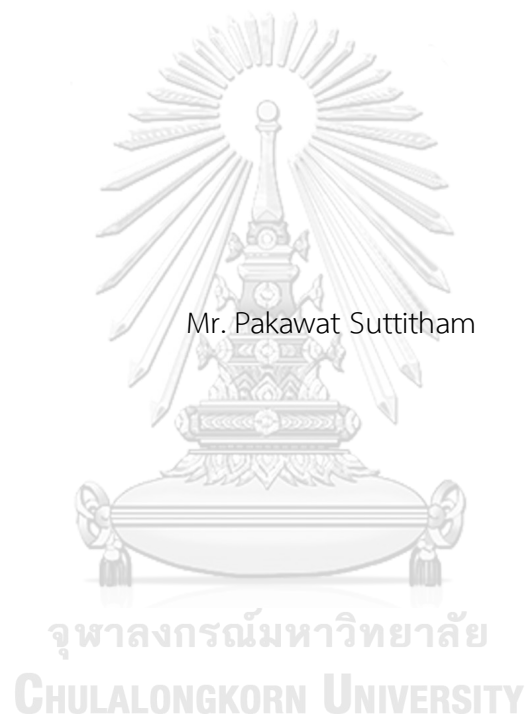


PREPARATION AND CHARACTERIZATION OF SEQUENTIAL CURING WITH OFF-
STOICHIOMETRIC AMINE-DIGLYCIDYL ETHER OF BISPHENOL A /NOVOLAC EPOXY
BLENDED SYSTEMS



A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering in Chemical Engineering

Department of Chemical Engineering

FACULTY OF ENGINEERING

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เทคนิคการบ่มแบบลำดับขั้นไม่ตามปริมาณสารสัมพันธ์ของเอมีน



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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ภควัต สุทธิธรรม : การเตรียมและการหาลักษณะเฉพาะของไดโกลซิคลีเอเทอร์ของบิสฟีนอลเอ/โนโวแลคอีพอกซี ที่ใช้เทคนิคการบ่มแบบลำดับขั้นไม่ตามปริมาณสารสัมพันธ์ของเอมีน. (PREPARATION AND CHARACTERIZATION OF SEQUENTIAL CURING WITH OFF-STOICHIOMETRIC AMINE-DIGLYCIDYL ETHER OF BISPHENOL A /NOVOLAC EPOXY BLENDED SYSTEMS) อ.ที่ปรึกษาหลัก : ศ. ดร.อนงค์นาฏ สมหวังธนโรจน์

การบ่มบิสเตจอีพอกซีมีการใช้งานอย่างหลากหลาย เช่น ในอุปกรณ์อิเล็กทรอนิกส์และพรีเพ็กคอมโพสิต โดยส่วนใหญ่แล้วบิสเตจอีพอกซีจะอยู่ในรูปของฟิล์ม ฟิล์มมัน แผ่นซีท หรือรูปร่างที่ต้องการ ในงานวิจัยนี้บิสเตจอีพอกซีถูกเตรียมขึ้นโดยใช้เทคนิคการบ่มแบบลำดับขั้นไม่ตามปริมาณสารสัมพันธ์ของเอมีน โดยไดเอทิลีนไดอะมีนเป็นสารบ่มลำดับที่หนึ่ง ไดไซยานไดเอไมด์เป็นสารบ่มแฉ่งสำหรับการบ่มลำดับที่สองและมีไดยูรอนเป็นตัวเร่งปฏิกิริยาเพื่อลดอุณหภูมิการบ่มของไดไซยานไดเอไมด์ โนวโอแลค (Novolac) อีพอกซีจะถูกผสมด้วยไดโกลซิคลีเอเทอร์ของบิสฟีนอลเอ (DGEBA) ในอัตราส่วน 0 ถึง 50 phr เพื่อปรับปรุงอุณหภูมิเปลี่ยนสถานะคล้ายแก้วและความเสถียรทางความร้อนให้ดีขึ้น ผลการทดลองจากดีพีเพอเรนเชียลสแกนนิ่งแคลอริมิเตอร์ในโหมดอุณหภูมิไม่คงที่ (Non-isothermal differential scanning calorimetry) แสดงให้เห็นถึงอุณหภูมิการบ่มของสารบ่มทั้งสองชนิดมีความแตกต่างและไม่มีการแทรกสอดกัน นอกจากนี้อุณหภูมิสถานะเปลี่ยนสถานะคล้ายแก้วและความเสถียรทางความร้อนเพิ่มขึ้นเมื่อโนโวแลคอีพอกซีเพิ่มขึ้น อย่างไรก็ตามเมื่ออัตราส่วนผสมของโนโวแลคมากกว่า 30 phr ความหนืดของสารผสมจะมีค่าเพิ่มขึ้นทำให้ยากต่อกระบวนการหล่อฟิล์ม (Film casting) ณ อุณหภูมิห้อง ดังนั้นอัตราส่วนผสมของ DGEBA/Novolac ที่ 70/30 จะถูกเลือกนำไปตรวจวิเคราะห์ต่อไป โดยมีความหนืดที่เหมาะสมสำหรับกระบวนการหล่อฟิล์มที่อุณหภูมิห้อง อุณหภูมิสถานะเปลี่ยนสถานะคล้ายแก้วและอุณหภูมิการสลายตัวทางความร้อนที่น้ำหนักของชิ้นงานหายไป 5 % (Thermal degradation at 5 % weight loss) คือ 144 และ 355 องศาเซลเซียส ตามลำดับ ผลการทดลองจากเทคนิคฟูเรียร์ทรานส์ฟอร์มอินฟราเรดสเปกโตรสโคปี (Fourier transform Infrared (FTIR) Spectroscopy) พบว่าสารบ่มแฉ่งและตัวเร่งปฏิกิริยายังคงไม่ถูกใช้งานในขั้นบิสเตจ การทดลองความเสถียรในการเก็บรักษาที่อุณหภูมิ -18 องศาเซลเซียส พบว่ามีการเปลี่ยนแปลงทางความร้อนของปฏิกิริยาการบ่มเพียง 8.72 % และยังสามารถยึดติดกับวัสดุได้หลังจากบ่มบิสเตจ ไปแล้ว 28 วัน

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Pakawat Suttitham : PREPARATION AND CHARACTERIZATION OF SEQUENTIAL CURING WITH OFF-STOICHIOMETRIC AMINE-DIGLYCIDYL ETHER OF BISPHENOL A /NOVOLAC EPOXY BLENDED SYSTEMS . Advisor: Prof. ANONGNAT SOMWANGTHANAROJ, Ph.D.

B-stage epoxy adhesives are used in many applications such as electronic devices and prepreg composites. The most common available form is in the film form, rolls, sheets, or custom preforms. In this work, B-staged epoxy adhesives were prepared by using sequential curing with off-stoichiometric amine technique. Diethylenetriamine (DETA) was used as the curing agent for the first curing step. While dicyandiamide (DICY) was used as the latent curing agent for the second curing step and 3-(3,4-dichlorophenyl)-1,1dimethylurea (DIURON) as accelerator for reducing the curing temperature of DICY. Novolac epoxy was blended in diglycidyl ether of bisphenol A (DGEBA) with various ratio of 0 – 50 phr to enhance the glass transition temperature (T_g) and thermal stability. Non-isothermal differential scanning calorimetry (Non-iso DSC) showed simultaneous presence of two curing agents with two different curing reaction without interference. In addition, thermal stability and T_g were improved with increasing in Novolac epoxy content. However, blending ratio more than 30 phr of Novolac epoxy was practically difficult to proceed due to high viscosity, which is not suitable for film casting process at room temperature. Therefore, the weight ratio 70/30 of DGEBA/Novolac blended was then selected for further investigation owing to its acceptable T_g of 144 °C, thermal degradation at 5 % weight loss (T_{d5}) of 355°C and suitable viscosity for use in film casting process at room temperature. Fourier-transform infrared (FTIR) spectroscopy showed that the inactivity of latent curing agent and accelerator in the B-staged. The storage stability test showed only 8.72 % change in heat of curing reaction and able to adhere with substrate after B-staged for 28 days storage at freezer (-18 °C).

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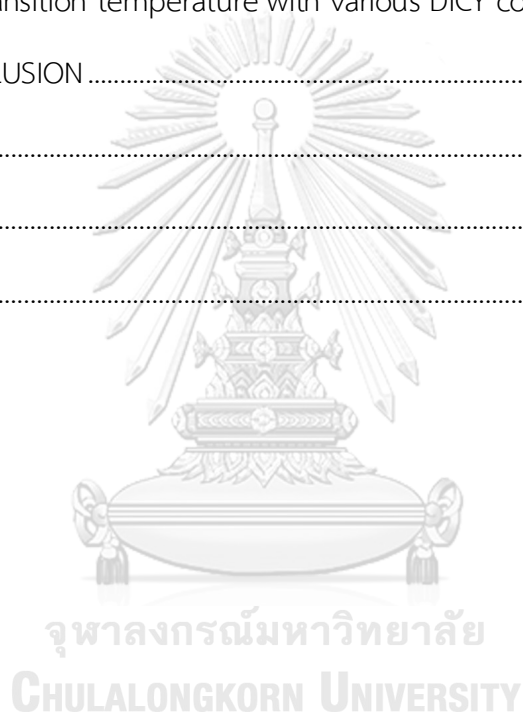
Pakawat Suttitham

TABLE OF CONTENTS

	Page
.....	iii
ABSTRACT (THAI).....	iii
.....	iv
ABSTRACT (ENGLISH).....	iv
ACKNOWLEDGEMENTS.....	v
TABLE OF CONTENTS.....	vi
LIST OF TABLES.....	ix
LIST OF FIGURES.....	ix
CHAPTER I INTRODUCTION.....	1
1.1 General Introduction.....	1
1.2 Objective.....	3
1.3 Scopes of the research.....	4
CHAPTER II THEORY AND LITERATURE REVIEWS.....	6
2.1 Flexible Circuit Technology.....	6
2.1.1 Material configuration.....	6
2.1.1.1 Base material (dielectric film/flexible substrate).....	7
2.1.1.2 Conductor (foil or conductive coating).....	7
2.1.1.3 Adhesive (optional).....	8
2.1.1.4 Cover lay (film or coating).....	8
2.2 Epoxy adhesives.....	8
2.2.1 Epoxy resin.....	9

2.2.1.1 Diglycidyl ether of bisphenol A (DGEBA).....	9
2.2.1.2 Epoxy Novolac resins.....	10
2.2.1.3 Flexible epoxy resin.....	12
2.2.2 Curing agent.....	13
2.2.2.1 Primary and Secondary aliphatic amines.....	14
2.2.2.2 Aromatic amines.....	16
2.2.2.3 Dicyandiamide and tertiary amine catalysts.....	17
2.3 B-staged epoxy adhesives.....	19
2.4 Stoichiometry & Non-stoichiometry.....	22
CHAPTER III EXPERIMENTS.....	26
3.1 Materials.....	26
3.2 Sample preparation.....	28
3.2.1 Surface preparation of aluminum substrates.....	28
3.2.2 Adhesive preparation.....	28
3.3 Characterization.....	30
3.3.1 Rheometer.....	30
3.3.2 Differential scanning calorimetry (DSC).....	30
3.3.3 Thermogravimetric analysis (TGA).....	31
3.3.4 Fourier transform infrared spectroscopy (FTIR).....	31
3.3.5 Peel test.....	31
CHAPTER IV RESULT AND DISCUSSION.....	32
4.1 Curing behavior and thermal properties by non-isothermal test.....	32
4.2 Thermal stability properties.....	34
4.3 FTIR characterization of each stage curing reaction.....	37

4.4 Pot-life time.....	39
4.5 Curing behavior by DSC iso-thermal mode.....	40
4.6 Storage stability	43
4.6.1 Curing of final staged epoxy by DSC.....	43
4.6.2 Tackiness after B-staged cure by peel strength test	46
4.7 Peel strength at C-staged cure.....	49
4.8 The glass transition temperature with various DICY content.....	51
CHAPTER V CONCLUSION	52
REFERENCES.....	55
Appendix.....	59
VITA.....	60



LIST OF TABLES

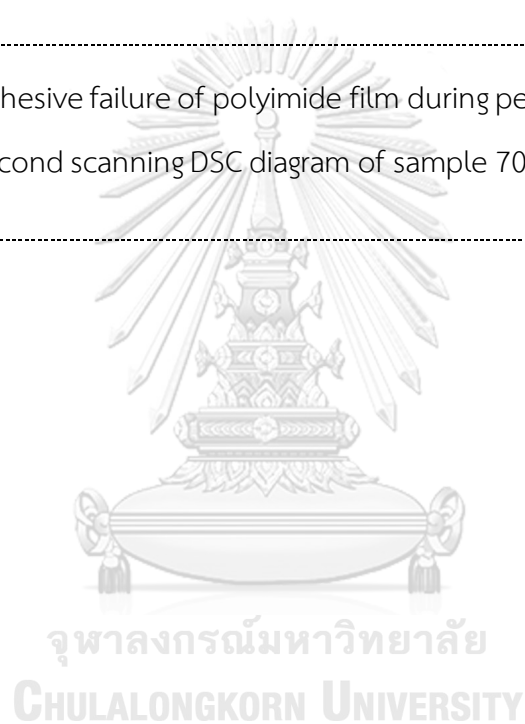
	Page
Table 2.2 Effect of curing temperature on bond strength of DGEBA cured with two different aliphatic polyamines [21].....	16
Table 3.1 The formulations of various ratio of DGEBA/Novolac epoxy content.....	29
Table 4.1 Degradation temperature at 5% weight loss (T_{d5}) and residual weight (%) at 600 °C of all sample.....	35
Table 4.2 Heat of curing reaction of sample 70/30 after B-staged cured for 0, 7, 14, 21 and 28 days stored at room temperature and freezer.....	44
Table 4.3 Mechanical properties of polyimide film.....	49

LIST OF FIGURES

	Page
Figure 2.1 Flexible printed circuit board make up.....	7
Figure 2.2 Oxirane or epoxide ring structure.....	9
Figure 2.3 Differential scanning calorimetry thermograms (the first scan (a) and the second scan (b)) of various DGEBA/Novolac epoxy blends cured with triethylenetetramine: neat DGEBA (●), DGEBA/Novolac (DN) 80/20 (■), DN 60/40 (◆), DN 40/60 (▲), DN 20/80 (▼), and neat Novolac epoxy (▴) [19].....	11
Figure 2.4 Chemical structures of BZPNE.....	12
Figure 2.5 Reaction mechanism between primary or secondary amine and epoxy.....	15
Figure 2.6. DSC heat flow curves for DICY-cured DGEBA accelerated by 2 phr of three different accelerators, BDMA, Monuron, and imidazole at heating rate of 5 °C/min [27].....	19

Figure 2.7 DSC diagram of the dual-curable formulation (S6) in comparison with individual curing agent's behavior in including DETA (S4) and DICY (S8) [7].....	22
Figure 2.8 Scheme of reactions: (a) epoxy & DIURON, (b) epoxy & DICY & DIURON [7].....	25
Figure 3.1 Diglycidyl ether of bisphenol A (DGEBA).....	26
Figure 3.2 Novolac epoxy.....	27
Figure 3.3 Diethylenetriamine (DETA).....	27
Figure 3.4 Dicyandiamide (DICY).....	27
Figure 3.5 and 3-(3,4-Dichlorophenyl)-1,1-dimethylurea (DIURON).....	27
Figure 4.1 The first scanning DSC diagram of samples 100/0, 80/20, 70/30, 60/40 and 50/50 with sequential curing in presence of two amine curing agents and accelerator systems.....	33
Figure 4.2 The second scanning DSC diagram of samples 100/0, 80/20, 70/30, 60/40 and 50/50 with sequential curing in presence of two amine curing agents and accelerator systems.....	34
Figure 4.3 TGA Thermogram of samples 100/0, 80/20, 70/30, 60/40 and 50/50 with sequential curing technique at C-stage.....	36
Figure 4.4 FTIR spectra of sample 70/30 with sequential curing technique at A-staged, B-staged, and C-staged.....	38
Figure 4.5 Viscosity profile of sample 70/30 in A-staged at 25 °C under constant shear rate of 1.0 s ⁻¹	40
Figure. 4.6 Degree of conversion versus time of sample 100/0, 70/30 and 0/100 at isothermal temperature 80 °C.....	41
Figure. 4.7 Degree of conversion versus time of sample 100/0, 70/30 and 0/100 at isothermal temperature 150 °C.....	42

Figure 4.8 The DSC diagram of sample 70/30 after B-staged cured for 0, 7, 14, 21 and 28 days stored at room temperature.....	45
Figure 4.9 The DSC diagram of sample 70/30 after B-staged cured for 0, 7, 14, 21 and 28 days stored at freezer.....	45
Figure 4.10 Average peel strength of adhesives after B-staged cure and stored at room temperature.....	47
Figure 4.11 Average peel strength of adhesives after cure and stored B-staged at freezer.....	48
Figure 4.12 The cohesive failure of polyimide film during peel strength test.....	50
Figure 4.13 The second scanning DSC diagram of sample 70/30 with various DICY content.....	51



CHAPTER I

INTRODUCTION

1.1 General Introduction

Epoxy adhesives are the most important of high-performance thermosetting polymers and have been widely used in many major industrials including automotive, construction, aerospace, and electronic packaging. This is due to their good mechanical properties, high resistance to chemicals and corrosion, high thermal stabilities, excellent electrical properties and bond well to many substrates [1]. However, manufacturing of electronic packaging/part assembly industry need to precisely control the parameters such as bond line thickness, dimension, and placement location of the adhesives. Commonly, epoxy adhesives prefer in liquid form which are difficult to control thickness and dimension of adhesives. It may be squeezed-out because the exceed liquid adhesives was used when joint with the substrates [2]. B-staged epoxy or partially cured epoxy is a one component epoxy type. From this stage, epoxy is semi-solid form with little or no flow, which provides uniform bond line thickness and precise placement in desired bond area. After applied onto the substrate, it can be later completely cured under proper heat [3]. B-staged epoxy adhesives the most typically available in film form, rolls, sheets, or custom preforms. It can be die cutting or laser cutting with desired dimensions [2]. The most common way to create the B-staged is heat cured for a short period time

to achieve 10 to 20 % of degree of cure (DOC) and then cool down to low temperature immediately to stop curing reaction. However, this method is complicated to specify certainly time and temperature of the curing system. Moreover, it can be risk over or less than DOC from desired level in B-staged, leading to lost tackiness of adhesive. In recently year, sequential curing with off-stoichiometric technique is methodology in which two different polymerization processes by dual curing agent, separately take place at different curing temperature. The advantages of this technique are in terms of control of the process by changing composition of formulation and minimize the risk of overcuring in common B-staged processing, which is subject to time-temperature specifications to control the extent of the polymerization. After materials were cured at first stage, it can be partially cured and obtained storage stable materials, which cannot be further cured after the end of the first stage. At later time, it can be achieved fully cured at second staged with the desired final properties [4-7].

One of the most general-purpose epoxy adhesives is diglycidyl ether of bisphenol A (DGEBA) epoxy resin which is a low-viscosity, good physical properties, low cost and good processability for casting. However, when using the same curing agents, the content of curing agents, and curing condition that cure neat DGEBA and compared to neat Novolac epoxy. The glass transition temperature (T_g) of fully cured DGEBA is lower than that of Novolac epoxy resin, due to low crosslink density and high flexible segment [8, 9], causing the main effect on coefficient of thermal

expansion (CTE) in electronic parts, which is T_g should be higher than 125 °C to keep lower CTE while in working temperature range [10, 11]. Thus, Novolac epoxy resin with high polyfunctional and high rigid segment that could generate highly crosslinked network become the candidate to use in this application. Furthermore, when Novolac epoxy resin was blended with DGEBA, the epoxy blends exhibited a synergistic effect and provide better adhesion properties, glass transition temperature, fracture toughness and high-temperature performance of epoxy adhesives [8, 12].

In this research, sequential curing technique is used to create B-staged epoxy by using diethylenetriamine (DETA) as first staged curing agent and dicyandiamide (DICY) as latent curing agent for final curing staged. Moreover, to improve thermal properties and adhesive strength of B-staged epoxy adhesives. Novolac epoxy resin was blended with DGEBA with various ratio, then the proper ratio of DGEBA/Novolac that can be processed in film casting at room temperature was selected to create the film specimen. Finally, the DICY content was varied to investigate the effect on thermal properties of B-staged epoxy adhesives.

1.2 Objective

The objective of this research is to use sequential curing technique to create B-staged epoxy with epoxy blended system and improve the glass transition

temperature, and thermal stability of B-staged epoxy adhesive. Then, the formulation with acceptable glass transition temperature, thermal stability and processability for film casting at 25 °C was selected to investigate curing behavior, peel strength, and storage stability of B-staged epoxy adhesive.

1.3 Scopes of the research

1.3.1 Preparation of B-staged epoxy adhesive by using DGEBA blends with Novolac epoxy 0 – 50 wt% and the optimal formulation a casting process was selected. DIURON was used as an accelerator and diethylene triamine (DETA) was used as the first step curing agent at constant concentration of 1.6 phr and 2.2 phr, respectively. Dicyandiamide (DICY) was used as the second step curing agent with various ratio.

1.3.2 Characterization of thermal properties and curing behavior of B-staged epoxy adhesive using differential scanning calorimetry (DSC).

1.3.3 Characterization of thermal degradation of B-staged epoxy adhesive using thermogravimetric analysis (TGA).

1.3.4 Characterization of adhesion strength of B-staged epoxy adhesive using universal testing machine (90° peeling mode).

1.3.5 Characterization of curing behavior of storage stability after B-staged 0, 7, 14, 21 and 28 days at 25 ± 2 °C and -18 °C using DSC.

1.3.6 Characterization of viscosity and pot lifetime of selected sample epoxy for film casting process at 25 °C using rheometer.

1.3.7 Characterization of curing reaction of selected sample with three different staged by Fourier transform infrared spectroscopy (FTIR).



CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Flexible Circuit Technology

Flexible printed circuit (FPC) plays an important role in microelectronic device such as cellular phone, cameras, LCD/OLED display and laptop. Moreover, it can be found in automotive, military, aerospace, and medical products. Due to thin, lightweight, small size and can be bent without breaking or damaging to both the circuit material and the component [13-15].

2.1.1 Material configuration

Flexible circuits consist of four distinct materials which are base material, conductor, adhesive, and cover lay. A simple typical flexible circuit make-up is shown in figure 2.1.



Figure 2.1 Flexible printed circuit board make up

2.1.1.1 Base material (dielectric film/flexible substrate)

Base material is the important part to perform a variety function. It must electrically insulate the conductive circuit tracks from one another and must be compatible with any adhesives used for conductor or cover-lay bonding. Materials that have been used as substrate materials include polyimide, polyester, fluorocarbon and aramid [15].

2.1.1.2 Conductor (foil or conductive coating)

The conductor material must provide proper electrical and mechanical performance in the various environment applications. The materials that have been used in conductor includes elemental metal foils, such as copper, aluminium, stainless steel, and metal compound. Both silver and carbon polymer thick-film (PTF) inks are also used [15].

2.1.1.3 Adhesive (optional)

Adhesives play an important role in extending the service life of FPC. They are used to joint between base material and the chosen conductor material, and protect cover lay over exposed conductors. Therefore, the properties of adhesive must be good mechanical strength, good chemical resistance, and be able to withstand the FPC manufacturing condition without delamination. In addition, they must be compatible with both base material and conductor materials. Typical adhesives used for FPC manufacture include polyester, polyimide, acrylic and epoxy [14, 15].

2.1.1.4 Cover lay (film or coating)

Cover lay is one type of protective films or coatings that applied to the surface of FPC to protect it from moisture, contamination, and abrasion, and reduce conductor stress during bending. The most common materials used to cover are polyester film with polyester adhesive, polyimide film with acrylic adhesive, and polyimide film with epoxy adhesive [15].

2.2 Epoxy adhesives

Adhesives based on epoxy resin can be formulated to fulfil a wide range of applications due to its easily modified to achieve desired application and bond well to many substrates. When they were cured, the 3D-crosslinked network between the molecular structures was formed and exhibit excellent mechanical strength

properties, and chemical, thermal, and electrical resistance, as well as low shrinkage. However, these properties depend on chemical structure of epoxies, curing agent, curing time/temperature and additives or modifiers [1]

2.2.1 Epoxy resin

Epoxy is an organic compound which contains greater than or equal to one oxirane ring functional group in molecular structure, as shown in Figure 2.2. Furthermore, epoxy equivalent weight (EEW) is the important parameter to determining curing agent concentrations. This term is defined as “the weight of resin in grams that contain the equivalent of one epoxy group”. As EEW increases, the amount of curing agent decreases.

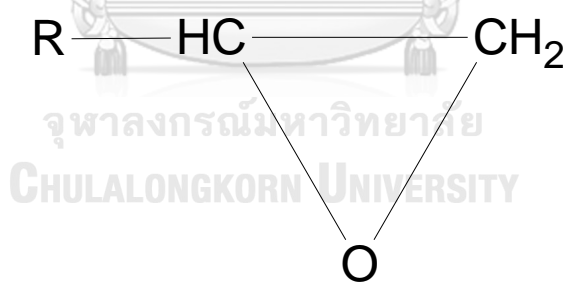


Figure 2.2 Oxirane or epoxide ring structure

2.2.1.1 Diglycidyl ether of bisphenol A (DGEBA)

Diglycidyl ether of bisphenol A or DGEBA is the most common commercial epoxy resin used, synthesized from the reaction of bisphenol A and epichlorohydrin.

The reasons for their popularity are the relatively low cost of raw materials used to synthesize, the ability to be cured by various type of curing agents and relatively good mechanical and chemical properties that are exhibited by the cured resins [16]. DGEBA can be used alone or blends with other epoxy resins, or even other types of polymeric resins. When compared to subtle variations in chemical structure with diglycidyl ether of bisphenol F (DGEBF) and 1,3 bis(4-isopropyl phenylglycidyl ether) benzene (DGEBM) cured with bi- and tri-aryl amines which was studied by Reyes Q. L. et al. (2019) [17]. The result show that DGEBA exhibited the highest T_g due to isopropyl group in central atom which is increase crosslink density and rigidity of the chain. Likewise, yield strength and yield strain were increased.

2.2.1.2 Epoxy Novolac resins

Epoxy Novolac resins are prepared by reacting epichlorohydrin with a Novolac resin. They generally have significantly different properties from DGEBA because of the presence of the phenolic structure and their multifunctionality, which is about 2.0 to 8.0 [18]. The multiplicity of epoxide group influences to increase crosslink density, resulting in good heat, chemical resistance and increase in T_g [8, 9]. However, epoxy Novolac resins are high-viscosity liquids or semisolids, and they are often mixed with other epoxy resins. They are cured more rapidly than DGEBA and have higher exotherms, but the incorporation of Novolac epoxy and DGEBA could lower curing temperature due to the higher functionality of Novolac epoxy when compared to neat DGEBA. Moreover, T_g were increased by increasing Novolac epoxy content as

shown in DSC thermograms in figure 2.3 studied by Chailee O. et al (2019) [19]. In industrial application, Novolac epoxy resins are used for adhesive, aerospace composites, coating of tanks, pipes, floors, automotive parts, and electronic parts.

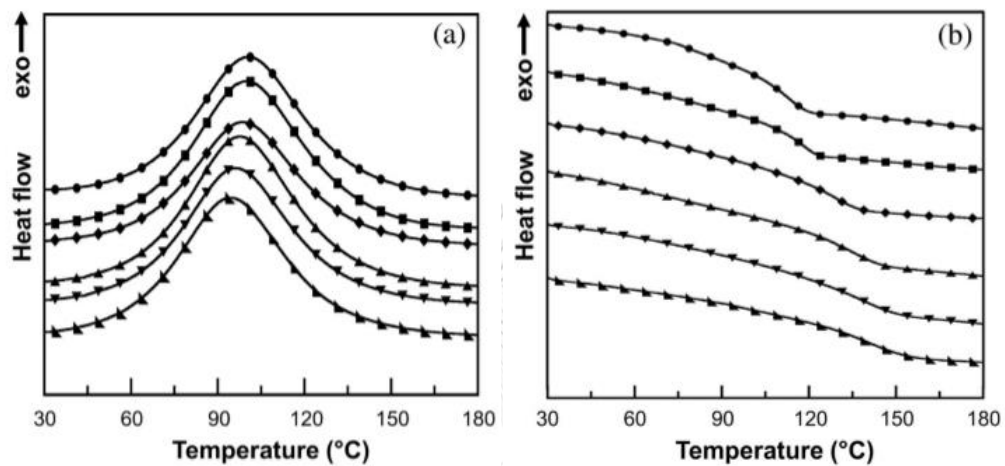


Figure 2.3 Differential scanning calorimetry thermograms (the first scan (a) and the second scan (b)) of various DGEBA/Novolac epoxy blends cured with triethylenetetramine: neat DGEBA (●), DGEBA/Novolac (DN) 80/20 (■), DN 60/40 (◆), DN 40/60 (▲), DN 20/80 (▼), and neat Novolac epoxy (▴) [19]

In addition to the Novolac epoxy resins, there are several other derivative types which is synthesized from different chemical-based structure. For example, bisphenol-S, bisphenol-A, and benzophenone. These structures improve flexibility of resins before cured by introducing methylene group between aromatic groups of bisphenols. Moreover, steric hindrances from central linkage between the two phenyl groups were increased chain rigidity, leading to higher crosslinked density after cured. Moreover, the coefficient of thermal expansion (CTE) has reduced 1.75-fold and 1.3-

fold enhanced T_g with 30% of 4,4-dihydroxybenzophenone Novolac resin (BZPNE) synthesized by Monisha B. et al (2017) [20] in DGEBA resin and using dicyandiamide (DICY) as curing agent. The enhancement of T_g and reduction in CTE may be explained the restrained or controlled molecular motion of the cured thermoset due to the rigid segment contributed by 4,4'-dihydroxybenzophenone part. Figure 2.4 shows the chemical structures of BZPNE.

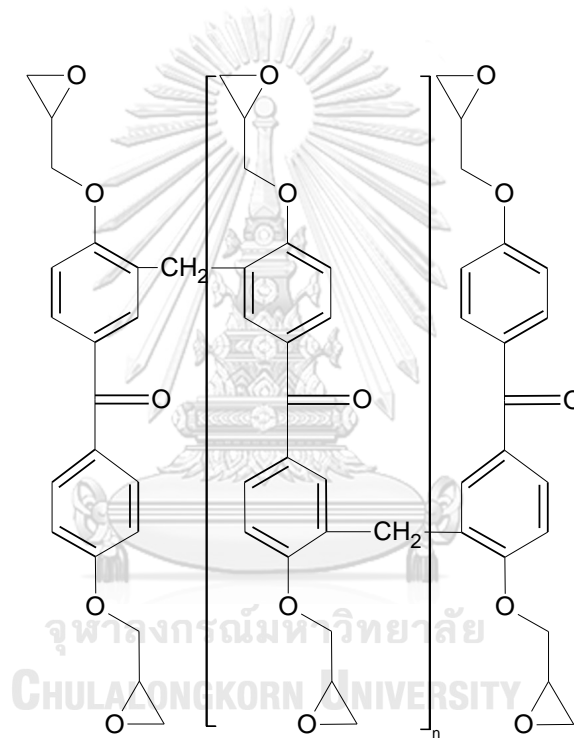


Figure 2.4 Chemical structures of BZPNE.

2.2.1.3 Flexible epoxy resin

Flexibility of epoxy resin can be provided by various ways. For instance, incorporating large groups in the molecular chain, which increases the distance

between crosslinks, changes aromatic structure to a more aliphatic hydrocarbon or by reducing functionality, insertion of long hydrocarbon side chains also can provide additional flexibility to the epoxy molecule [1]. Example of modifier for improved flexibility includes acid functional oils (dimer acid, cashew nut oil, and castor oil), and polyalkylene glycol (polyethylene or polypropylene glycol)

However, the increment of flexibility of epoxy decreases in crosslink density of epoxy molecules results in a decrease in T_g and significantly decrease in tensile and shear strength as well as a decrease in other performance properties, such as chemical and heat resistance [1].

Applications where flexible epoxy resins are included

1. Adhesives to laminate safety glass
2. Adhesives and sealants to damp vibration and sound in addition to providing joining
3. Encapsulants for electrical components and other delicate components where thermal cycling is expected

2.2.2 Curing agent

To convert epoxy resins to rigid, infusible thermoset and form 3D- crosslinked networks. Crosslinking agent or curing agent is needed, which are generally reacted

with the available epoxide ring or hydroxyl groups by chemical bonding. These cross-linkers, hardeners or curing agents as they are widely known, promote cross-linking or curing of epoxy resins. There are various types of curing agents, some can be used to improve the flexibility of epoxy resins, one can double the impact resistance and increase in tensile elongation at break of epoxy adhesives [1]. In fact, it mainly depends on the processing requirements (e.g., viscosity, pot life, application method, curing temperature, reactivity, mix ratio) and the end-use requirements (e.g., thermal, chemical resistance, shear strength, toughness). The examples of curing agent are amine, polyamides, anhydrides, polysulfides and mercaptans. But in this chapter, amine and their sub classifications are only mentioned.

2.2.2.1 Primary and Secondary aliphatic amines

Amine curing agents has been one of the most common types of curing agents for epoxy resins and can be primary or secondary one due to a rapid reaction with epoxide ring at room or lower temperature to form three-dimensional crosslinked structures. The reaction mechanism between primary or secondary amine and epoxy is illustrated in figure 2.5; i.e., (1) the primary amine is added to the epoxy ring forming a secondary amine, (2) the secondary amine is added to the epoxy ring, forming a tertiary amine and (3) the formed hydroxyl groups are accelerated with excess epoxy presented, the secondary hydroxyl groups can be also added to the epoxy ring. The resulting cured epoxy have relatively high moisture resistance, good chemical resistance, and heat resistance with a heat distortion temperature in the

range of 70 to 110 °C. These aliphatic amines can also be cured at elevated temperatures to provide a highly cross-linked density with better mechanical properties, elevated-temperature performance, and chemical resistance. The effect of curing temperature on the bond strength of DGEBA with two different aliphatic amines is shown in table 2.2.

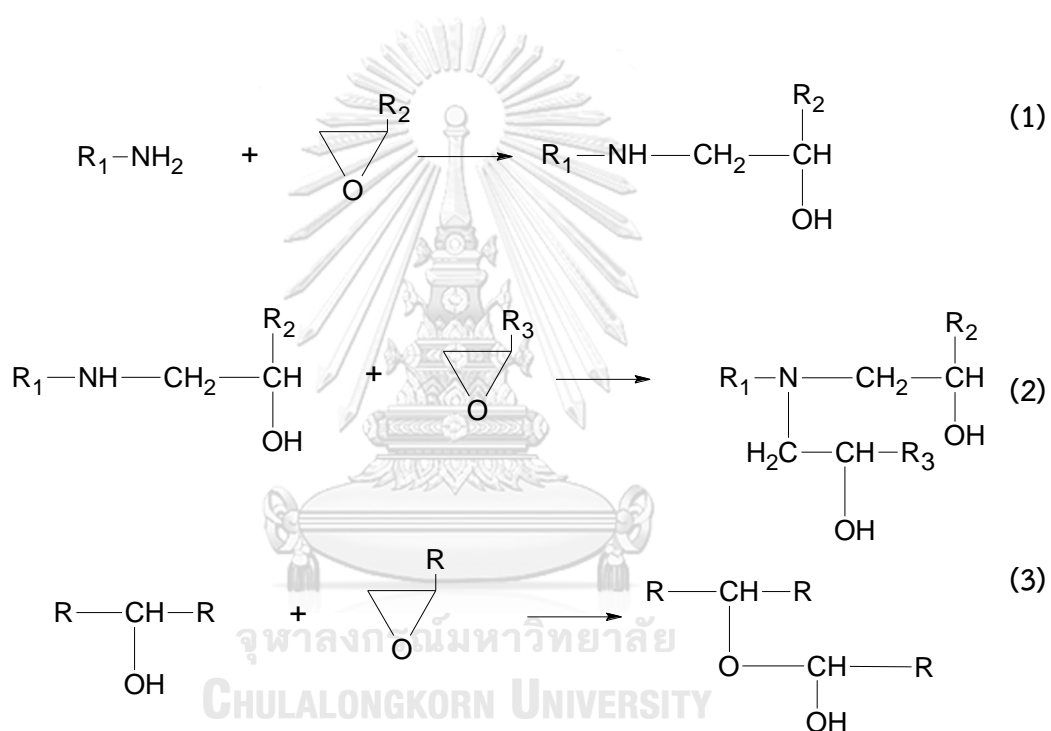


Figure 2.5. Reaction mechanism between primary or secondary amine and epoxy

Table 2.2 Effect of curing temperature on bond strength of DGEBA cured with two different aliphatic polyamines [21]

Curing condition	Bond strength on aluminum, psi	
	Triethylenetetramine (TETA)	Diethylaminopropylamine (DEAPA)
RT for 3 days	1162	-
RT for 15 days	1690	-
95°C for 30 min	3172	-
145°C for 30 min	3426	-
40°C for 16 hrs.	-	702
40°C for 16 hrs. plus 14 days at RT	-	840
95°C for 5 hrs.	-	3236
145°C for 30 min	-	4056

2.2.2.2 Aromatic amines

Aromatic amines are widely used as curing agents for epoxy resins. They offer cured epoxy structures with good heat and chemical resistance. The main advantages of aromatic amines over aliphatic amines are the longer pot life as well as the enhancement of higher heat, chemical resistance and mechanical strength

[17]. Since the lower reactivity of the aromatic amines in epoxy resin mixture, they can be B-staged epoxy adhesives at room temperature and will not be fully cured for months. Therefore, films and one-component adhesives can be formulated as elevated-temperature curing with long shelf life. The disadvantages are that they are solids at room temperature and generally require high temperature for processing and curing. Likewise, added heat required for mixing and cure are increased the dermatitis and toxicity potential by releasing irritating vapors [1].

2.2.2.3 Dicyandiamide and tertiary amine catalysts

Dicyandiamide (DICY or 1-cyanoguanidine) is used as a latent curing agent that form crystals and have a high melting point of 207 to 210 °C and reacts with both the epoxy terminal groups and the secondary hydroxyl groups. DICY does not react with epoxy resins at room temperature or low temperatures, only reacts on heating beyond an activation temperature, typically require 145–165 °C to initiate curing reaction [1, 22]. It is widely used for film epoxy adhesives and for B-staged epoxy adhesive prepregs with long shelf life up to 6 months at ambient temperatures and up to 12 months for storage under refrigeration [23]. Because of its low solubility in the epoxy resins, DICY is often first dissolved in organic solvents. Nevertheless, when dissolved in epoxy resins using a solvent, shelf life has decreased to 24 hours [24].

To reduce curing time and temperature as well as enhance its reaction rate, catalysts or accelerators are usually used for DICY e.g., Fenuron, Monuron, Diuron,

Benzyl dimethyl amine (BDMA), DMP and imidazole which have tertiary amine group and no active hydrogen in structure, neither react with the epoxide ring nor participate themselves in the epoxy polymerization reactions. Generally, it acts as a catalyst to accelerate other curing reactions by stabilizing the transition state [25, 26]. The amounts of catalyst used with epoxy resins are generally several parts per hundred (phr) of catalyst. Excess amounts of catalyst can result in poor physical properties and degraded resin. Hayaty M. et al. (2013) [27] studied the effects of DICY concentration, type and amount of three different accelerators including BDMA, 2-methyl imidazole (Im) and 3-(4-chlorophenyl)-1,1-dimethylurea (Monuron) on curing behavior of DICY/DGEBA system by DSC method in which DGEBA epoxy resin with EEW 230 was used in this work. The results showed that the best curing characteristic and glass transition temperature are obtained at the stoichiometric ratio of DICY to epoxy of 0.65 or 7 phr of DICY. From the cured characteristic by DSC as shown in figure 2.6, it can be concluded that BDMA had a broader peak in DSC and starts the curing reaction earlier than other two accelerators, but Monuron showed narrow curing reaction peak which is difficult to control B-staging in making for prepregs or molding compounds. In addition, increasing amount of Monuron content, the T_g were decrease.

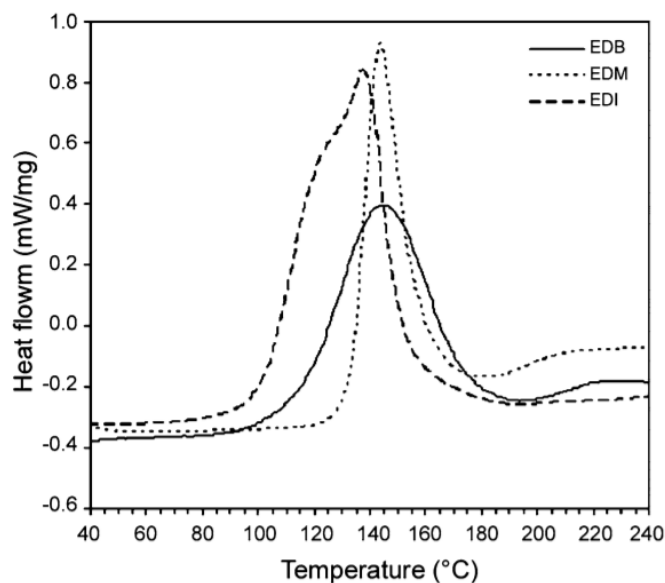


Figure 2.6. DSC heat flow curves for DICY-cured DGEBA accelerated by 2 phr of three different accelerators, BDMA, Monuron, and imidazole at heating rate of 5 °C/min [27]

In addition, the bulkiness, number of nitrogen atoms and the electron density of accelerator influence on curing behavior of DGEBA/DICY systems [28]. The result showed that the number of nitrogen atoms in the molecular structure has more remarkable accelerating effect than the electron density. By comparing with equal number of nitrogen atoms in the trimolecular structure, the accelerating superiority is determined by the bulkiness.

2.3 B-staged epoxy adhesives

Most commonly, B-staged refers to an epoxy resin that has been cured for a short period of time and then cooled down immediately (quenched) to prevent complete polymerization of the resin system. At this stages epoxy adhesive is almost

solid that has been partially cured, typically 10-20% degree of cured (DOC) [2, 29] and still be available for bonding adherend together. At later time, it can be completely cured under heat and pressure. Film form, either as rolls, tape die cutting sheets, laser cutting sheets or custom preforms are the most commonly available in B-staged epoxy adhesives with thickness range from 10-200 μm . The advantage of B-staged over liquid epoxy is the ability to precisely control both bond line thickness and placement location of the adhesive, which eliminates squeeze-out problems when joint substrate together by excess liquid epoxy. The applications of B-staged epoxy adhesives are usually in microelectronic, seal lids for electronic packages, semiconductor packaging, fiber optic bonding in ferrules, and pre-applying epoxy on heat sinks. According to heat and quenched method, it is complicated way to create B-staged. Because certainly time and specific temperature of the curing system are needed, otherwise it can be risk to over or less than DOC from desired level in B-staged, leading to lost tackiness of adhesive.

Another way to create a B-staged epoxy adhesive is blending epoxy resin in a solvent carrier, preparing a homogeneous liquid slurry that can be coated or laminated on a substrate surface and then evaporated excess solvent at a temperature below the polymerization. Although, this process creates a stable solid in the desired configuration, which can be cured at later time. It has not been advanced and arguably not a true b-stage epoxy, technically. Dual-curable off-stoichiometric formulation introduced by Fernandez-Francos et al. (2016) [6] is a

modification method to reach custom-tailored epoxy structures. In this method, two controllable curing agents are carried out simultaneously or sequentially polymerization. Sequential dual curing has many advantages in terms of process which cause a better control over the final properties. In these systems, the resin can be partially cured with the first curing agent before storing or processing. Since these systems remarkably reduce the risk of passing the degree of cure from desired level in B-staged. Pouladvand A. et al. (2020) [7] successful by created a B-staged epoxy prepreg based on amine dual-curable systems. Herein, DGEBA with EEW 183–188 g/mol as epoxy resin, DIURON as accelerator and two curing agents with off-stoichiometric, which are diethylene triamine (DETA) as primary aliphatic amine and DICY as latent curing agent. The first curing of DETA can be converted to the tertiary amine which acts as the catalyst for the final curing stage of DICY. This catalytic activity leads to a 25 °C decreasing in the DICY-epoxy curing temperature and there still is a separation of peak between the two stages as shown in figure 2.7. In addition, it is evident that the presence of DIURON 1.6 phr can reduce the curing temperature of DICY around 45 °C leading the final curing temperature to 132 °C. Moreover, after storage at ambient temperature for 21 days, only 7% increase in conversion. Thus, this formulation provides an acceptable one with high storage stability of the prepreg.

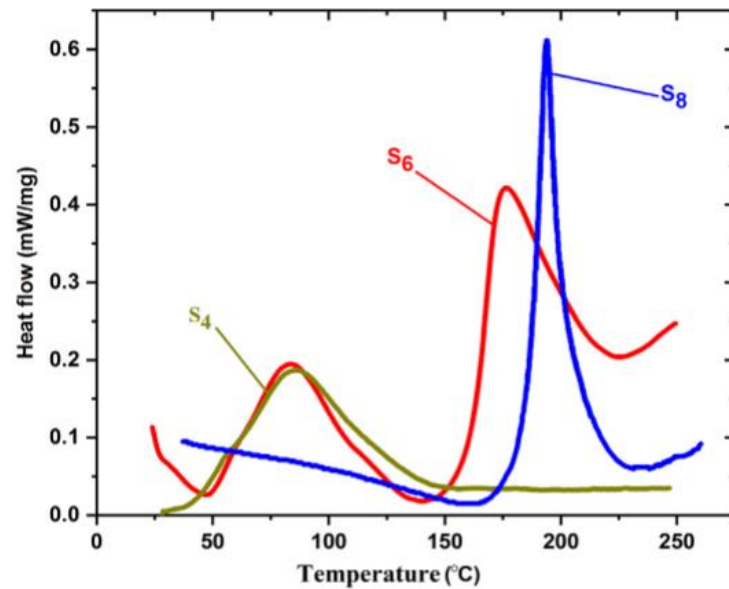


Figure 2.7 DSC diagram of the dual-curable formulation (S6) in comparison with individual curing agent's behavior including DETA (S4) and DICY (S8) [7].

2.4 Stoichiometry & Non-stoichiometry

Optimum properties are achieved when the amount of curing agent used is stoichiometric. For catalyst, their no meaning in stoichiometric calculation since their action is truly catalytic and often added at low levels (0 to 5%). The stoichiometric quantity of amine can be calculated from amine-equivalent weight (AEW) which is the molecular weight of the amine divided by the number of active hydrogens in the amine as shows in Eq. 2.2, and using the epoxy equivalent weight (EEW) to obtain theoretical amount of curing agent (A_c), which can be calculated as in Eq. 2.1

$$A_c = \frac{AEW}{EEW} \times 100 \quad (2.1)$$

where A_c is the curing agent required to cure 100 parts of resin (phr).

For example, using diethylenetriamine ($\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH-CH}_2\text{-CH}_2\text{-NH}_2$) and DGEBA epoxy resin having an EEW of 189.

1. Calculate the amine equivalent weight

$$AEW = \frac{\text{MW of amine}}{\text{Number of active hydrogens}} \quad (2.2)$$

$$AEW = \frac{103.2}{5} = 20.6$$

2. Calculate the stoichiometric ratio of amine to use with the epoxy resin.

$$A_c = \frac{20.6}{189} \times 100 = 10.9 \text{ phr}$$

Thus, diethylenetriamine should be added 10.9 part for 100 part of DGEBA to achieve the optimum properties.

Mixing ratios of resin to curing agent is unnecessarily to be stoichiometric ratios, it depends on chemical functionality and chemical structure of resins and curing agent. Moreover, specific application to end-user conditions are included. For non-stoichiometric amine-curing agents, for example in using diethylenetriamine greater than stoichiometric amine, tend to stop polymer chain building from polymerization and produce low-molecular-weight polymers with high degree of cure (DOC) that tend to be brittle. On the other hand, less than stoichiometric amine results in incomplete and low DOC, but flexibility was increased [1, 22]. Petterson

[30] has shown that the use of only 50 percent of the stoichiometric amount of hexamethylenediamine imparts to a cured DGEBA adhesive the maximum strength, bulk tensile strength, and flexural moduli, whereas higher proportions of the diamine give lower properties.

For DICY latent curing agent, the stoichiometric amount is arguably, because the mechanism of DICY curing process is complicated. In addition to the four active hydrogen atoms, the nitrile group of DICY could react with hydroxyl group and epoxide ring, then rearrangement to form the cyclic amide structure [31] or decomposed to cyanamide then the active hydrogen atoms react with epoxide ring [32]. Moreover, the mechanism of DICY in the presence of DIURON as accelerator is different as shown in figure 2.8. First, DIURON decomposed and react with epoxide ring to generate dimethylamine and 2-oxazolidone (Figure 2.8a). Then, dimethylamine removes a proton from DICY and hence the conjugated anion will be more nucleophilic which reacted with epoxide groups at lower temperatures (fig. 2.8b) [7]. Lee Y. D. et al. [33] reported the effects of ratio of DICY/DGEBA (EEW 195) on the lap shear and T-peel strengths in which the stoichiometry ratio of DICY/DGEBA is as 11 phr. The result showed that, the ratio of DICY/DGEBA 6 phr produced the highest value of lap shear and T-peel strengths on aluminium substrate. When the DICY/DGEBA ratio which is greater or less than 6 phr, both lap shear and T-peel strength would decrease.

CHAPTER III

EXPERIMENTS

3.1 Materials

DGEBA (EPOTEC YD 128) with EEW = 185 – 194 g/eq. and semi-solid phenol Novolac based multifunctional epoxy resin (YDPN 638) with EEW = 175 – 182 g/eq. were obtained from Aditya Birla Chemical (Thailand) Ltd. Diethylenetriamine (DETA) was used as low temperature curing agent, Dicyandiamide (DICY) as latent curing agent and 3-(3,4-Dichlorophenyl)-1,1-dimethylurea (DIURON) as accelerator were purchased from Tokyo Chemical Industry Co., Ltd. The chemical structures of epoxy resins, curing agent, and catalysts are shown in figure 3.1-3.5.

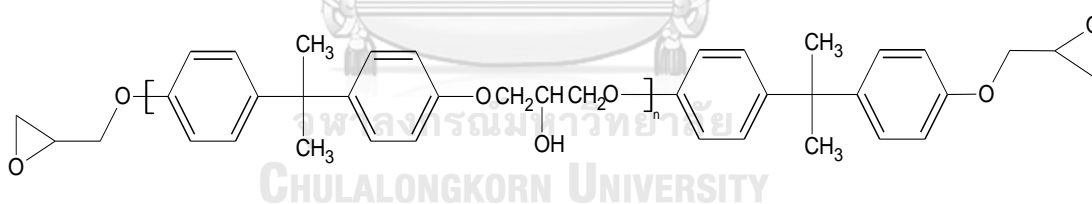


Figure 3.1 Diglycidyl ether of bisphenol A (DGEBA)

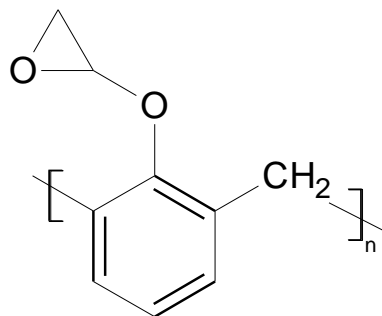


Figure 3.2 Novolac epoxy

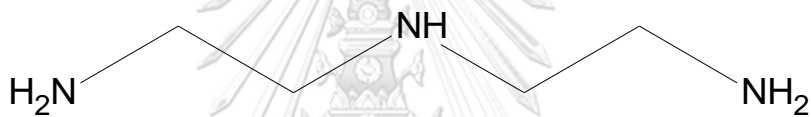


Figure 3.3 Diethylenetriamine (DETA)

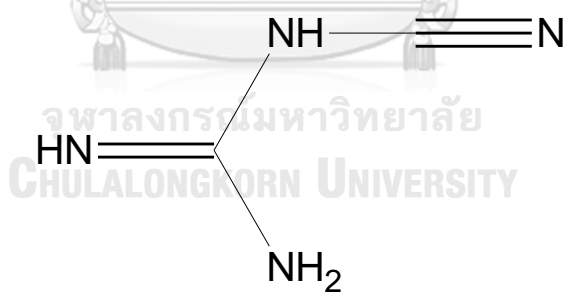


Figure 3.4 Dicyandiamide (DICY)

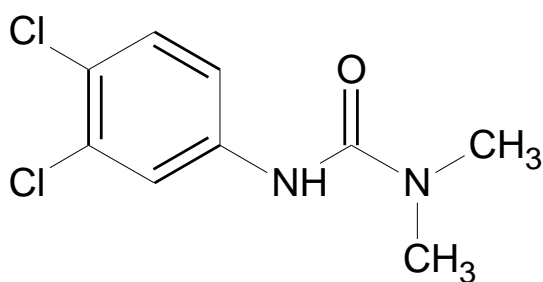


Figure 3.5 and 3-(3,4-Dichlorophenyl)-1,1-dimethylurea (DIURON)

3.2 Sample preparation

3.2.1 Surface preparation of aluminum substrates

In this work, AA 1100 4 x 4 aluminum alloy sheets were used to study the adhesion between epoxy adhesive and aluminum sheet. The surface preparation was performed by chemical treatment followed ASTM D2651 standard. At first, aluminum sheets were immersed in 5 % w/w NaOH solution (alkaline etching) at 50 °C for 3 mins. In this method, the aluminum oxide layer on the surface can be removed. Then, the etched samples were washed with distilled water and then were immersed in the acid etching solution composed of 50% v/v nitric acid solution for 1 min at ambient temperature. Finally, the samples were washed with distilled water and dried in a vacuum oven at 60 °C for 15 mins. All samples were kept in a desiccator before using, for preventing the occurrence of further corrosion on these samples.

3.2.2 Adhesive preparation

For preparation, DGEBA was blended with Novolac epoxy at ratio DGEBA/Novolac 100/0, 80/20, 70/30, 60/40 and 50/50 for 20 mins at 70 °C. Blend ratio containing more than 60 of Novolac epoxy in DGEBA was practically difficult to film casting process due to almost solid consistency. Then, the epoxy blend was mixed with DICY at the stoichiometric ratio for 4 hrs at 70 °C. This mixture can be stored at room temperature for several weeks or at freezer for longer shelf life, since no reaction occurs between epoxy and DICY at this condition. After that, the mixture

of epoxy/DICY was mixed with DIURON by mechanical stirrer at 200 rpm for 30 mins. at 50 °C. Then, DETA were dissolved in the mixture with softly stirred for 5 mins at room temperature and the mixture was laminated on aluminum backup board by film casting technique with adhesive thickness about 30 μm . Afterward, aluminum backup board was attached by polyimide film and placed in an oven at 80 °C for 20 mins to obtained B-staged epoxy. Then, the samples were cooled down at room temperature. Finally, they were placed in an oven at 150 °C for 30 mins to reach fully cured of the adhesive film. The adhesive formulations of various Novolac epoxy content are shown in table 3.1.

Table 3.1 The formulations of various ratio of DGEBA/Novolac epoxy content

Sample	Formulation				
	DGEBA (g)	Novolac (g)	DETA (phr)	DICY (phr)	DIURON (phr)
100/0	100	0	2.2	6.0	1.6
80/20	80	20	2.2	6.0	1.6
70/30	70	30	2.2	6.0	1.6
60/40	60	40	2.2	6.0	1.6
50/50	50	50	2.2	6.0	1.6

3.3 Characterization

3.3.1 Rheometer

The flow experiments for film casting process investigation were done on the rheometer (model AR-G2 manufactured by TA instruments). Viscosity of the adhesive sample was measured as a function of time. A 25 mm diameter parallel plate was used, and the instrument settings were as follows: a gap of 1000 microns, frequency of 1 Hz, temperature of 25 °C and a constant shear rate of 1.0 s⁻¹.

3.3.2 Differential scanning calorimetry (DSC)

The curing behavior, glass transition temperature and storage stability after B-staged at 25 °C and -18 °C of the epoxy adhesives were evaluated by a differential scanning calorimeter (DSC). In this work, both non-isothermal and isothermal temperature scanning were evaluated by using DSC, model DSC1 module, Mettler-Toledo (Thailand) and Perkin Elmer Diamond DSC for storage stability test after B-staged testing. Temperature scanning was from 0 °C to 250 °C at a heating rate of 10 °C/min. Isothermal curing method was performed at a heating rate of 150 °C/min. The first staged of curing a temperature was raised up to 80 °C, then cool down to 25 °C and raised up 150 °C for the final staged of curing. All of measurements were performed under nitrogen atmosphere at a flow rate 50 ml/min.

3.3.3 Thermogravimetric analysis (TGA)

Thermal stability of epoxy adhesives was analyzed by a thermogravimetric analyzer (model SDT Q600 manufactured by TA instruments). The samples were heated from 25 °C to 600 °C at a heating rate of 10 °C/min under a nitrogen atmosphere with a constant flow rate of 50 ml/min. The degradation temperature of the samples was reported at 5% weight loss (T_{d5})

3.3.4 Fourier transform infrared spectroscopy (FTIR)

The curing reaction was further confirmed by Fourier transform infrared spectroscopy (FTIR). FTIR spectra of the uncured epoxy, B-staged epoxy and completely cured epoxy were measured in a spectral range of 4000-400 cm^{-1} with 128 scans at a resolution of 4 cm^{-1} .

3.3.5 Peel test

The 90° peel strength was measured by a universal testing machine (Instron, model 5567) based on ASTM D-6862 from Instron (Thailand) Co., Ltd. At least five samples (5 mm width of a peel test) were tested for adhesives joints with 30 μm thickness between a polyimide film with 12.5 μm thickness and aluminum backup board with peel rate 50 mm/min. The peel strength was the average peel force divided by specimen width.

CHAPTER IV

RESULT AND DISCUSSION

In this chapter, the epoxy blended adhesive with various ratio of Novolac epoxy was investigated. Then, the formulation with acceptable glass transition temperature, thermal stability, and proper viscosity to film casting process at room temperature was selected to further investigation such as reaction mechanism, pot-life time, curing behavior by iso-thermal test, storage stability and peel strength.

4.1 Curing behavior and thermal properties by non-isothermal test

The curing behavior of formulations of neat DGEBA and DGEBA blends with Novolac epoxy in presence of two curing agents and accelerator were investigated by DSC first temperature scanning as shown in figure 4.1. Two-separation curing peak are observed which indicate that curing reaction of each stage occur at different temperature. The first curing peak at 88 °C is attributed to the reaction between epoxide ring and the primary and secondary amine of DETA. At this concentration of DETA, percent cure is approximately 17-18 %. Likewise, the second curing peak is attributed to the reaction between epoxide ring and primary and secondary amine of DICY. The second curing peak of sample 100/0 is located at 154 °C while the second curing peak of the 80/20, 70/30, 60/40 and 50/50 epoxy blends are 152, 151, 150 and 149 °C, respectively. The second curing peak temperature of blended epoxy containing Novolac epoxy are reduced to lower temperature due to higher

functionality and reactivity of Novolac epoxy when compared to DGEBA [19]. The second temperature scanning was used to determine the glass transition temperature (T_g) measured at the mid-point of slope as shown in figure 4.2. T_g of samples 100/0, 80/20, 70/30, 60/40 and 50/50 are 130, 139, 144, 147 and 150 °C, respectively. The results showed that T_g of cured samples increased with increasing the content of Novolac epoxy in DGEBA because higher functionality of Novolac epoxy along with their chemical structure caused highly crosslinked network of epoxy [20]. Moreover, steric groups of Novolac epoxy such as the benzene ring are also contributed to restrain or control molecular motion of the cured thermoset.

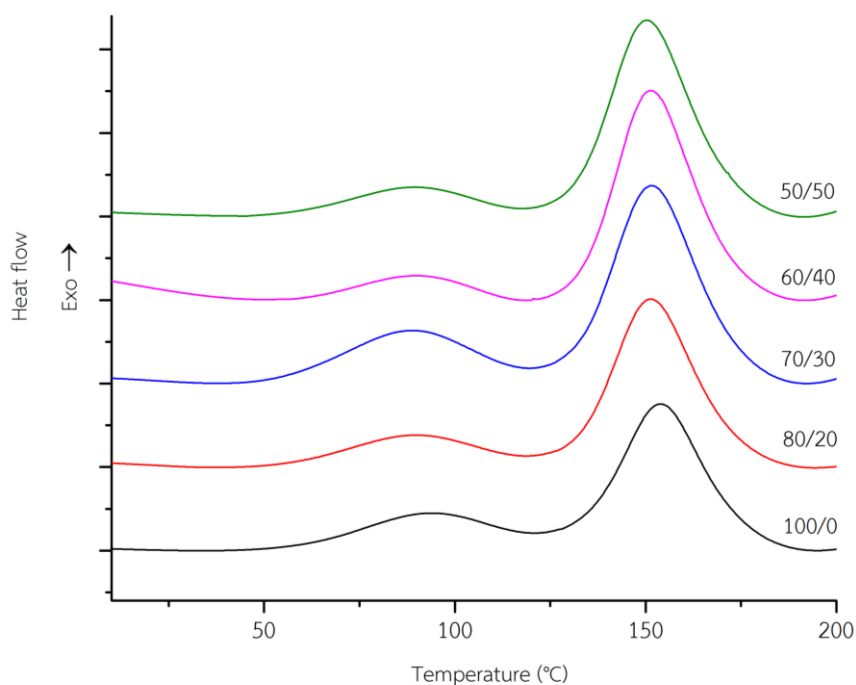


Figure 4.1 The first scanning DSC diagram of samples 100/0, 80/20, 70/30, 60/40 and 50/50 with sequential curing in presence of two amine curing agents and accelerator systems.

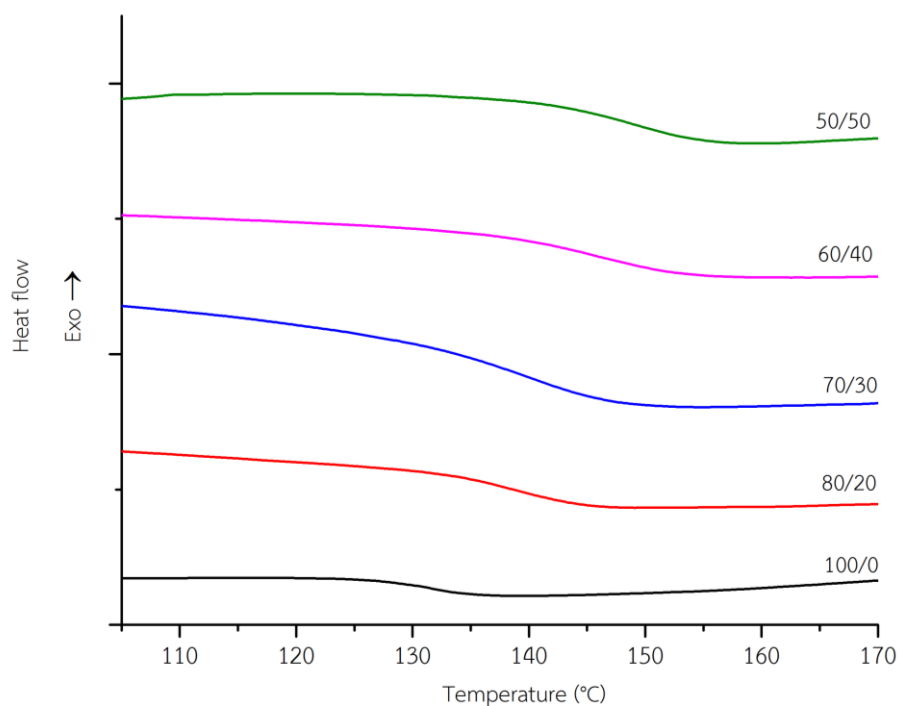


Figure 4.2 The second scanning DSC diagram of samples 100/0, 80/20, 70/30, 60/40 and 50/50 with sequential curing in presence of two amine curing agents and accelerator systems.

4.2 Thermal stability properties

Thermal stability of adhesives at different compositions was measured at C-stage of all sample. The degradation temperature is reported at 5% weight loss (T_{d5}) and residual weight (%) is reported at 600 °C. Both T_{d5} and residual weight were determined by thermogravimetric analysis under nitrogen atmosphere. Figure 4.3. shows TGA thermograms of sample 100/0, 80/20, 70/30, 60/40 and 50/50. The T_{d5} and residual weight (%) at 600 °C value of all sample are summarized in table 4.1. T_{d5} value of sample 100/0 is 350 °C and epoxy blended samples are in range of 355 – 357 °C. This can be concluded that when Novolac epoxy content was blended, the

T_{d5} value of formulation was increased when compared to neat DGEBA due to high structure of benzene ring of Novolac epoxy and higher crosslinked density when epoxy were cured. However, the incorporation of higher content of Novolac epoxy were not significantly affected thermal degradation temperature. Whereas the residual weight at 600 °C were trendy improved with increasing Novolac epoxy content in composition, which is 14 %, 17 %, 19 %, 21 % and 24 % of sample 100/0, 80/20, 70/30, 60/40 and 50/50, respectively. Therefore, enhanced crosslinked density or increment of benzene ring in the backbone chain of the cured thermoset could retard the degradation at high temperature.

Table 4.1 Degradation temperature at 5% weight loss (T_{d5}) and residual weight (%) at 600 °C of all sample.

Sample	Degradation temperature at 5% weight loss (T_{d5})	Residual weight (%) at 600 °C
100/0	350 °C	14 %
80/20	356 °C	17 %
70/30	355 °C	19 %
60/40	356 °C	21 %
50/50	357 °C	24 %

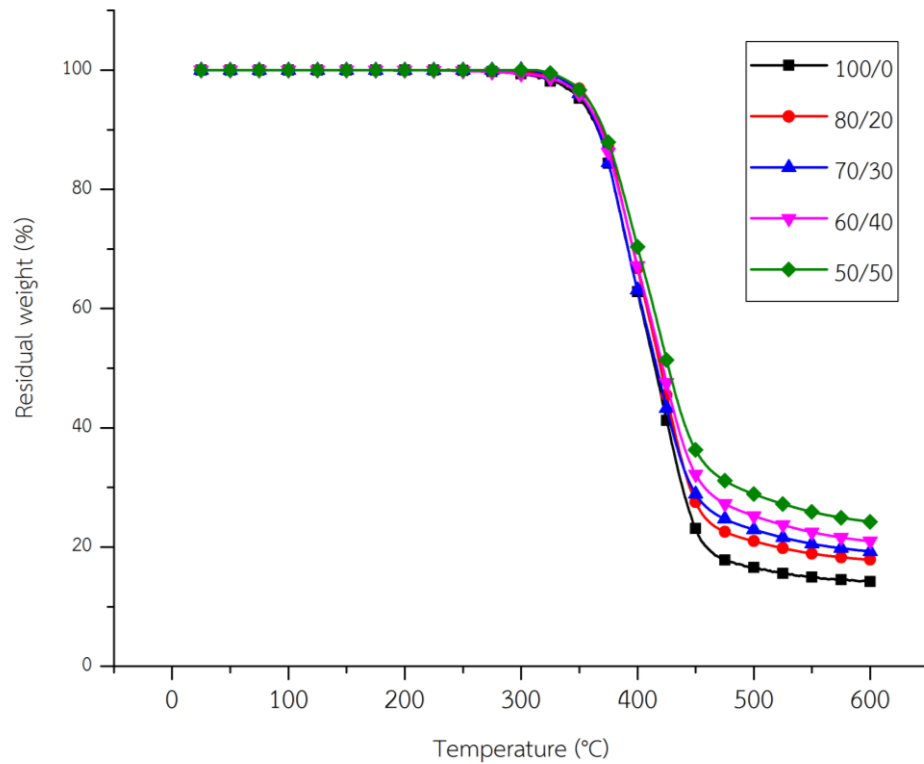


Figure 4.3 TGA Thermogram of samples 100/0, 80/20, 70/30, 60/40 and 50/50 with sequential curing technique at C-stage.

As a result of DSC and TGA test, the sample 70/30 was selected to further investigation, i.e., reaction mechanism, pot lifetime, curing behavior by isothermal scan, peel strength, and storage stability of B-staged epoxy adhesive due to acceptable glass transition temperature, thermal stability and processability viscosity for film casting process at room temperature.

4.3 FTIR characterization of each stage curing reaction

The reaction mechanism of sample 70/30 with sequential curing technique of three different stages including uncured (A-staged), partially cured (B-staged) and final cured (C-staged) were investigated by FTIR spectroscopy. According to figure 4.4., the peak at 915 cm^{-1} is attributed to epoxide ring ($-\text{CH}(\text{O})\text{CH}-$) in epoxy resin by moving from A-staged to B-staged one, the absorption band has decreased from 0.3934 to 0.2757. In the meantime, the sharp peak around 3378 cm^{-1} and 3421 cm^{-1} which correspond to primary amine ($-\text{NH}_2$) and secondary amine ($-\text{NH}$) in DETA and DICY were developed into broader peak around 3435 cm^{-1} attributed to hydroxyl group ($-\text{OH}$) which indicate the consumption of epoxide ring which was reacted by only DETA. The twin peak at around 2182 cm^{-1} and 2209 cm^{-1} correspond to nitrile ($-\text{C}\equiv\text{N}$) group of DICY molecules. These bonds are converted to a single absorption band at 2200 cm^{-1} during the subsequent curing process which occurs from changing in molecular structure around nitrile group [7]. Wu et al. [16] found that if there were both nitrile group and carbon–nitrogen double bond ($-\text{C}=\text{N}$) in the molecular structure, only when the $\text{C}=\text{N}$ bond directly connects with the primary amine, the nitrile group peak splits up into two peaks around 2200 cm^{-1} owing to the Fermi resonances. For this reason, it can be proved that DICY does not have any reaction with epoxide ring between this stage. In addition, the absence of any peak at 1745 cm^{-1} and 1650 cm^{-1} , corresponding to 2-oxazolidone and imino groups, respectively. It could be reflected that DIURON accelerate for only DICY and inactive in A-staged

and B-staged ones. In the chemical reaction at C-stage the twin peak at around 2182 cm^{-1} and 2209 cm^{-1} were converted to a single peak at 2162 cm^{-1} indicating the consumption of DICY. Also, the peak at 1742 cm^{-1} and 1646 cm^{-1} reflect to the formation of carbonyl group ($-\text{C}=\text{O}$) of 2-oxazolidone and imino groups ($-\text{C}=\text{N}$) which could be proved that the DIURON accelerator was activated only at C-stage. Moreover, the peak at around 3435 cm^{-1} of B-stage converted to broader peak at C-stage indicate that reaction between epoxide ring and primary amine and secondary amine in DICY have occurred and transform to $-\text{OH}$ groups at this stage.

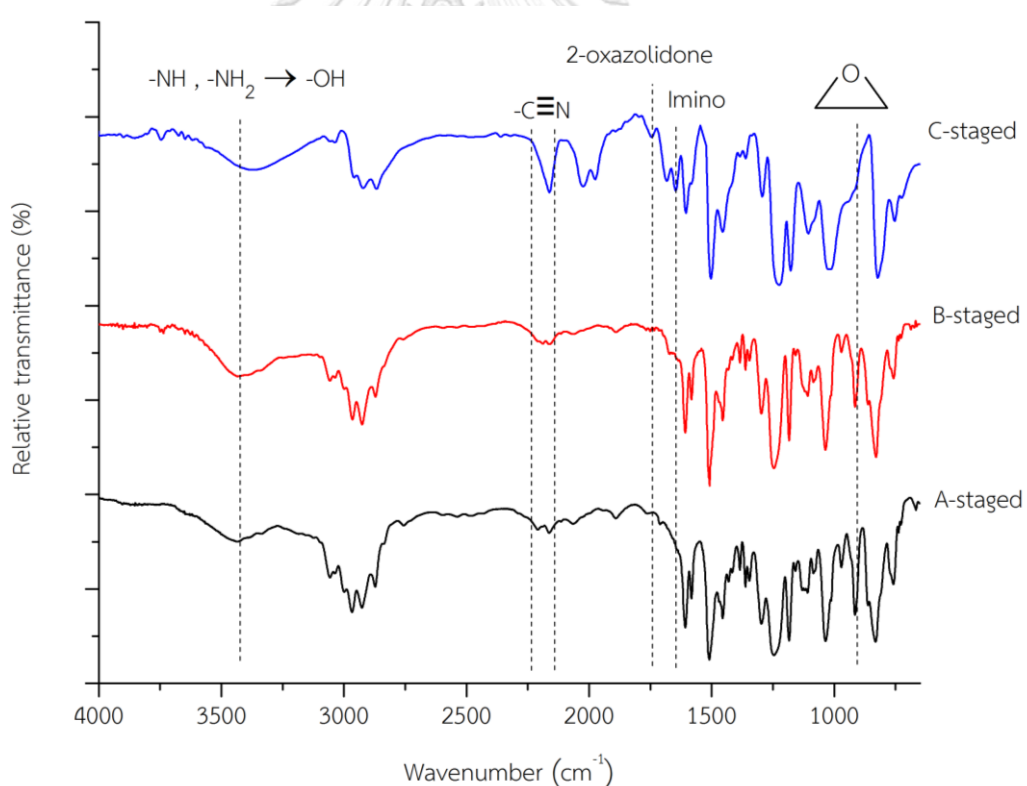


Figure 4.4 FTIR spectra of sample 70/30 with sequential curing technique at A-staged, B-staged, and C-staged

4.4 Pot-life time

Pot-life time is also known other names, including usable life, and working life. It is defined as the length of time in which the initial mixed viscosity of adhesives changed to double at processing temperature. Pot-life is very important parameter that must be known before starting the process which could prevent failure in manufacturing. According to figure 4.5, the sample 70/30 was measured in A-staged one. The initial viscosity at 25 °C under constant shear rate of 1.0 s^{-1} is 35770 cP, and then greatly increased to 72550 cP within 20 minutes. This is because DETA is a room-temperature curing agent, whose primary amine and secondary amine of its could rapidly react with epoxide ring without any heating [24]. Therefore, the 3D-crosslinked networks were generated resulting in viscosity build up. As a result, the amount of processing time at room temperature should be in range of 20 minutes, to avoid an adhesive stick with applicator.

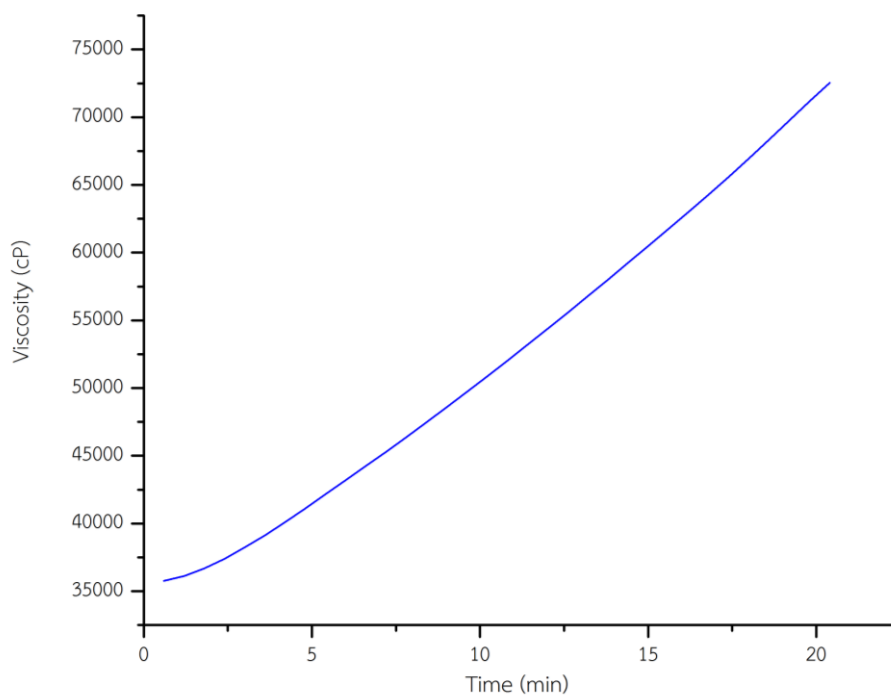


Figure 4.5 Viscosity profile of sample 70/30 in A-staged at 25 °C under constant shear rate of 1.0 s⁻¹

4.5 Curing behavior by DSC iso-thermal mode

The curing behavior were also carried out by DSC in iso-thermal mode with heating rate of 150 °C/min. At the first stage, a temperature was raised up to 80 °C, then cooled down to 25 °C and raised up again to 150 °C for the final stage of curing.

The degree of conversion was determined with the following equations.

$$x = \Delta H_{(t)} / \Delta H_{(0)} \quad (3.1)$$

where $\Delta H_{(t)}$ is the amount of heat released at time t, and $\Delta H_{(0)}$ is the total reaction heat in the system.

In this work, sample 70/30 was selected to study the degree of conversion and compare with sample 100/0 and 0/100. The first step of curing which is the

reaction between epoxide ring and primary amine and secondary amine of DETA performed at 80 °C and, also at 150 °C is the final step of curing between epoxide ring and primary amine and secondary amine of DICY which was accelerated by DIURON. Figure. 4.6 shows the degree of conversion as a function of time of sample 100/0, 70/30 and 0/100 at iso-thermal temperature 80 °C, and figure. 4.7 at 150 °C, respectively.

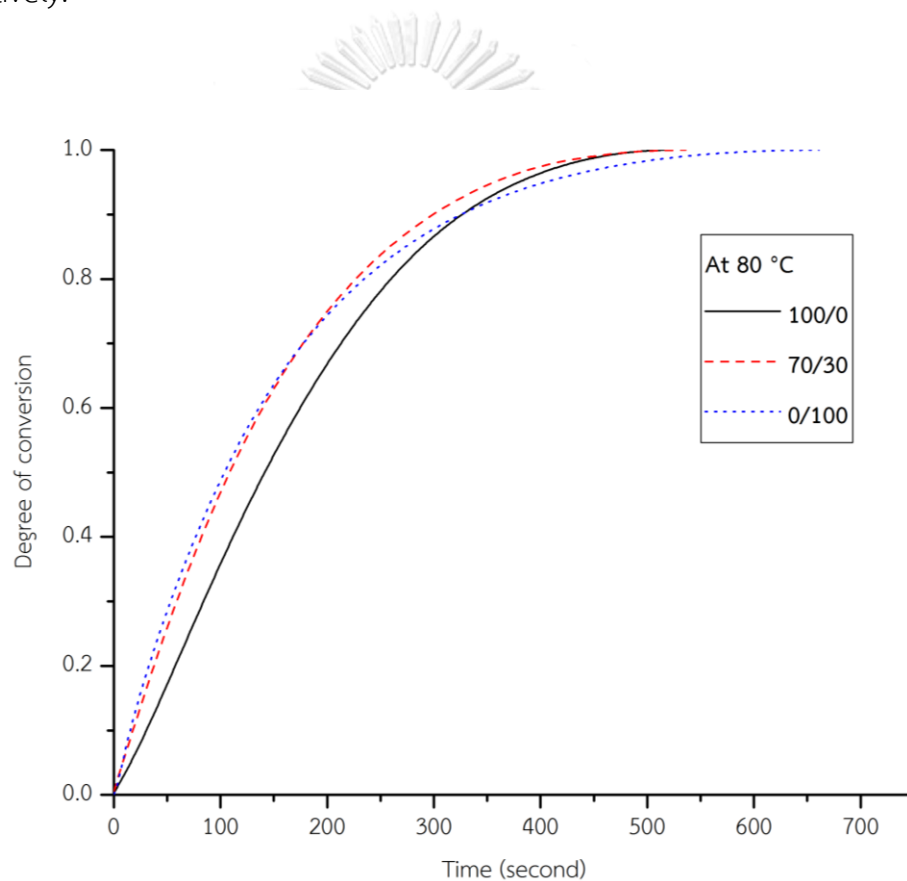


Figure. 4.6 Degree of conversion versus time of sample 100/0, 70/30 and 0/100 at iso-thermal temperature 80 °C

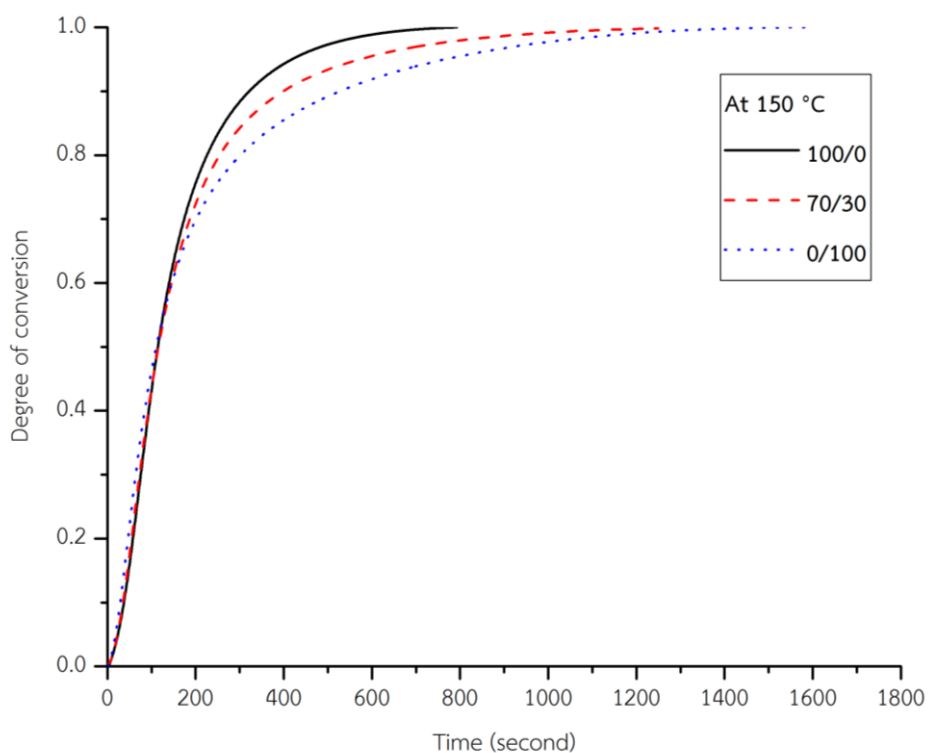


Figure. 4.7 Degree of conversion versus time of sample 100/0, 70/30 and 0/100 at isothermal temperature 150 °C

In this test, only DETA and epoxide ring reacted at 80 °C. However, when the heating proceeded longer than 3 hours, DICY with accelerator systems could initiate the reaction with epoxide ring [23]. As shown in figure 4.6 that the reaction rate of sample 70/30 is faster than that of 100/0. This may be attributed to multifunctional and higher reactivity of Novolac epoxy. But at degree of conversion close to 1, the time of ending reaction of both are not significantly different. Likewise, the reaction of sample 0/100 is faster than that of 70/30 and 100/0 for 197 and 310 second, respectively. After that time, the reaction rate change to slower and take a longer time to achieve the end of the reaction. Nevertheless, as shown in figure 4.7, at 150

°C, the initial curing rate of three samples are similar. However, when time passes 190 sec, the degree of conversion of 70/30 and 0/100 remarkably slow down and spend more time to reach the end of reaction. As reaction begins the rate of systems is controlled by chemical reaction. Afterwards, the molecular mobility is rapidly reduced due to crosslinked network were generated. The time that DICY molecules meet epoxide ring molecules and reacted will take longer, leading to slowly cure and chemical reaction becomes diffusion controlled [16]. As mentioned above, Novolac epoxy greatly generate higher crosslinked density than DGEBA during curing and after curing. Hence, the formulation that containing Novolac epoxy and crosslink density at partial curing stage might be affected on the rate of reaction of the final curing stage and make it slowly for this reason.

4.6 Storage stability จุฬาลงกรณ์มหาวิทยาลัย

4.6.1 Curing of final staged epoxy by DSC

The storage stability of sample 70/30 after B-staged cure for 0, 7, 14, 21 and 28 days were performed by non-isothermal DSC and measured in the heat of curing reaction (ΔH) of second stage curing. In this work, the samples were kept in the two different conditions, which are stored at room temperature ($25 \pm 2^\circ\text{C}$ with humidity $30 \pm 5\%$) and at freezer (-18°C) to investigate the proper temperature that change % conversion from day 0 to day 28 steadily or slightly. The DSC diagram of sample

stored at room temperature and freezer were shown in figure 4.8 and 4.9, respectively. The summarized data of heat of curing reaction of all sample were shown in table 4.2.

Table 4.2 Heat of curing reaction of sample 70/30 after B-staged cured for 0, 7, 14, 21 and 28 days stored at room temperature and freezer.

Day after B-staged	Heat of curing reaction for sample kept at R.T. (J/g)	% Change from day 0	Heat of curing reaction for sample kept at freezer (J/g)	% Change from day 0
0	276.0808	-	276.0808	-
7	208.8959	24.33 %	276.0509	0.01 %
14	156.6939	43.24 %	273.3941	0.93 %
21	72.8921	73.59 %	264.5122	4.19 %
28	69.7958	74.71 %	251.9943	8.72 %

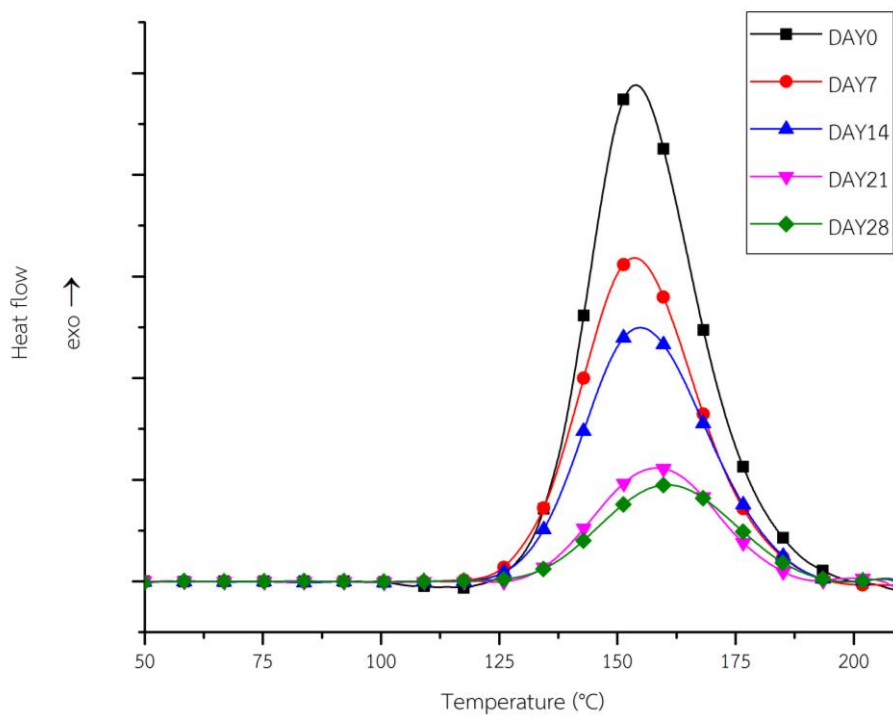


Figure 4.8 The DSC diagram of sample 70/30 after B-staged cured for 0, 7, 14, 21 and 28 days stored at room temperature

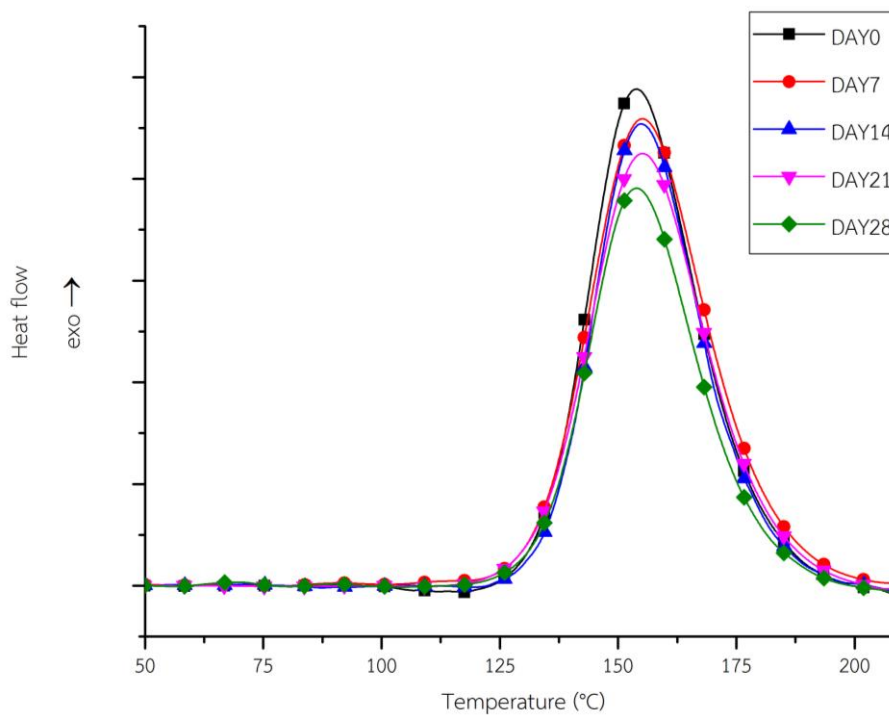


Figure 4.9 The DSC diagram of sample 70/30 after B-staged cured for 0, 7, 14, 21 and 28 days stored at freezer

According to both DSC diagram in figure 4.8 and figure 4.9, the first exothermic peak at around 90 °C disappeared, indicate that the adhesives completely turn into B-staged one. The DSC profile of samples that were stored at room temperature show dramatically decrease in area under peak every seven days. But between 21 and 28 day the DSC profile shows hardly change in value which is changed in range of 73 - 74 % from day 0, since the diffusion rate has controlled the overall reaction. However, the heat of curing reaction of sample stored at freezer was slightly reduced in % changed from day 0 and acceptable values in every seven days of testing. At this temperature, the reaction of final staged of curing was retarded which is epoxide ring and DICY with DIURON accelerator. When compared to those non-accelerator system, shelf life of accelerator system was shorter. However, the curing temperature and curing time that chemical reaction occurred between epoxide ring and DICY was reduced than that of non-accelerator system, which is useful in term of energy and time saving. However, shelf life of samples could be longer by stored them below -18 °C, to stop the reaction between epoxide ring and DICY with DIURON accelerator system.

4.6.2 Tackiness after B-staged cure by peel strength test

The peel strength was performed to evaluate the possibility of tackiness between polyimide film and aluminum substrate of adhesives after B-staged cure for 7, 14, 21 and 28 days at room temperature ($25\pm 2^{\circ}\text{C}$ with humidity $30\pm 5\%$) and at

freezer (-18 °C). The adhesives were cast on aluminum backup board and kept in super lock boxes before storage, then polyimide film was attached on the testing date. Figures 4.10 and 4.11 show the average peel strength of adhesives after B-staged cure at room temperature and at freezer, respectively.

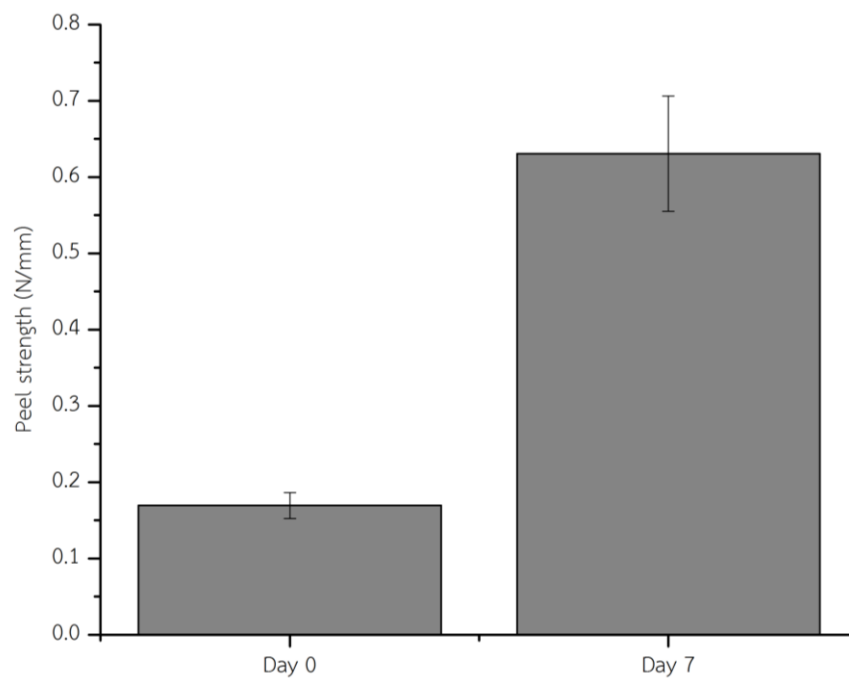


Figure 4.10 Average peel strength of adhesives after B-staged cure and stored at room temperature

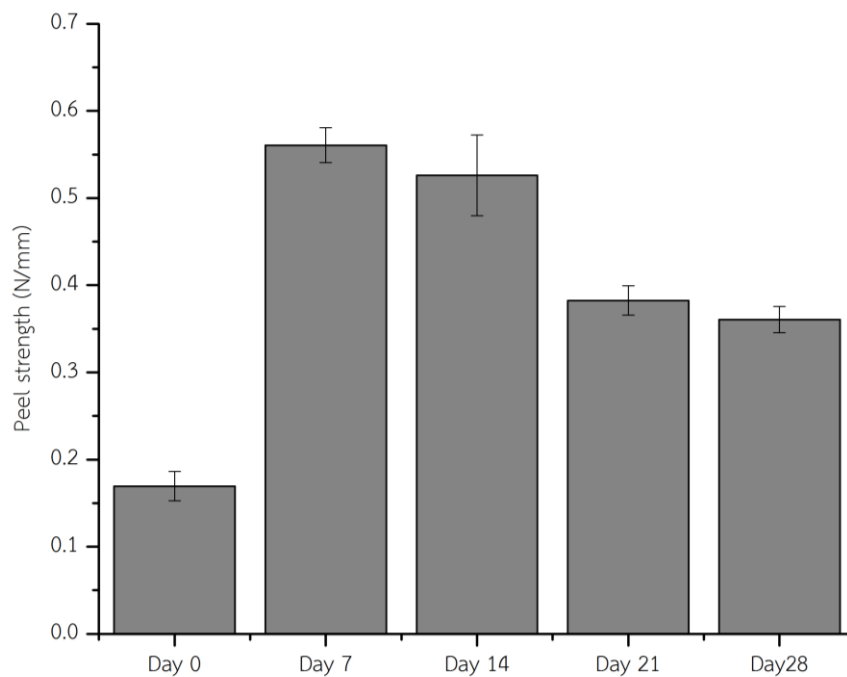


Figure 4.11 Average peel strength of adhesives after B-staged cure and stored at freezer

According to figure 4.10, the peel strength of samples stored at room temperature could be measured only in day 7 whose value was 0.6307 N/mm. This is due to the solidification of the surface which could not be tacked with polyimide film in day 14 after storage. Because the reaction between epoxide ring and DICY with DIURON accelerator still carry-on, the degree of pre-cure increase as obviously be seen in table 4.2. The more increasing in the degree of cure, the higher in the glass transition temperature of adhesive. Therefore, the glass transition temperature of samples in day 14 and after that day were higher than that of testing temperature (25 ± 2 °C) resulting in change from semi-solid to fully solid and cannot be attached

by polyimide film. The lowest value in day 0 which is 0.1695 N/mm might be too soon for testing while the molecular mobility still occur. It causes those part of the chains that are not cross-linked to move and could reduce the tackiness of sample in day 0 [7]. As shown in figure 4.11, the peel strength of adhesive that was stored at freezer for 7 days shows the highest value of 0.5606 N/mm because the viscosity of sample was increased to a semi-solid state which increased bond strength and tackiness. However, after day 7 the peel strength of adhesive slightly decreased in peel strength. As mentioned above, the reaction at final staged cure still carry-on. The glass transition temperature of samples might increase to higher than the testing temperature but not solidify to the surface of the adhesive to fully solid, resulted in decreased of peel strength in day 14, 21 and 28.

4.7 Peel strength at C-staged cure

The peel strength of adhesives at C-staged cure was unable to measure. Due to cohesive failure of polyimide film which adhere with adhesive was torn during peel testing as shown in figure 4.12. The adhesive-polyimide film bonding is remarkably strong which might be affected by the bonding of epoxy-DICY molecules, so that the failure occurs in one of the adherend away from the bond. This failure can be called a cohesive failure in the adherend [34]. However, the bond strength of adhesive-polyimide film could measure indirectly by tensile strength at break of polyimide film which is defined as the maximum stress that required to break a

specimen. According to table 4.3, the mechanical properties of polyimide film were measured at the same condition of peel strength testing. The tensile strength at break of polyimide film is about 97.23 MPa. Therefore, it can be extrapolated that the force required to separate adhesive-polyimide film bonded should be equal to or greater than 97.23 MPa

Table 4.3 Mechanical properties of polyimide film

Tensile strength at break (MPa)	97.23 ± 1.65
Elongation at break (%)	50.31 ± 12.67
Maximum load (N/mm)	3.05 ± 0.21

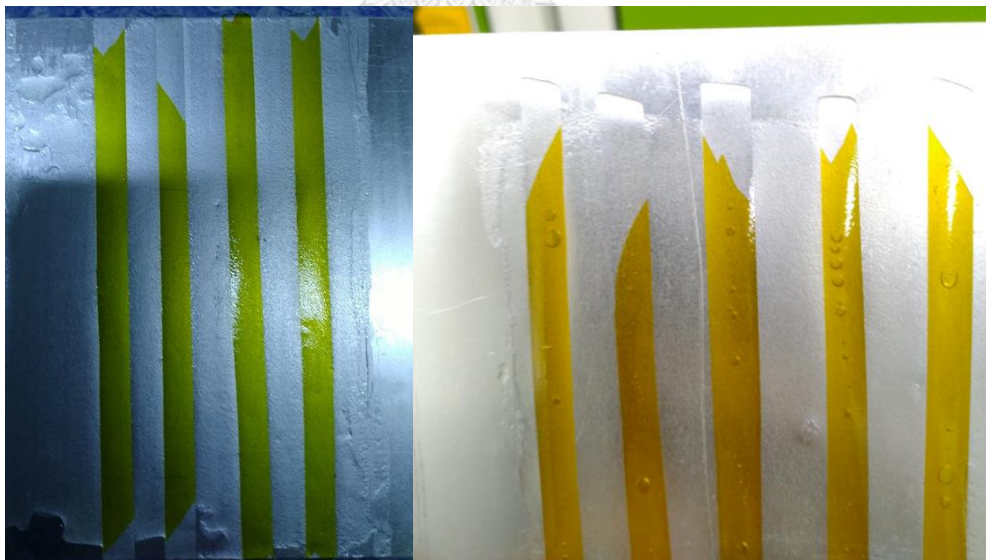


Figure 4.12 The cohesive failure of polyimide film during peel strength test

4.8 The glass transition temperature with various DICY content

The glass transition temperature (T_g) of sample 70/30 with different content of DICY; i.e., 4, 6, 8 phr was measured at the mid-point of slope. Second scanning DSC diagram of various DICY in figure 4.13 show that the T_g of adhesive formulation with DICY 4, 6 and 8 phr were 142, 144 and 144 °C, respectively. It can be concluded that increasing in DICY content from 4 to 6 phr the T_g is slightly increased. However, increasing in DICY content from 6 to 8 phr were not affect T_g of the sample. It might be said that with 6 phr of DICY, it gives the optimal formulation and the cross-linked density in molecules reach to the maximum which could not further increased with increasing in DICY content of formulation.

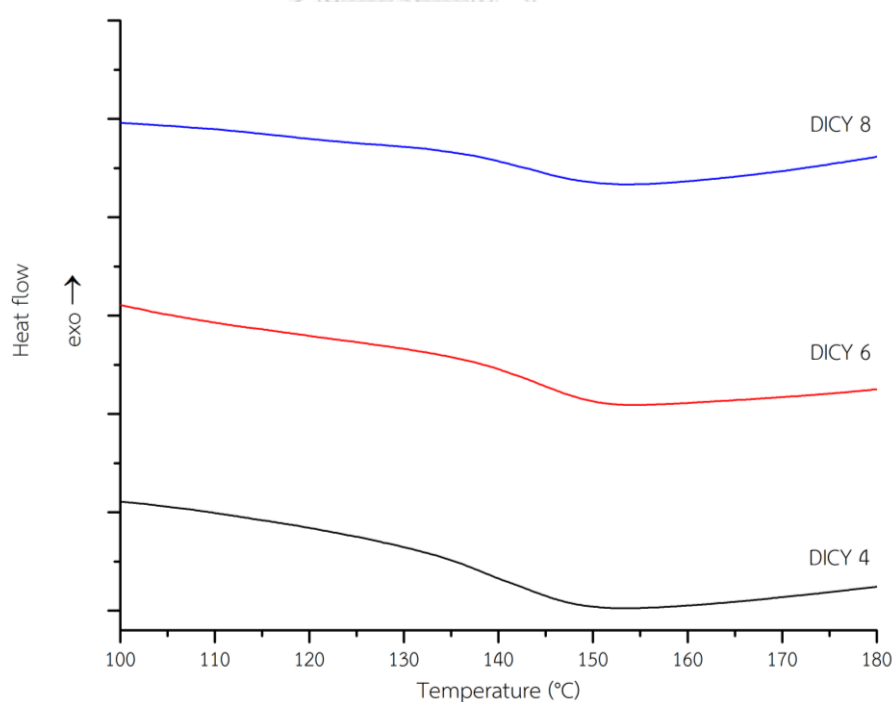


Figure 4.13 The second scanning DSC diagram of sample 70/30 with various DICY content.

CHAPTER V

CONCLUSION

In this work, the sequential curing with off stoichiometric amine technique was used to create B-staged epoxy adhesive and Novolac epoxy was blended in DGEBA to improve thermal properties of B-staged epoxy adhesive. The result shown that, the increasement of Novolac epoxy content tend to decrease the second to lower temperature. Moreover, the glass transition temperature and residual weight (%) at 600 °C were trendy increased with increasing in Novolac epoxy content. But higher content of Novolac epoxy were not significantly affect degradation temperature at 5% weight loss which is in range of 355 - 357 °C. However, blending more than 30 phr of Novolac epoxy was difficult to perform film casting process at room temperature. Therefore, the sample 70/30 was selected to further study due to acceptable of glass transition temperature, degradation temperature at 5% weight loss and viscosity to processability for film casting process at room temperature.

Isothermal DSC profile showing data reaction rate of sample 70/30 is faster than that of neat DGEBA (100/0) but slower than neat Novolac epoxy (0/100) at partial curing staged due to multifunctional and higher reactivity of Novolac epoxy. However, at final curing stage, the reaction rate of sample containing Novolac epoxy

becomes slowly cure due to diffusion rate controlled mechanism. The storage stability of sample was only 8.72% changed in heat of curing reaction for 28 days after B-staged cure stored at freezer (-18 °C) and be still acceptable of tackiness which was able to adhere with substates, as proved by the peel strength test. However, the peel strength of sample after B-staged cure and stored for 28 days was 74.71% changed. The adhesive which was stored at room temperature (25±2 °C) for 7 days still can adhere to the substrate. However, these sample that has been stored for longer than 7 days cannot adhere to another surface due to solidify of the adhesive surface. The peel strength of adhesive at C-staged cure shows very strong bonding between adhesives and polyimide film. The peel strength test cannot be completed due to the cohesive failure in the adherend. Although the peel strength could not be measured in numerical values, but indirectly way it could be extrapolated that to separate bonding of adhesive-polyimide film the required force should be equal to or greater than 97.23 MPa. Eventually, the sequential curing technique with DGEBA/Novolac blended system can be used to enhance B-staged epoxy adhesives and making them useful material at elevated temperature.

Recommendations

1. Dicyandiamide (DICY) curing agent should be kept in humidity-controlled room and remove some moisture by hot air oven at 50 - 60 °C before mixing with epoxy resin.

2. The method to extend the pot lifetime should be studied by varying types of the first curing agent.
3. Encapsulation system of accelerator is interesting to study, that it would be possible to extend the shelf lifetime at room temperature.



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Appendix

Calculation of epoxy equivalent weight (EEW) for epoxy blended

Epoxy equivalent weight (EEW) is the amount of resin (grams) that contains one molecule of an epoxy group as calculated by following equation.

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

For epoxy mixtures,

$$EEW \text{ of epoxy mixtures} = \frac{\text{Total weight of epoxy mixture}}{\frac{\text{Epoxy weight 1}}{EEW \text{ of epoxy 1}} + \frac{\text{Epoxy weight 2}}{EEW \text{ of epoxy 2}}}$$

For example: formulation 70/30 on basis 10 grams mass of epoxy mixture

$$\begin{aligned} EEW \text{ of epoxy mixtures} &= \frac{10}{\frac{7.0 \text{ g of DGEBA}}{189.5} + \frac{3.0 \text{ of Novolac epoxy}}{178.5}} \\ &= 186.11 \end{aligned}$$

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