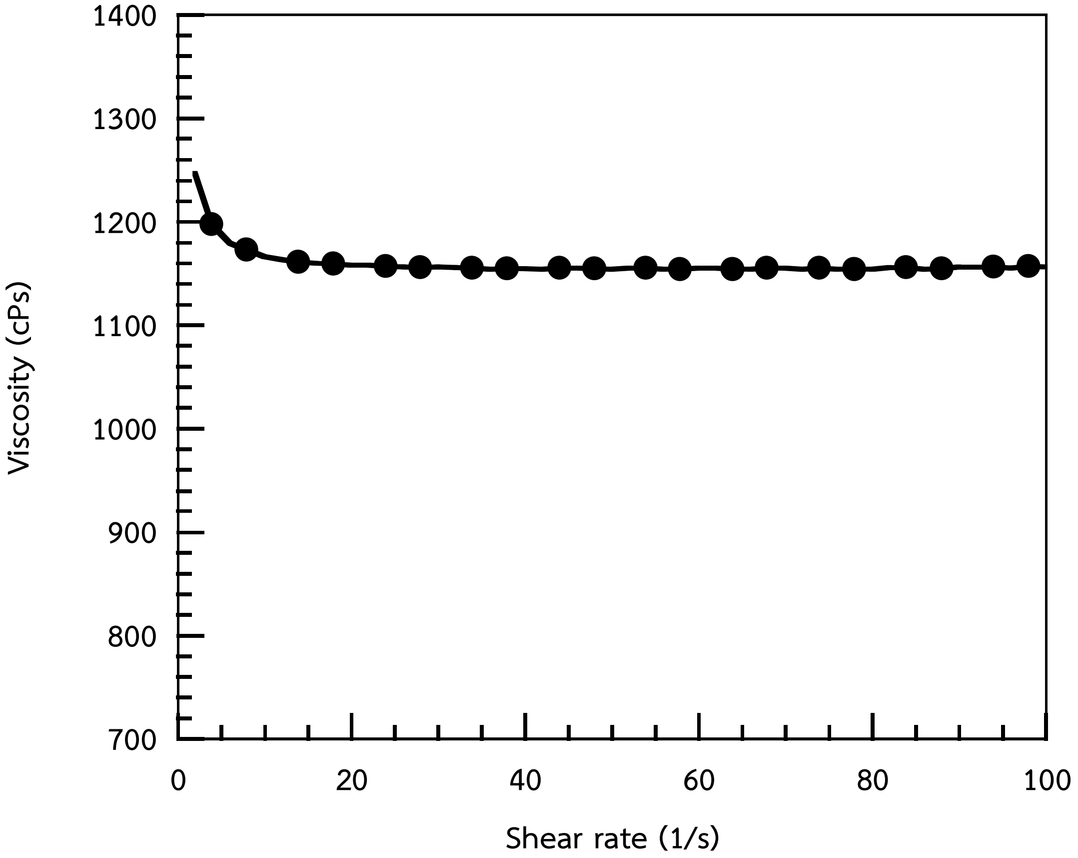


Figure 5.19 Viscosity of EPN/PPGDE/CTBN blends at 5 phr of CTBN as a function of shear rate.

CHAPTER VI

CONCLUSIONS

Epoxy based adhesives in binary system of aromatics epoxy and aliphatic epoxy was successfully used as the adhesive between aluminum boards and polyimide films in flexible printed circuit (FPC). In sample preparation, DGEBA/PPGDE and EPN/PPGDE system cured at 170^{o}C for 15 min with m-PDA used as curing agent and the aromatics epoxies were varied in a range of 50 to 90wt%. From the results, DSC thermograms show the fully-cured polymerization of each epoxy system and curing temperature of both systems increased with increasing PPGDE mass content. However, glass transition temperature (T_g), thermal degradation temperature (T_d) and residual weight of both polymeric blends also increased with increasing aromatic epoxies mass fraction due to a great thermal stability of aromatic structures in the epoxy matrix.

In part of peel strength testing, it was found that the 90^{o} peel strength of EPN/PPGDE blends was higher than DGEBA/PPGDE system. For all that, the highest 90^{o} peel strength of the DGEBA/PPGDE blends was 0.411 N/mm at mass ratio of 70/30 and EPN/PPGDE binary blends exhibits the maximum value of 0.561 N/mm at 50/50 mass ratio. Therefore, both mass ratios have been selected to develop adhesive strength by filling CTBN rubber with a varying of 5 to 20 phr in epoxy matrix. From the results, carboxylic groups of CTBN rubber can interact with epoxide rings in epoxy structure and generated ester linkage on the polymer chain that confirmed by FTIR spectra. Meanwhile, the thermal properties composed of T_g, T_d and residual weight were higher when filling CTBN in small amount in the epoxy matrix.

For peeling test, the DGEBA/PPGDE that filled with 10 phr of CTBN rubber shows the maximum 90° peel strength at 0.246 N/mm and the 5 phr of CTBN rubber filled EPN/PPGDE blends exhibits maximum value of 0.706 N/mm. After the peeling test of all systems, the adhesion behavior of DGEBA/PPGDE and EPN/PPGDE blends were observed that can be adhere well on the aluminum substrates. On the other hand, CTBN modified both of epoxy systems show the great adherence on PI films due to the difference of adhesive mechanism of each substrate. From the observation, the two layers epoxy adhesive was interesting to develop the adhesive strength of this epoxy system. On laminating steps, the binary blends of each system was laminated on aluminum substrates as the first layer and the epoxy systems of each system that modified by CTBN rubber was also laminated above as the second layer. The 90° peel strength of two layers epoxy adhesive in 70/30 mass ratio of DGEBA/PPGDE and 10 phr of CTBN rubber filled 70/30 mass ratio of DGEBA/PPGDE systems was measured to be 0.246 N/mm. Whereas, The 90° peel strength of two layers of 50/50 mass ratio of EPN/PPGDE and 5 phr of CTBN rubber filled 50/50 mass ratio of EPN/PPGDE systems was 0.813 N/mm. From this result, it can be conclude that the two layers epoxy adhesive in the system of 50/50 mass ratio of EPN/PPGDE and 5 phr of CTBN rubber filled 50/50 mass ratio of EPN/PPGDE blends was an appropriate system that has enough potential to use as adhesive for screen printing on FPC.

Moreover, the viscosity of EPN/PPGDE/CTBN blends at 5 phr of CTBN rubber remained constant as varying the shear rate. The viscosity value of this sample was 1,159 cPs at shear rate of 1 s^{-1}. The pot life time of EPN/PPGDE/CTBN blends at 5 phr of CTBN rubber had pot life of 228 minutes at room temperature.

APPENDIX

APPENDIX A

Calculation of epoxy adhesive formula

Calculation of equivalent weight of epoxy mixtures:

To calculate the desired stoichiometric quantity of amine in weight parts per gram epoxy resin the following formula can be used:

$$\text{Amount of amine needed (g)} = \text{AHEW} \times \frac{\text{1 g mass of epoxy resin}}{\text{EEW}}$$

Where Amine hydrogen equivalent weight, AHEW refers to as equivalent weight per active hydrogen of amine as followed by:

$$\text{AHEW}\left(\frac{\text{grams}}{\text{equivalent}}\right) = \frac{\text{Molecular weight of hardener}}{\text{number of active hydrogen per molecule}}$$

Whereas Epoxy Equivalent Weight, EEW is the amount of resin (grams) that contains one molecule of an epoxy group as calculated by:

$$\text{EEW}\left(\frac{\text{grams}}{\text{equivalent}}\right) = \frac{\text{Molecular weight of epoxy resin}}{\text{number of epoxide ring}}$$

For the epoxy mixtures,

$$\text{EEW of epoxy mixture} = \frac{\text{total weight of epoxy mixture}}{\dfrac{\text{Weight 1}}{\text{EEW 1}} + \dfrac{\text{Weight 2}}{\text{EEW 2}}}$$

For example: 50/50 with mPDA system on basis 1 gram mass of epoxy mixture

$$\text{EEW of epoxy mixture} = \frac{\text{1 g of epoxy mixture}}{\dfrac{\text{0.5 g of EPN}}{172.7} + \dfrac{\text{0.5 g of PPGDE}}{335.8}} = 228.1$$

Therefore,

$$\text{Amount of mPDA needed }(\text{g}) = 27.035 \times \frac{\text{1 g mass of epoxy resin}}{228.1} = 0.12\text{ g}$$

APPENDIX B

90° peel strength of epoxy adhesive

APPENDIX B1 90° peel strength of DGEBA/PPGDE blends

DGEBA/PPGDE mass ratio	Peel strength	
	(lb_f/in)	(N/mm)
90/10	0.35 ± 0.04	0.061 ± 0.008
80/20	0.66 ± 0.02	0.117 ± 0.004
70/30	0.69 ± 0.01	0.121 ± 0.002
60/40	0.63 ± 0.02	0.110 ± 0.004
50/50	0.57 ± 0.06	0.099 ± 0.011

APPENDIX B2 90° peel strength of DGEBA/PPGDE blends with CTBN rubber and two layers adhesive of DGEBA/PPGDE and DGEBA/PPGDE/CTBN blends.

DGEBA/PPGDE/CTBN mass ratio	Peel strength	
	(lb_f/in)	(N/mm)
70/30/0	0.69 ± 0.03	0.121 ± 0.007
70/30/5	1.04 ± 0.05	0.182 ± 0.009
70/30/10	1.40 ± 0.06	0.246± 0.011
70/30/15	1.04 ± 0.03	0.183 ± 0.007
70/30/20	0.92 ± 0.04	0.161 ± 0.008
2 Layers (70/30/0 and 70/30/10)	2.29 ± 0.08	0.401 ± 0.014

APPENDIX B3 90° peel strength of EPN/PPGDE blends

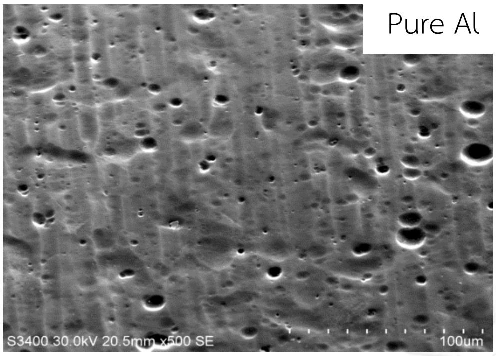
EPN/PPGDE mass ratio	Peel strength	
	(lb_f/in)	(N/mm)
90/10	1.97 ± 0.03	0.345 ± 0.007
80/20	2.05 ± 0.05	0.359 ± 0.009
70/30	2.35 ± 0.07	0.411 ± 0.012
60/40	2.45 ± 0.04	0.429 ± 0.008
50/50	3.20 ± 0.05	0.561 ± 0.009

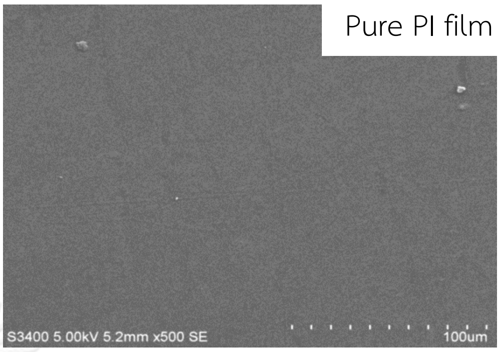
APPENDIX B4 90^{o} peel strength of EPN/PPGDE blends with CTBN rubber and two layers adhesive of EPN/PPGDE and EPN/PPGDE/CTBN blends.

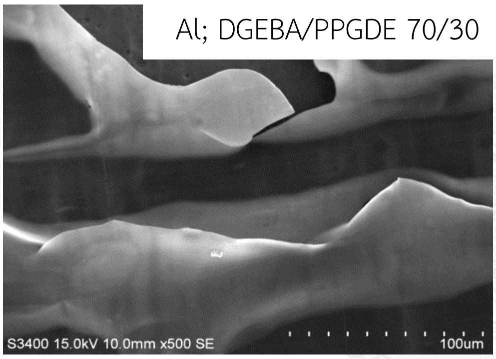
EPN/PPGDE/CTBN mass ratio	Peel strength	
	(lb_f/in)	(N/mm)
50/50/0	3.20 ± 0.05	0.561 ± 0.009
50/50/5	4.03 ± 0.03	0.706 ± 0.007
50/50/10	2.59 ± 0.07	0.454 ± 0.012
50/50/15	0.15 ± 0.06	0.026 ± 0.011
50/50/20	0.11 ± 0.05	0.020 ± 0.009
2 Layers (50/50/0 and 50/50/5)	4.64 ± 0.06	0.813 ± 0.011
50/50/0 with Al/Al	20.31 ± 0.24	3.557 ± 0.043

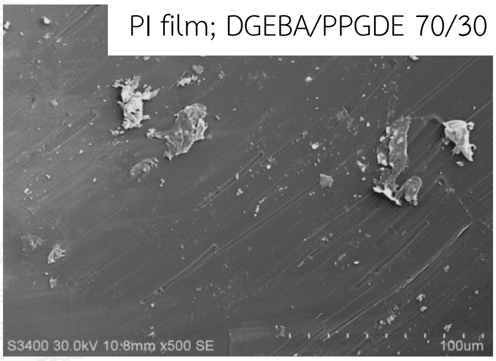
APPENDIX C

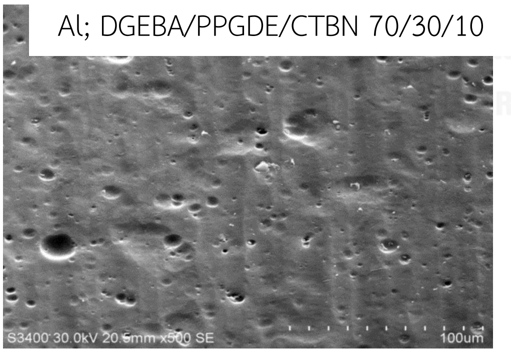
SEM micrographs of epoxy adhesives on aluminum (Al) and polyimide (PI) substrates after peeling test


Pure Al

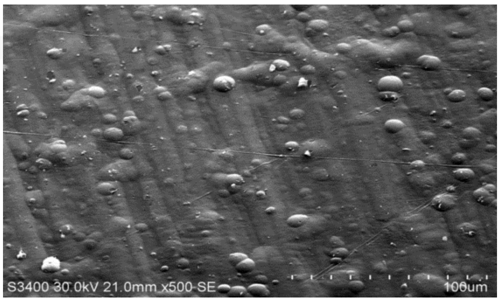

Pure PI film

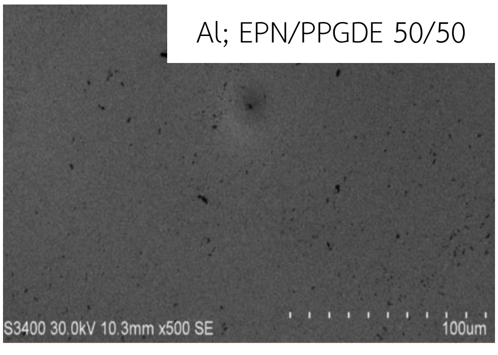

Al; DGEBA/PPGDE 70/30

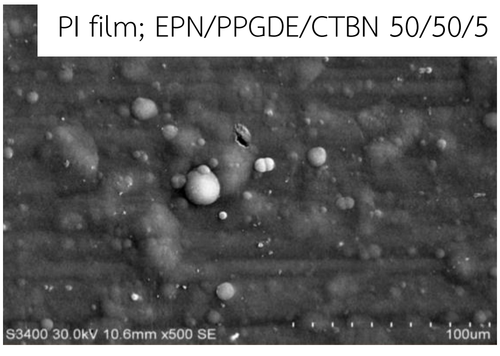

PI film; DGEBA/PPGDE 70/30


Al; DGEBA/PPGDE/CTBN 70/30/10

PI film; DGEBA/PPGDE/CTBN 70/30/10




Al; EPN/PPGDE 50/50


PI film; EPN/PPGDE/CTBN 50/50/5

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APPENDIX

VITA

Ms. Piyarat Leeium was born on October 23rd, 1991 in Bangkok, Thailand. She studied high school at Joseph Upatham School. In 2014, she received the Bachelor's degree of Engineering in Chemical Engineering from Srinakharinwisot University. After gratulation, she entered study for a Master's Degree in Chemical Engineering at the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University. Some part of this research was selected for oral presentation in The International Polymer Conference of Thailand (PCT-6) which was held during June 30 - July 1, 2016 at Pathumwan Princess Hotel Korea, Bangkok, Thailand.