การสังเคราะห์และวิเคราะห์คุณลักษณะของกาวอิพอกซีเอไมด์อิไมด์ที่มีความแข็งแรงสูง

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SYNTHESIS AND CHARACTERIZATION OF HIGH STRENGTH AMIDE-IMIDE-EPOXY ADHESIVE

Mr. Vayo Malithong

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
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Thesis Title	SYNTHESIS AND CHARACTERIZATION OF HIGH STRENGTH AMIDE-IMIDE-EPOXY ADHESIVE
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Field of study	Chemical Engineering
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วาโย มะลิทอง: การสังเคราะห์และวิเคราะห์คุณลักษณะของกาวอิพอกซีเอไมด์อิไมด์ที่มีความแข็งแรงสูง. (SYNTHESIS AND CHARACTERIZATION OF HIGH STRENGTH AMIDE-IMIDE-EPOXY ADHESIVE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. มล. ศุภกนก ทองใหญ่, 86 หน้า.

โอลิโกเมอร์เอไมด์อิไมด์สามารถสังเคราะห์ได้จากไตรเมลลิติกแอนไฮไดรด์หรือจากกรดเทอรีพทาลิก อุณหภูมิการเสื่อมสลายของกาวอิพอกซีเอไมด์อิไมด์ลดลง เมื่อลดปริมาณของโอลิโกเมอร์เอไมด์อิไมด์ลง อุณหภูมิการเสื่อมสลายของกาวอิพอกซีเอไมด์อิไมด์ที่มีการใส่ยางไนไตรล์บิวตะไดอีนสูงกว่าของกาวอิพอกซีเอไมด์อิไมด์ที่ไม่มีการใส่ยางไนไตรล์บิวตะไดอีน อุณหภูมิการเสื่อมสลายของกาวอิพอกซีเอไมด์อิไมด์ที่สังเคราะห์จากกรดเทอรีพทาลิกกับ 4,4’ ไดฟีนิลมีเทนไดไอโซไซยาเนต(ทีดีไอ) สูงกว่าที่สังเคราะห์จากกรดเทอรีพทาลิกกับโทลีลีน 2,4 ไดไอโซไซยาเนต (เอ็มดีไอ) คุณสมบัติเชิงกล(ค่าอิลองเกชัน, ค่าต้านทานแรงดึงและค่าความเหนียว)ของกาวอิพอกซีเอไมด์อิไมด์ ที่มีการใส่ยางไนไตรล์บิวตะไดอีนสูงกว่ากาวอิพอกซีเอไมด์อิไมด์ที่ไม่มีการใส่ยางไนไตรล์บิวตะไดอีนลงไป คุณสมบัติเชิงกล(ค่าอิลอกเกชัน, ค่าต้านทานแรงดึงและค่าความเหนียว) ของกาวอิพอกซีเอไมด์อิไมด์ ที่สังเคราะห์จากกรดเทอรีพทาลิกกับ 4,4’ ไดฟีนิลมีเทนไดไอโซไซยาเนต(ทีดีไอ) สูงกว่าที่สังเคราะห์จากกรดเทอรีพทาลิกกับโทลีลีน 2,4 ไดไอโซไซยาเนต(เอ็มดีไอ) คุณสมบัติเชิงกล(ค่าอิลองเกชัน, ค่าต้านทานแรงดึงและค่าความเหนียว)ของกาวอิพอกซีเอไมด์อิไมด์ ที่สังเคราะห์จากกรดเทอรีพทาลิกสูงกว่ากาวอิพอกซีเอไมด์อิไมด์ที่สังเคราะห์จากไตรเมลลิติกแอนไฮไดรด์

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต
สาขาวิชา วิศวกรรมเคมี ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์หลัก
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VAYO MALITHONG: SYNTHESIS AND CHARACTERIZATION OF HIGH STRENGTH OF AMIDE-IMIDE-EPOXY ADHESIVE. ADVISOR: ASSOC. PROF. ML. SUPAKANOK THONGYAI, Ph.D., 86 pp.

An oligomer amideimide was synthesized from trimellitic anhydride (TMA) / terphthalic acid (TPA). The degradation temperature of the amide-imide-epoxy adhesives decreased when the OPAI content decreased. The amide-imide-epoxy adhesives with NBR rubber are degraded at higher temperature than amide-imide-epoxy adhesives without NBR rubber. The amide-imide-epoxy adhesives from terphthalic acid with MDI are degraded at higher temperature than from terphthalic acid with TDI. The mechanical properties (elongation, tensile strength and toughness) of amide-imide-epoxy adhesives with NBR rubber are higher than amide-imide-epoxy adhesives without NBR rubber. The mechanical properties (elongation, tensile strength and toughness) amide-imide-epoxy adhesives from terphthalic acid with TDI are higher than amide-imide-epoxy adhesives with MDI. The mechanical properties (elongation, tensile strength and toughness) of amide-imide-epoxy adhesives from terphthalic acid are higher than from trimellitic anhydride.

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Finally, I would like to dedicate this thesis to my parents and my families, who generous supported and encouraged me through the year spent on this study.

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CHAPTER I

INTRODUCTION

Polyamideimide is one of the thermoplastic amorphous polymers that have exceptional mechanical, thermal and chemical resistant properties. It holds, as the name suggested, a positive synergy of properties from both polyamides and polyimides, such as high strength, good melt processabilty, exceptional high heat capability, and broad chemical resistance. Polyamideimide polymers can be processed into a wide variety of forms, from injection or compression molded parts and ingots to coatings, films, fibers and adhesives. Generally these articles reach their maximum properties with a subsequent thermal cure process. Polyamideimide resins have excellent electrical and mechanical properties and high heat resistance and therefore are widely used as adhesives for printed circuit boards. Polyamideimide have the N-H bonds that can be further react with epoxy to generate the cross-linked between molecules. Recently, the *US patent application 200602/0241239 A1: Polyoxyalkylene amine – modified polyamideimide resin and composition thereof* issued oligomer amideimide with epoxy as one component of the hardener strictly with the cooperation of the tri-carboxylic acid component.

Epoxy systems containing functional additives have been studied extensively in recent year to overcome and improve the inherent brittleness and low thermal degradation of the epoxy matrix. Functional additives can be organic (polyimide, small molecule amine, small molecule anhydride), inorganic (Phosphorous, Silica, Alumina) or hybrid material (POSS). Organic–inorganic hybrid materials have been recognized as a new class of advanced materials because they can exhibit superior properties over the parent organic or inorganic materials.

In this research, the synthesis and characterization of the adhesive from the oligomer of polyamideimide produced from di-carboxylic acid were examined. The amide-imide-epoxy adhesive will be developed in order to have a stronger adhesive strength for printed circuit boards. And then improve epoxy by oligomer amideimide to enhance thermal, mechanical properties.

1.1 The Objectives of This Thesis

1.1.1 To synthesize oligomer amideimide.

1.1.2 To synthesize amide-imide-epoxy adhesive to improve thermal and mechanical properties.

1.2 The Scope of This Thesis

1.2.1 Synthesize oligomer amideimide from trimellitic anhydride (tri-carboxylic acid) or terephthalic acid (di-carboxylic acid).

1.2.2 Synthesize amide-imide-epoxy adhesive.

1.2.3 Characterize of amide-imide-epoxy adhesive by fourier transform infrared spectroscopy (FT-IR), thermal gravimetric analysis (TGA), Differential Scanning Calorimetry (DSC) and adhesion peel test properties.

This thesis is divided into six chapters as follows:

Chapter I provide an overview of the polyamideimide and objective and scope of this thesis.

Chapter II explains the basic theory about this work such as polyamideimide definition, type of polyamideimide polymerization and epoxy

Chapter III presents literature reviews of the previous works related to this research.

Chapter IV shows the experimental equipments and experimental procedures to synthesis oligomer amideimide and preparation of amide-imide-epoxy adhesive. Including, instruments and techniques used for characterizing the resulting polymers.

Chapter V exhibits the experimental results of oligomer amideimide from trimellitic anhydride (tri-carboxylic acid) or terephthalic acid (di-carboxylic acid), and effects of various ratio of acid on the properties of the synthesized amide-imide-epoxy adhesive.

Chapter VI, the last chapter, shows overall conclusions of this research and recommendations for future research.

CHAPTER II

THEORIES

2.1 Polyamideimides

Polyamideimides contained both amide and heterocyclic imide structures along the main chain of the polymer backbone, shown in Figure 2.1, and hence constitute a polymer class with average properties between aromatic polyamides and polyimides.

The best know polyamideimides are polytrimellitamideimides, shown in Figure 2.2, derived from trimellitic acid or its derivatives, and are of major commercial and industrial importance due to their outstanding mechanical properties and excellent thermal and oxidative stability [1-3].

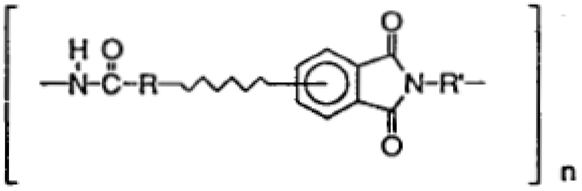

Figure 2.1 Polyamideimide

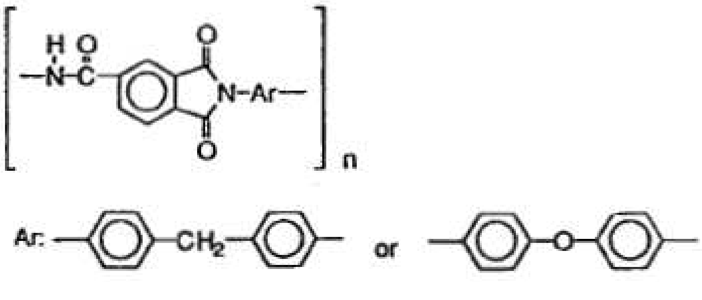

Figure 2.2 Polytrimellitamideimides

The knowledge and experience accumulated over many years in the synthesis of aromatic polyamides [4-6] and polyimides [7-9]. Thus they have greatly helped in developing synthetic routes for polyamideimides. A number of polyamideimides have been synthesized through two main routes; via amide-imide-forming reaction from aromatic tricarboxylic acids, and through amide-forming reaction from imide-containing monomers such as dicarboxylic acids and diamines. Little is known about the approach through imide-forming reaction from amide-containing diamines. Thus, polyamide-imides can be synthesized readily by general synthetic methods similar to those for both aromatic polyamides and polyimides.

2.2 Typical property of polyamideimide

Table 2.1 Typical property of polyamideimide

Property	Value
Density (g/cm^3)	1.40
Surface Hardness	RM109
Tensile Strength (MPa)	185
Flexural Modulus (GPa)	4.58
Notched Izod (kJ/m)	0.13
Linear Expansion (/°C x 10^{-5})	3.6
Elongation at Break (%)	12
Strain at Yield (%)	8
Max. Operating Temp. (°C)	210
Water Absorption (%)	0.28
Oxygen Index (%)	43
Flammability UL94	V0
Volume Resistivity (log ohm.cm)	17
Dielectric Strength (MV/m)	23
Dissipation Factor 1kHz	0.001
Dielectric Constant 1kHz	3.5
HDT @ 0.45 MPa (°C)	260+
HDT @ 1.80 MPa (°C)	274
Material. Drying hrs @ (°C)	16@150
Melting Temp. Range (°C)	315 – 360
Mould Shrinkage (%)	0.7
Mould Temp. Range (°C)	180 – 260

2.3 Synthesis of polyamideimide

2.3.1 Fundamentals of polyamideimide synthesis from trimellitic acid and its derivatives

The polycondensation of trimellitic acid with aromatic diamines at a temperature below 200^{o}C generally gives polyamideimides with low molecular weights due to low reactivity of both monomers. Therefore, the activation of either of the monomers, trimellitic acid or aromatic diamines, is needed to produce higher-molecular-weight polyamideimides. Two major methods were developed in the 1960s for the synthesis of polyamideimides. One is the diamine route using trimellitic anhydride chloride (4-chloroformylphthalic anhydride) and aromatic diamines [10,11]. The other is the diisocyanate route using trimellitic anhydride and aromatic diisocyanates derived from aromatic diamines [12-14]. These methods are very useful for laboratory preparations as well as the commercial production of polyamideimides (Figure 2.2). The method of direct polycondensation between trimellitic anhydride and aromatic diamines giving polyamideimides was later developed [15].

A. Diamine Route

One of the simplest methods for the synthesis of polyamideimides is the polycondensation of trimellitic anhydride chloride with appropriate diamines (Figure 2.3), because both acid chloride and anhydride are the most reactive class of functional groups among carboxylic acid derivatives.

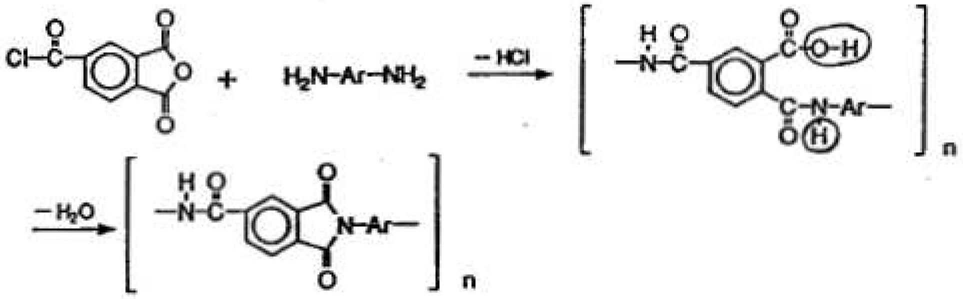

Figure 2.3 Polycondensation of trimellitic anhydride chloride with appropriate diamines

In the first step of this reaction, poly(amide amic acid)s are produced via two simultaneous reactions: the condensation of an amino group with the acid chloride and the ring-opening addition of an amino group to acid anhydride. In second step, this polymers is subsequently converted into polyamideimide by thermally (heating above 200^{o}C) or by chemical means. For the synthesis of poly(amide amic acid)s, the low-temperature solution method is usually used; however, the interfacial method is also applicable.

i) Low-Temperature Solution Method

The solution polymerization of trimellitic anhydride chloride with aromatic diamines (Figure 2.3) is effectively achieved in highly polar aprotic solvents [16-18]. Amide-type solvents such as N, N-dimethyl acetamide (DMAc) and N-methyl-2-pyrrolidone (NMP) are the most commonly used reaction media, which acts as solvents for both the monomers and the resulting poly(amide amic acid)s and as hydrogen chloride acceptor as well. The polymerization is generally carried out by the addition of solid trimellitic anhydride chloride to a stirred solution of an aromatic diamine in such solvents at room temperature or below, and it proceeds in a homogeneous solution leading to the formation of poly(amide amic acid) with high molecular weight.

The polymer structure is usually described as having head-to-tail amide-imide (A-I) structure (Figure 2.4), but in the strict sense the polymer also contain head-to-head and tail-to-tail structures, that is, amide-amide (A-A) and imide-imide (I-I) structures as shown in Figure 2.4. The microstructure of the polyamideimides from bis(4-aminophenyl)methane formed by the above method (structure given in Figure 2.4, where Ar is 4,4'-methylenediphenylene) was determined by ^{1}H nuclear magnetic resonance (NMR), and the polymer was found to have 40/30/30% of A-I/A-A/I-I units in the main chain [18].

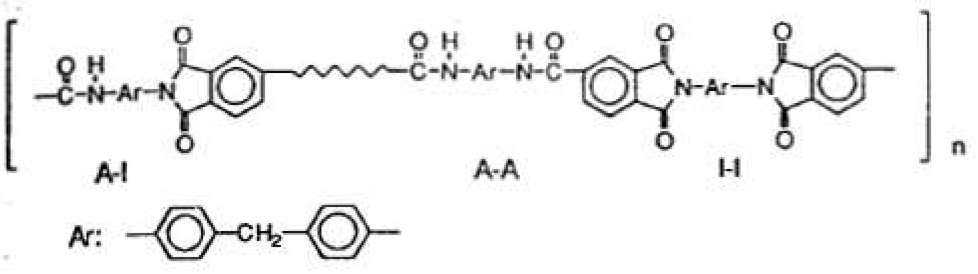

Figure 2.4 The polyamideimide structure

ii) Interfacial Method

In the case of the polymerization in polar aprotic amide-type solvents such as DMAc mentioned above, rigorous exclusion of water is essential for the synthesis of poly(amide amic acid)s with high molecular weights. The polymerization of trimellitic anhydride chloride with bis(4-amiophenyl)methane in DMAc containing a small amount of water indeed drastically reduced inherent viscosity of the resulting polymer.

A solution of trimellitic anhydride chloride in a certain solvent was added to a rapidly stirred solution of an aromatic diamine and triethylamine (acid acceptor) in a mixture of the solvent and water all at once at room temperature. The poly(amide amic acid) formed immediately and precipitated out of the reaction mixture. Vigorous stirring was continued for 20 min, and the precipitated polymer was collected by filtration.

B. Diisocyanate Route

The second useful method for the synthesis of polyamideimides is the polycondensation of trimellitic anhydride with aromatic diisocyanates (Figure 2.5). The polymers are obtained in a once-step process with fully imidized form [17,19,20].

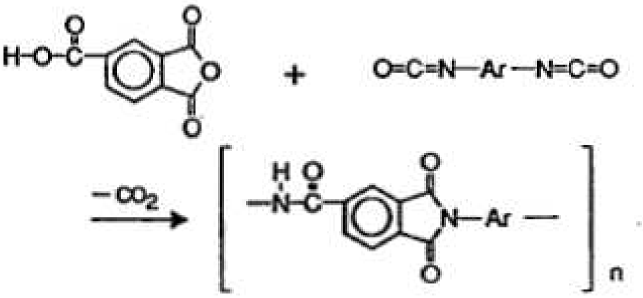

Figure 2.5 Polycondensation of trimellitic anhydride with aromatic diisocyanates

Since the isocyanate group reacts with both carboxylic acid and anhydride functionalities with subsequent loss of carbon dioxide to give amide and imide functions, respectively, aromatic diisocyanates were used for the preparation aromatic polyamides [21,22] and polyimides [23-26] by the polymerization with aromatic dicarboxylic acids and tetracarboxylic dianhydrides, respectively, in addition to the synthesis of polyamideimides from trimellitic anhydride.

These polyamideimides are usually synthesized by solution polymerization at relatively low temperatures, around 150°C in highly polar amide-type solvents such as DMAc or NMP [17,19]. The polymers remain in solution at the end of the polymerization. A proper choice of reaction temperature is essential for the preparation of polyamideimides with moderate inherent viscosity of 0.4 dl/g [17], because these amide-type solvents are known to react with isocyanate functionality at 230°C [19].

C. Direct Polycondensation Method

The direct synthesis of polyamideimides starting from trimellitic anhydride and aromatic dimines is the simplest and most desirable method (Figure 2.6).

However, the preparation of high-molecular-weight polyamideimides is rather difficult compared with both diamine and diisocyanate methods described above.

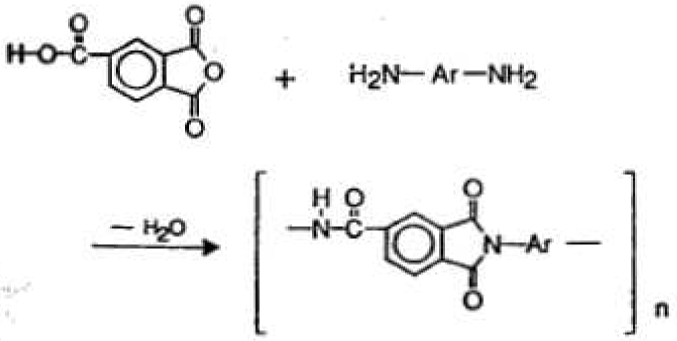

Figure 2.6 The direct synthesis

This is because aromatic amine function is normally too weak to react with carboxylic acid to give amide linkage even at high temperatures. Therefore, it is essential to select a suitable dehydrating catalyst and reaction conditions to promote direct polyamide formation. Thus the synthesis of polyamideimides was achieved by the solution polycondensation of trimellitic acid with bis(4-aminophenyl)methane in NMP in the presence of boric acid as a catalyst at 200^oC [15].

D. Miscellaneous Method

The following two routes, the N-silylated diamine route where N,N'-bis(trimethylsilyl)-sub-stituted aromatic diamines are used in place of the parent diamines [27], and the thioanhydride route in which aromatic tricarboxylic acid thioanhydride derivatives are employed in place of the parent tricarboxylic anhydride [28], are not very common methods, but have been developed for the preparation of polyamideimides.

i) N-Silylated Diamine Route

Recently a novel N-Silylated diamine route has been developed for the synthesis of high-molecular-weight aromatic polyamides [29-31] and polyimides [32,33] starting from N,N'-bis(trimethylsilyl)-substituted aromatic diamines. This method was extended to the preparation of polyamideimides by the polymerization of N-silylated aromatic diamines with trimellitic anhydride chloride (Figure 2.7)[27]. The process is almost identical with that for the low-temperature solution method in the diamine route mentioned above.

The solution polymerization of N-silylated diamines with trimellitic anhydride chloride was carried out at room temperature in various organic solvents giving silylated poly(amide amic acid)s [poly(amide amic acid trimethylsilyl ester)s], which were followed by thermal imidization. When N,N’-bis(trimethylsilyl)-substituted bis(4-aminophenyl) ether was used (Figure 2.7, where Ar is 4,4’-oxydiphenylene), the polymerization in an amide-type solvent such as DMAc or NMP proceeded in homogeneous solution yielding the poly(amide amic acid) with high inherent viscosity of 1.4-1.8 dl/g. The other less polar aprotic solvent auch as benzene, chloroform, tetrahydrofuran, and acetronitrile also afforded a polymer with inherent viscosity of 0.5-1.1 dl/g, despite the fact that polymer precipitation occurred during the polymerization. This is because silylated poly(amide amic acid)s, the precursors for polyamideimides, have good solubility, and/or high affinity to these none polar aprotic solvents due to the lack of carboxylic acid functionality capable of forming strong hydrogen bonding [27].

Since the polymerization progressed under neutral reaction conditions with the elimination of trimethylsilyl chloride, transparent and flexible films of silylated precursor polymers were directly prepared by casting from the polymer solutions. The desilylation of the silylated polymers, if necessary, proceeded smoothly by the reaction with aprotic solvent such as methanol, resulting in the corresponding poly(amide amic acid)s. The silylated precursor polymers were subsequently converted thermally at 300^{o}C to polyamideimides with the elimination of trimethylsilanol. All the reactions show no side reactions and proceed cleanly. The rate of thermal imidization of the silylated polymers was almost the same as that of the poly(amide amic acid)s prepared by the conventional diamine route using the parent diamines [27].

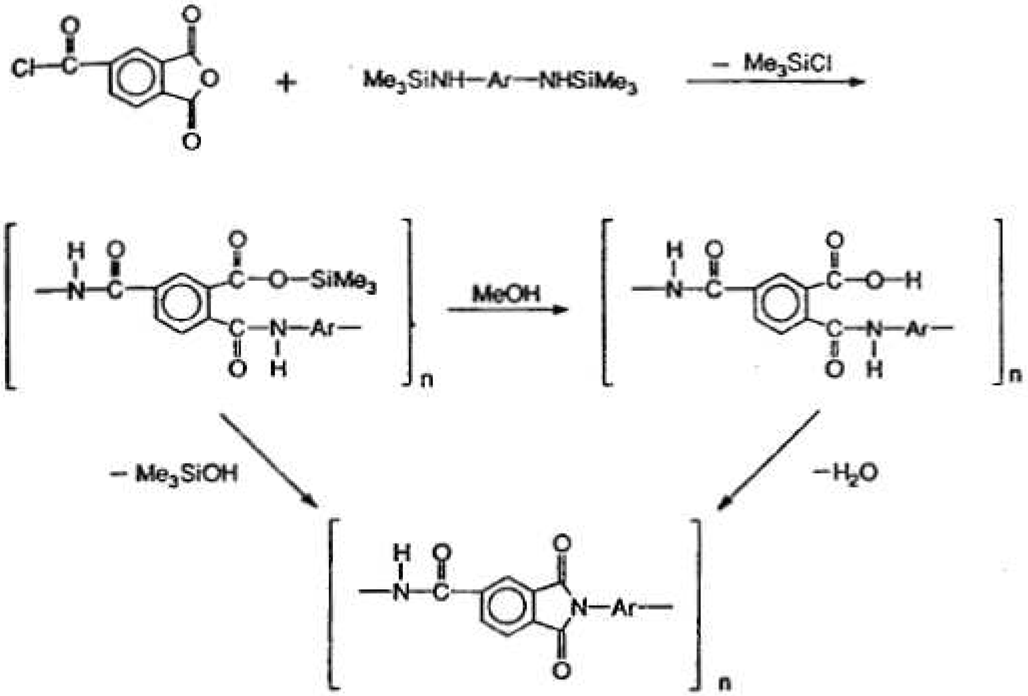

Figure 2.7 N-Silylated Diamine Route

ii) Thioanhydride Route

It is known that aromatic polyimides were synthesized in one step by the solution polycondensation of aromatic tetracarboxylic dithioanhydrides with aromatic diamines, with the elimination of hydrogen sulfide at moderately low temperatures (around 100-150^{o}C) [34,35]. This thioanhydride route was also applicable to the one-step synthesis of polyamideimides starting from trimellitic thio-anhydride derivatives and aromatic diamines(Figure 2.8) [28].

The polycondensation of trimellitic thioanhydride chloride (4-chloroformylphthalic thioanhydride) with bis(4-aminophenyl) ether in pyridine at 80^{o}C proceeded along with precipitation of the resultant polyamideimide (Figure 2.8, where Ar is 4,4'-oxydiphenylene and X is chloride). During the course of the reaction, elimination of both hydrogen sulfide and hydrogen chloride took place. The polymerization of trimellitic thioanhydride phenyl thioester (4-phenylthiocarbonylphthalic thioanhydride) with the same diamine in NMP at 140^{o}c progressed in homogeneous solution with the eliminations of both hydrogen sulfide and benzenethiol (Figure 2.8 where Ar is 4,4'-oxydiphenylene and X is phenylthio group). Both polymerizations gave the polyamideimides with inherent viscosity of around 0.5 dl/g [28].

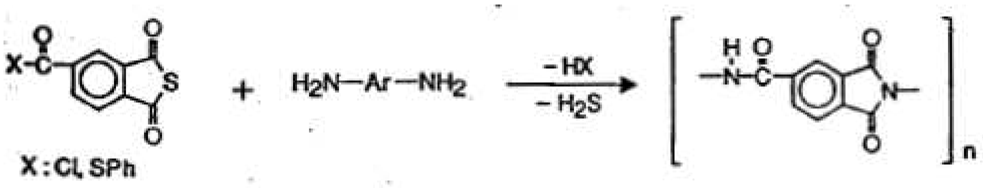

Figure 2.8 Thioanhydride Route

2.3.2 Synthesis of polyamideimides from tricarboxylic acids via amide-imide-forming reaction

A number of polyamideimides have been synthesized from trimellitic acid derivatives and various aromatic diamines (and their derivatives) either by the diamine route (Figure 2.3) or by the diisocyanate route (Figure 2.5). Aromatic tricarboxylic acids other than trimellitic acid used for the synthesis of polyamideimides are 3,4,4’-biphenyltricarboxylic acid [36] and 3’,4’,4’’-terephthaloyldiphenyl-tricarboxylic acid [37]. The chemical structure, inherent viscosity, and thermal properties of polyamide-imides from these tricarboxylic acids by the diamine route (Figure 2.9). In addition, 3,4,4’-sulfonyldiphenyltricarboxylic acid (Figure 2.10) has also been employed for preparing polyamideimides [38].

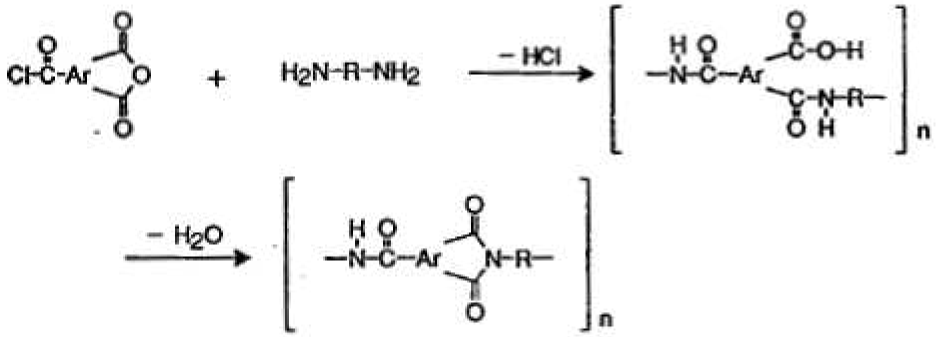

Figure 2.9 PAI from tricarboxylic acid by the diamine route

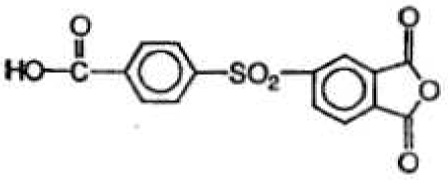

Figure 2.10 3,4,4’-sulfonyldiphenyltricarboxylic acid

2.3.3 Synthesis of polyamideimides from imide-containing monomers via amide-forming reaction

Another approach for the synthesis of polyamideimides is the use of monomers having preformed imide rings. The advantage of this synthelic route is that polyamide-forming polycondensation is more facile than polyimide-formation reaction. In other words, the monomers already carry the imide ring and hence post-curing at high temperatures to ring-close the poly(amic acid)to polyimide is not needed.

A. From imide-containing Dicarboxylic Acids

Polyamideimides can be readily prepared starting from imide-containing dicarboxylic acids via general synthetic methods used to prepare aromatic polyamides. Aromatic diamines are weakly basic (pKa: 2~6) to produce high – molecular-weight aromatic polyamides by reacting directly with dicarboxylic acids. Therefore, the activation of either aromatic diamines or dicarboxylic acids is usually essential to execute this synthesis pathway.

The best known is the low-temperature solution polycondensation method, in which the most reactive dicarboxylic acid chlorides are employed as dicarboxylic acid components and are coupled to aromatic diamines as shown in Figure 2.11 (Im, imide-containing unit). The use of aromatic diisocyanates, which are one of the activated diamine derivatives, together with dicarboxylic acids is less known for the preparation of aromatic polyamides (diisocyanate route) [21,22]. This is shown in Figure 2.12 [39]. The method of in situ activation of dicarboxylic acids by using activating (or condensing) agents, usually referred to as the direct polycondensation method, is easier for the preparation of aromatic polyamides [40]. The above mentioned methods, along with the direct polycondensation method (Figure 2.13), have been used for the synthesis of a variety of polyamideimides of high molecular weights.

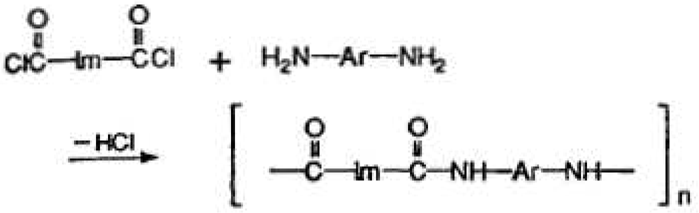

Figure 2.11 Low temperature solution polycondensation method

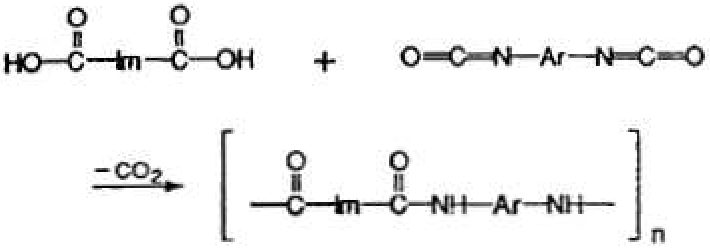

Figure 2.12 The preparation of aromatic polyamides

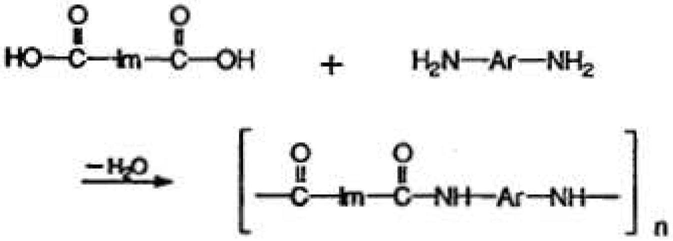

Figure 2.13 The direct polycondensation of imide-containing diamine with aromatic dicarboxylic acid chloride

B. From imide-containing Diamines

Some polyamide-imides have been obtained by the low-temperature solution polycondensation of imide-containing diamines with aromatic dicarboxylic acid chlorides (Figure 2.14). This route has the shortcoming that some imide-containing diamines are poorly soluble in the reaction medium, such as DMAc or NMP, for performing the polycondensation in homogeneous solution.

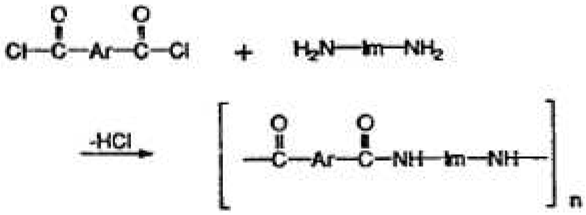

Figure 2.14 Low temperature polycondensation of imide-containing diamines with aromatic dicarboxylic acid chloride

C. From imide-containing Bis-N-Hydroxymethyl Compounds

The reaction of secondary or tertiary alcohols with nitriles in the presence of concentrated sulfuric acid at room temperature to give amides is known as the Ritter reaction [40]. This reaction is not so common, but could be applied to the synthesis of polyamideimides from bis-N-hydroxymethylimide compounds and dinitriles (Figure 2.15). Pyromellitic acid-based and 4,4’-azodiphthalic acid-based bis-N-hydroxymethyl compounds (Figure 2.16,12.7) were used for this type of polycondensation, and they were reacted with both aliphatic and aromatic dinitriles, to give polyamideimides with inherent viscosities up to 1.1 dl/g [41,42]. Most of these polyamideimides are not thermally very stable and start to decompose at around 300°C in air due to the presence of N-methylene unit in the polymer main chain [41,42].

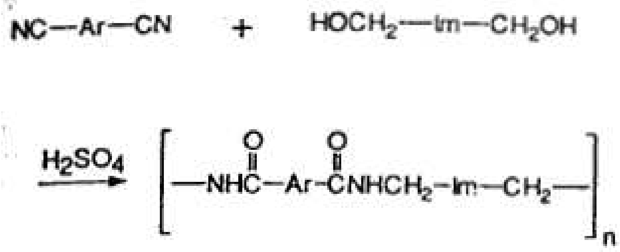

Figure 2.15 Polyamideimides from bis-N-hydroxymethylimide compounds and dinitriles

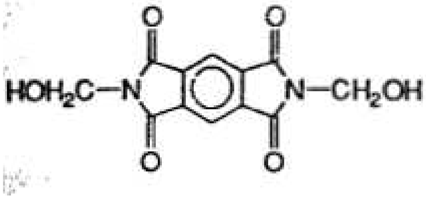

Figure 2.16 Pyromellitic acid-based

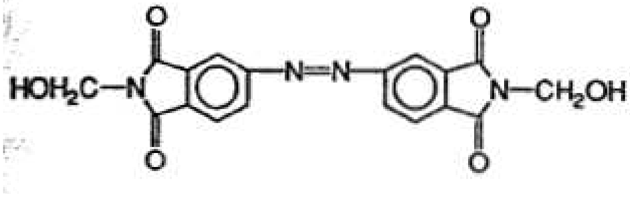

Figure 2.17 4,4’-azodiphthalic acid-based bis-N-hydroxymethyl compounds

2.3.4 Synthesis of polyamideimides from amide-containing monomers via imide-forming reaction

The classic synthetic route for polyimides is the two-step process, which consists of synthesis of poly(amic acid)s by the ring-opening polyaddition of aromatic diamines to tetracarboxylic dianhydrides, followed by cyclodehydration by thermal or chemical means. The one-step synthesis from aromatic diisocyanates and tetracarboxylic diamhydrides is also known. These methods are applicable to the synthesis of polyamideimides from amide-containing diamines and their derivatives.

A. From amide-containing Diamines

The two-step diamine route has been used for the synthesis of polyamideimides starting from various amide-containing diamines (Figure 2.18, where Am is amide-containing unit).

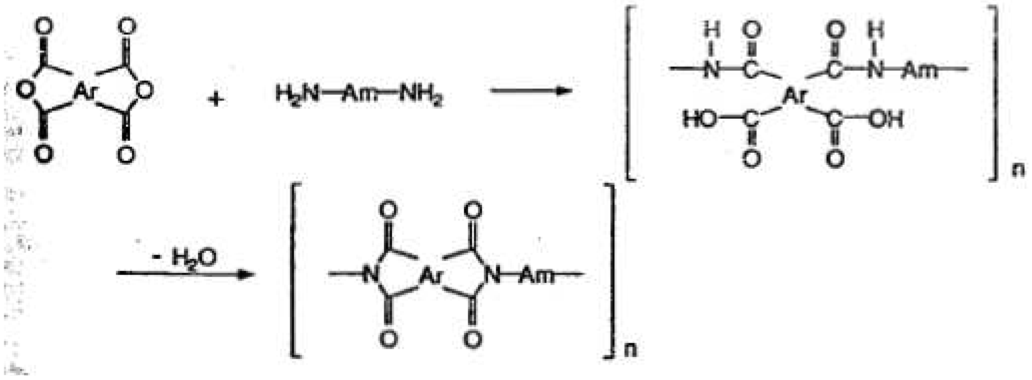

Figure 18 Polyamideimides starting from various amide-containing diamines

B. From Dihydrazides

Properly substituted dihydrazides are known to act like amide-containing diamines and have been utilized for the preparation of polyamideimides by the two-step polymerization with tetracarboxylic dianhydrides (Figure 2.19). Both aliphatic and aromatic dihydrazides shown in Figure 2.21-2.22 were employed for the polymerizations, and gave precursor poly(amic acid) like intermediates with inherent viscosities up to 0.9 dl/g [43-46]. The precursor polymers were then readily converted to polyamide-imides by heating at 250^{o}C. The thermal statibility of the resulting polyamide-imides is not very good and begins to decompose at around 300^{o}C. Thus, this type of polyamideimide is less thermally stable than conventional polyamideimides, due to the existence of nitrogen-nitrogen single linkage with low bond dissociation energy along the polymer backbone [43-46].

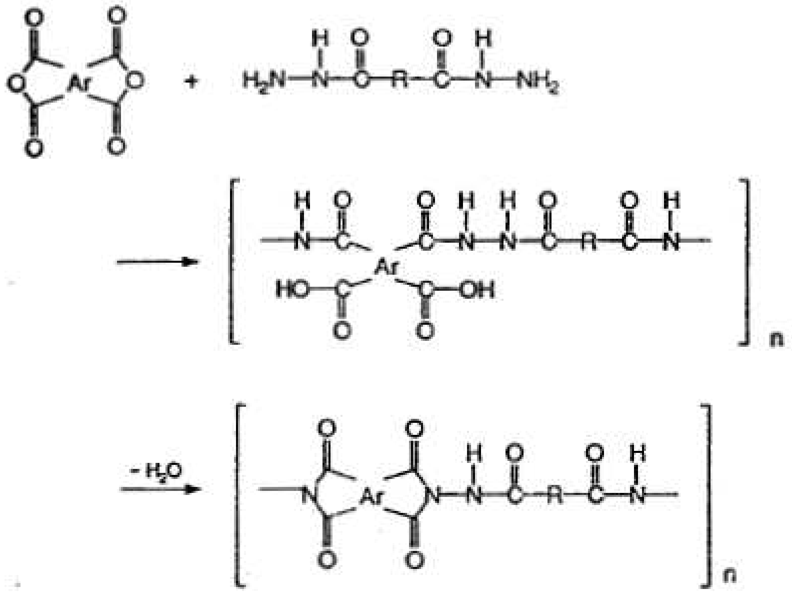

Figure 2.19 Polyamideimides by the two-step polymerization with tetracarboxylic dianhydrides

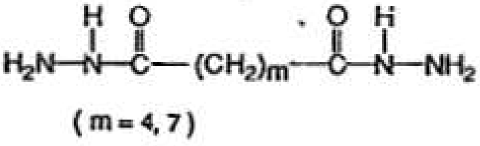

Figure 2.20 Aliphatic dihydrazides

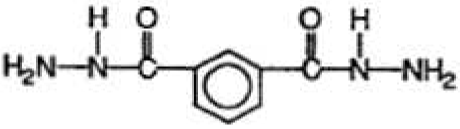

Figure 2.21 Aromatic dihydrazides

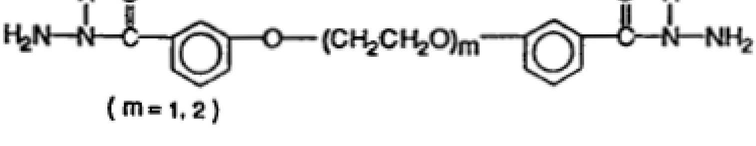

Figure 2.22 Aromatic dihydrazides

2.4 EPOXY RESINS

Epoxy resins are one of the versatile thermosetting polymers that, before curing, have one or more active epoxide or oxirane groups at the end(s) of the molecules and a few repeated units in the middle of the molecules. Chemically, they can be any compounds that have one or more 1,2-epoxy groups and can convert to thermosetting materials. Their molecular weights can vary greatly depend on the combination ingredient and formulation method. The Epoxy resin usually exist either as liquids with lower viscosity or as solids depend on the functionality and molecular weight of the resin. Through the ring opening reaction, the active epoxide groups in the uncured epoxy can react with many curing agents or hardeners that contain hydroxyl, carboxyl, amine, and amino groups. Compared to other materials, epoxy resins have several unique chemical and physical properties. Epoxy resins can be produced to have excellent chemical resistance, excellent adhesion, good heat and electrical resistance, low shrinkage, and good mechanical properties, such as high strength and toughness. These desirable properties result in epoxy resins having wide markets in industry, packaging, aerospace, construction, etc. They have found remarkable applications as bonding and adhesives, protective coatings, electrical laminates, apparel finishes, fiber-reinforced plastics, flooring and paving, and composite pipes.

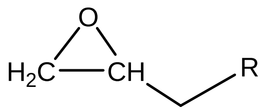

Figure 2.23 Epoxied groups

2.4.1 Curing Agents

Curing agents play an important role in the curing process of epoxy resin because they are crucial to the curing kinetics, reaction rate, gel time, degree of cure, viscosity, curing cycle, and the final properties of the cured products. Thus many researchers have investigated the effects of curing agents on the curing process.

2.4.2 Three main types of curing agents

The first type of curing agents includes active hydrogen compounds and their derivatives. Compounds with amine, amides, hydroxyl, acid or acid anhydride groups belong to this type. They usually react with epoxy resin by poly-addition to result in an amine, ether, or ester. Aliphatic and aromatic polyamines, polyamides, and their derivatives are the commonly used amine type curing agents. The aliphatic amines are very reactive and have a short lifetime. Their applications are limited because they are usually volatile, toxic or irritating to eyes and skin and thus cause health problems. Compared to aliphatic amine, aromatic amines are less reactive, less harmful to people, and need higher cure temperature and longer cure time. Hydroxyl and anhydride curing agents are usually less reactive than amines and require a higher cure temperature and more cure time. They have longer lifetimes. Polyphenols are the more frequently used hydroxyl type curing agents. Polybasic acids and acid anhydrides are the acid and anhydride type curing agents that are widely used in the coating field.

The second type of curing agents includes the anionic and cationic initiators. They are used to catalyze the homopolymerization of epoxy resins. Molecules, which can provide an anion such as tertiary amine, secondary amines, and metal alkoxides are the effective anionic initiators for epoxy resins. Molecules that can provide a cation, such as the halides of tin, zinc, iron and the fluoroborates of these metals, are the effective cationic initiators**.** The most important types of cationic initiators are the complexes of BF_3.

The third type of curing agents is called reactive crosslinkers. They usually have higher equivalent weights and crosslink with the second hydroxyls of the epoxy resins or by self-condensation. Examples of this type of curing agents are melamine, phenol, and urea formaldehyde resins.

2.4.3 Curing Reactions

The curing reaction of epoxide is the process by which one or more kinds of reactants, i.e., an epoxide and one or more curing agents with or without the catalysts, is transformed from low-molecular-weight to a highly crosslinked structure. As mentioned earlier, the epoxy resin contains one or more 1,2-epoxide groups. Because an oxygen atom has a high electronegativity, the chemical bonds between oxygen and carbon atoms in the 1,2-epoxide group are the polar bonds, in which the oxygen atom becomes partially negative, whereas the carbon atoms become partially positive. Because the epoxide ring is strained (unstable), and polar groups (nucleophiles) can attack it, the epoxy group is easily broken. It can react with both nucleophilic curing reagents and electrophilic curing agents. The curing reaction is the repeated process of the ring-opening reaction of epoxides, adding molecules and producing a higher molecular weight and finally resulting in a three dimensional structure. The chemical structures of the epoxides have an important effect on the curing reactions.

CHAPTER III

LITERATURE REVIEWS

This chapter presents the literature reviews of the previous works related to this research.

M.H. Tsai *et al.* [47] prepared high thermal durability and good mechanical properties of Poly(amide-imide), PAI, hybrid films by using sol–gel techniques. The poly(amide amic acid), both with controlled block chain length of 5000 and 10,000 g/mol and with uncontrolled chain length, were synthesized by condensation reaction from 4,4’-diaminodiphenyl ether (ODA), 3,3’,4,4’-benzophenonetetracarboxylic dianhydride (BTDA), trimellitic anhydride chloride (TMAC) and terminated with p-aminopropyltrimethoxysilane (APrTMOS). Then, the imidization reactions of poly(amide amic acid) were proceeded to obtain the poly(amide-imide) hybrid film. The characteristic absorption peak of C=O groups were obviously increased as the imidization reaction temperature increased. The degradation temperature of 5 wt% loss of all hybrid films were well above 540^{o}C and increased as the increase of TMAC content. It means that hybrid films maintain superior heat properties at room condition. The storage modulus, damping intensity and Tg of PAI hybrids are all increased as the PAI chain block length decreased. While the storage modulus increased, the tan δ peak shifted to higher temperature and damping intensity decreased, the TMAC content increased. Hybrid films with 5000 g/mol block chain length possess higher storage modulus, lower glass transition temperature and lower damping intensity compared to the films with 10,000 g/mol block chain length. The better effects of TMAC addition to the poly(amide-imide) hybrids toughness was enhanced by the increase of intermolecular hydrogen bonding, which was increased the average strength of intermolecular bonding. The intermolecular bonding strength depended on the hydrogen-bonded fraction (f_{bonded}), frequency difference ($\Delta\upsilon$) and shiftment. Meanwhile, PAI hybrid films containing more APrTMOS and TMAC content possessed higher thermal and mechanical properties. On the other hand, hybrid films with 10,000 g/mol block chain length and more TMAC content had higher gas permeabilities than other films, while the O_2/N_2 selectivities were only slightly decreased and the values are all above 8.3.

K.Y. Hwang *et al.* [48] provided a polyoxyalkylene amine-modified polyamide-imide resin with various polyamide-imide resin compositions. A polyoxyalkylene amine-modified polyamide-imide resin, produced by reacting a mixture of a polyalkylene amine and a multi-phenyl diamine compound with trimellitic anhydride to obtain a di-imido-dicarboxylic acid compound then reacting the di-imido-dicarboxylic acid compound with a diisocyanate compound to obtain a polyoxyalkylene amine-modified polyamide-imide resin. The polyamide-imide resin composition of the present invention had high resistance and high bond strength, and can achieve good adhesion at low temperature as 160 to 180^{o}C.

Y.W. Park *et al.* [49] conducted the reaction of Polyamideimide (PAI)–epoxysilane (coupling agent) composites with oligomeric polydimethylsiloxane (PDMS), a condensation product of difunctional silane, by using the sol– gel process, and then dried the solution into films. After these procedures, the surface, mechanical, and thermal properties were measured. The FTIR study showed that PDMS existed in the PAI matrix. Addition of epoxysilane increased the cohesiveness between PAI and oligomeric PDMS. When the content of oligomeric PDMS in PAI was increased with a fixed amount of epoxysilane, the maximum tensile strength decreased slightly, whereas maximum elongation and toughness increased regardless of the slightly decreased maximum tensile strength. In those experiments, PAI–30 wt% epoxysilane composite had the best mechanical properties. The intensive dispersion of the silane groups (Si-O) on the surface of PAI was confirmed through XPS measurement. As a function of the siloxane contents, the TGA curve shows less thermal stability in terms of their initial weight loss. However, in an oxygen atmosphere at about 700^{o}C, the series of PAI–siloxane composites indicated a significant increase in char concentration. In the end, PAI with a relevant amount of silane groups was improved in both toughness and surface properties. These experiments showed that the addition of PDMS to PAI gave better properties than those of classical materials.

T.C. Chang *et al.* [50] synthesized Hydrogen-bonded acidic poly(siloxane amideimide)s (PSAIs) by partial imidization of 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) with 2,2',bis(3-amino-4-hydroxyphenyl) hexafluoropropane (AHHFP) and 1,3-bis(3-aminopropyl) tetramethyldisiloxane (APrTMDS). They used Infrared (IR) and ^{13}C nuclear magnetic resonance (NMR) spectroscopy to characterize the structure of PSAI copolymers. With the addition of the flexible disiloxane as a segment in polyimide structure, a higher extent of imidization and a lowering of Tg were observed. The incorporated disiloxane segments enhance the thermo-oxidative stability of AHHFP imide segments, but lesser affect the thermal stability. The apparent activation energies of thermo-oxidative degradation, Ea from the AHHFP imide moiety of PSAIs (≈250 kJ/mol) evaluated by van Krevelen method were larger than that of unmodified PAI (232 kJ/mol), but decrease with increasing APrTMDS. It suggested that the degradation products of the disiloxane segments retard the degradation of PSAIs and the higher thermal conductivity of the silica induces the decrease of decomposition threshold when APrTMDS increases. The higher Ea of the PSAIs in air than that of the PAI suggested that the disiloxane enhanced the stability of the polyamideimide, and the smaller spin–spin relaxation time T2 of the PSAI copolymers than that of the PAI revealed that the PSAI had more closely packed structure with increasing APrTMDS.

T.C. Chang *et al.* [51] synthesized Hydrogen-bonded acidic fluorinated poly(siloxane-amideimide-silica) hybrid materials (FPSAI–SiO_2) using the sol-gel technique by polycondensation of tetramethoxysilane (TMOS) in diethoxysilane-terminated amic acid solution. The preparation of diethoxysilane terminated amic acid with 6FDA, DMAc/toluene mixture, a solution of AHHFP in cosolvent (DMAc/toluene = 3:1), DAPrTMDS and APrMDEOS. IR, ^{29}Si- and ^{13}C-NMR spectroscopy and thermogravimetric analysis (TGA) were used to study hybrids containing various proportions of TMOS. The abundant Q4 structures implied that in the absence of HCl the degree of condensation of TMOS was enhanced by hydrogen-bonded acidic fluorinated poly(siloxane amideimide). The microstructure and chain mobility of the hybrids were investigated by measurements of the spin-lattice relaxation time in the rotating frame ($T^{H}_{1\rho}$) and the time constant for energy exchange between ^{1}H and ^{29}Si spin systems (T_{SiH}). The IR spectra of the hybrids reveal that the imidization of the hybrid becomes incomplete as the TMOS is above 30 wt%. ^{29}Si- and ^{13}C-NMR spectroscopy confirmed the fluorinated poly(siloxaneamideimide-silica) hybrids structure. The high degree of condensation Dc (~95%) in the absence of HCl revealed that fluorinated poly(siloxane amideimide) segment is acidic. The higher T_{SiH} values of the M^1 and D^2 species suggested that the rate of polarization transfer in fluorinated siloxane amideimide segment in hybrids was depended on the local motion. On the other hand, the spin-diffusion path length (L) in FPSAI–SiO_2 hybrids was clearly around 3.6 nm, almost the same as that of the hybrids. This revealed that the flexible DAPrTMDS coupling agent causes the same chain mobility of the hybrids. The apparent activation energy (Ea) for degradation of the hybrids was studied by the van Krevelen method. The Ea of the FPSAI–SiO_2 hybrids in thermal degradation decreased with increasing silica content, whereas those in thermo oxidative degradation were almost unchanged. The results suggest that silica enhanced the aliphatic n-propyl segment degradation and the flexible DAPrTMDS coupling agent does not change the free volume of the fluorinated polyamideimide.

Y.B. Lee *et al.* [52] synthesized Polyamideimide-branched siloxanes (PAIBrSs) from 4, 4’-(hexafluoroisopropyllidene)diphthalic anhydride (6FDA), *p,p*’-oxydianiline (ODA), and aminopropyl-terminated oligomeric dimethylsiloxane (ODMS). In this investigation, a mixture of *N*-methylpyrrolidinone (NMP) and tetrahydrofuran (THF) was used as a cosolvent for the homogeneous mixing of poly(amic acid) (PA) and the ODMS solution. Thionyl chloride ($SOCl_2$) was used for the acylation of PA to activate the reaction between PA and ODMS. FTIR spectra showed an increase in the intensity of characteristic absorption peaks of dimethylsiloxane units with the reacted amount of ODMS. From thermogravimetric analysis (TGA), PAIBrSs showed good thermal stability, but relatively low thermal stability when compared with that of block poly(imide siloxane) (PIBlS) or poly(amideimide siloxane) (PAIBlS). The char contents at over 600°C increased with the amount of ODMS incorporated. During the process of thermal curing, the amorphous region of the polymers increased as evidenced from the WAXD patterns. A solubility test showed that dipolar aprotic solvents such as NMP, DMAc, DMF, and DMSO, were relatively good solvents for the polymer. However, the deterioration increased with increase of the ODMS contents. Gas separation was performed by single gas-permeation equipment and showed that the permeability of oxygen increased while the selectivity of oxygen over nitrogen decreased with the amount of ODMS incorporated. The permeabilities of PAIBrS membranes were higher than those of PIBlS membranes and the selectivities of PAIBrS membranes were lower than those of PIBlS membranes. PAIBrSs exhibited good gas-permeation properties compared with those other silicone-containing polymers.

S.Y. Ha *et al.* [53] prepared poly(amideimide siloxane) block copolymer from oligo(dimethylsiloxane) (ODMS), trimellitic anhydride chloride (TMAC) and oxylene diamine (ODA) using trimethylsilyl chloride (TMSC) as the reaction activator. Trimethylsilyl chloride (TMSC) enhanced the reactivity of oligo(dimethylsiloxane) (ODMS) , resulting in a higher yield and higher viscosity of the siloxane-containing PAIs (SPAI). The high reactivity of N-trimethylsilylated siloxane diamine stem from the silicon σ-π effect, and a nucleophilic addition-elimination reaction was proposed. The addition of a small amount of N-methylpyrrolidone (NMP) in tetrahydrofuran (THF) led to a higher yield of product. The inherent viscosities of SPAIs ranged between 0.41 and 0.45 dl g^{-1}. FTIR and NMR spectra suggested the successful preparation of SPAIs. The temperatures of 10% weight loss for the products were exceeded 355°C according to thermogravimetric analysis. A transient change in the contact angle of water on the sample surface was observed, suggesting surface segregation of the hydrophobic component in the polymer.

CHAPTER IV

EXPERIMENT

4.1 Materials and chemicals

1. Trimellitic anhydride (TMA) purchased from Fluka Company ,Inc.
2. Terphthalic acid (TPA) purchased from Fluka Company ,Inc.
3. 4,4´- Oxydianiline (ODA) purchased from Aldich chemical Company, Inc.
4. 4,4'-diphenylmethane diisocyanate (MDI) purchased from Aldich chemical Company, Inc.
5. Tolylene 2-4-diisocyanate (TDI) purchased from Aldich chemical Company, Inc.
6. Benzene-1,2,4,5-tetracarboxylic dianhydride (PMDA) purchased from Aldich chemical Company, Inc.
7. N-Methyl-2-pyrrolidinone (NMP) purchased from Merck KGaA Germany.
8. Toluene commercial grade was donated from Exxon Chemical Ltd.,Thailand.
9. Argon gas (Ultra high purity grade, 99.999 %) was purchased from Thai Industrial Gas Co.,Ltd.(TIG) and further purified by passing through columns packed with copper catalyst, NaOH, P_2O_5 and molecular sieve 4A to remove traces of oxygen and moisture.
10. Acetone (Analytical grade) was purchased from SR lab.
11. Diglycidyl ether of bisphenol-A (DGEBA) EEW 170 from Dow Chemical Company.
12. Nitrile butadiene rubber (NBR) from Multi-Chemical & Engineering Company.

4.2 Equipments

4.2.1 Oligomer amideimide synthesis part

Since most of the reagents were very sensitive to the oxygen and moisture therefore the special techniques were taken during the handling of reagents and the loading of ingredient into the reactor. Such equipments utilized for this purpose are listed as follows:

(a) Glove box (Vacuum Atmospheres) with oxygen and moisture analyzer for handling solid reagents under inert atmosphere and for storing air-sensitive reagents. Inside the glove box, oxygen and moisture levels are normally controlled to below 0.1 ppm. The glove box is shown in Figure 4.1.

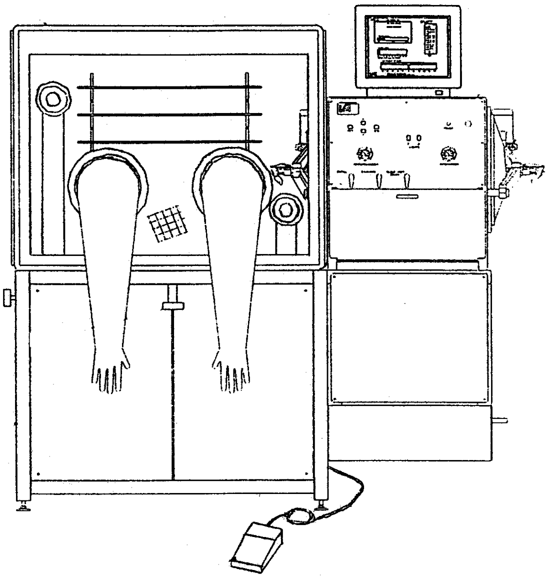

Figure 4.1 Glove box

(b) Schlenk line included of vacuum line connected to vacuum pump and argon line for purging when reagents are transferred. The schlenk line was shown in Figure 4.2.

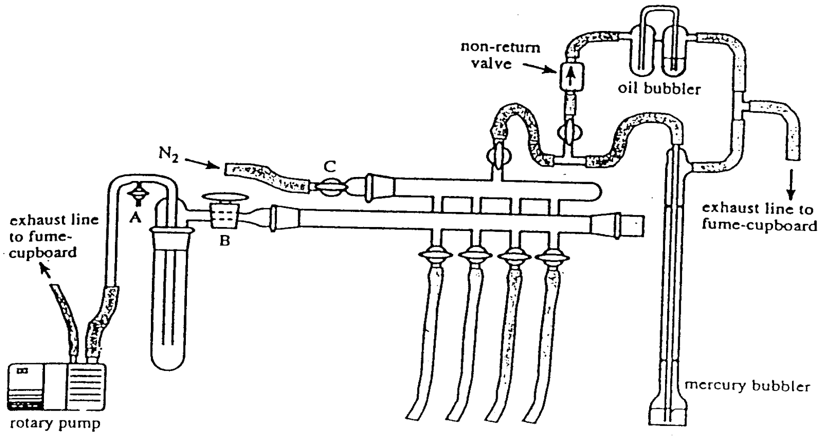

Figure 4.2 Schlenk line

(c) Schlenk tube for keeping reagents under argon atmosphere outside the glove box. It was used accompanied with the Schlenk line. Schlenk tube is the tube with a ground joint and a side arm which connected with three ways glass valve. The Schlenk tube picture is shown in Figure 4.3.

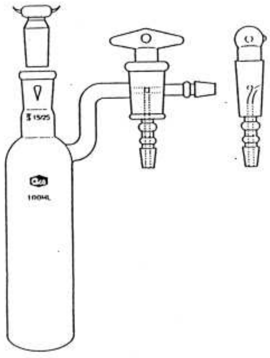

Figure 4.3 Schlenk tube

(d) The inert gas (argon) from the cylinders was passed through columns of oxygen trap (BASF catalyst, R3-11G), moisture trap (molecular sieve), sodium hydroxide (NaOH) and phosphorus pentaoxide (P_2O_5) in order to purifying the argon gas to obtain ultra high purity argon which was used in Schlenk line and solvent distillation column. The inert gas supply system can be shown in Figure 4.4.

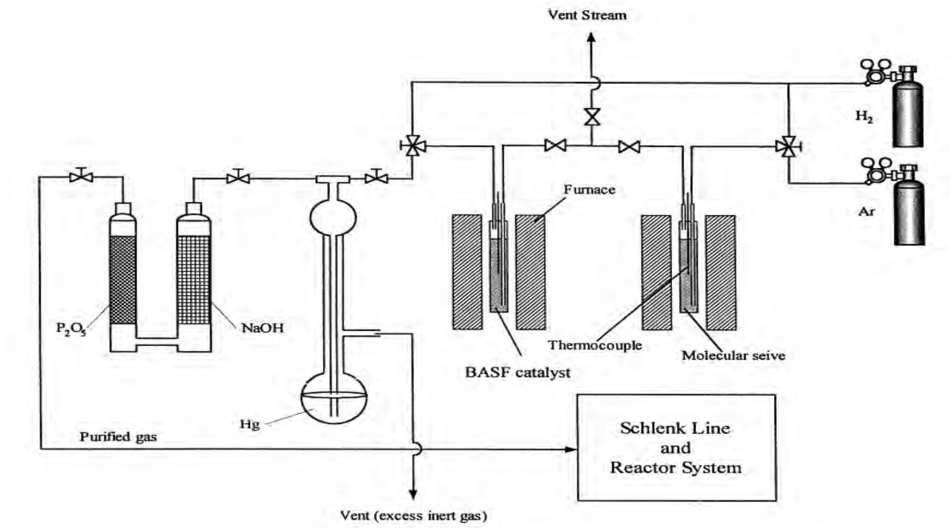

Figure 4.4 Inert gas supply system

(e) Magnetic Stirrer and Hot Plate

The magnetic stirrer and hot plate model RCT basic from IKA Labortechnik were used.

(f) Syringe, Needle

The syringe used in these experiments had a volume of 10, 5 ,1 ml and 100 µl, respectively.

(g) Dean Stark apparatus

The Dean Stark used in these experiment for azeotropic reflux with toluene to brought out water.

Figure 4.5 Dean Stark

(H) Stud test

The stud test used in the adhesion peel test was aluminum cylindrical with diameter 1.9 cm.

Figure 4.6 Stud test

4.2.2 Adhesive preparation Part

(a) High temperature oven

A Cole-Parmer high temperature oven model 282A were used for removing solvent from freshly cast films and used for thermal treated the film photosensitive polyimide. This high temperature oven can be programmed. All functions can be set from digital panel and display their status on LCD. The temperature, pressure and time are controllable variables. The maximum working temperature of this machine is 500°C.

4.3 Oligomer amideimide polymerization

4.3.1 Oligomer amideimide from trimellitic anhydride(tri-carboxylic)

A solution of ODA (0.04 mol, 8.0092 g) in NMP (65 g) was charged into a 3-neck flask equipped with a stirrer. A solution of TMA (0.084 mol, 16.13 g) in NMP (25 g) was charged into a 3-neck flask and the reaction mixture was heated at a temperature of 80^{o}C for an hour. The 3-neck flask was equipped with Dean Stark Apparatus and toluene (30 g) was added to the flask. The byproduct, water was brought out by azeotropic reflux with toluene at 190^{o}C. The reaction continued until no water was brought out. Toluene was then evaporated off and the reaction mixture was cooled to room temperature. MDI (0.048 mol, 12.012 g) was added to the reaction mixture. The temperature was slowly raised to 190^{o}C and the reaction was preformed at this temperature for 2 hours. The Oligomer of polyamideimide (OPAI) was obtained.

4.3.2 Oligomer amideimide from terphthalic acid(di-carboxylic)

Example1 A solution of ODA (0.04 mol, 8.0092 g) and TPA (0.01 mol, 1.66167 g) in NMP (32.76 g) was charged into a 3-neck flask equipped with a stirrer. A solution of PMDA (0.074 mol, 16.14088 g) in NMP (49.14 g) was charged into a 3-neck flask and the reaction mixture was heated at a temperature of 80^{o}C for an hour. The 3-neck flask was equipped with Dean Stark Apparatus and toluene (30 g) was added to the flask. The by product, water was brought out by azeotropic reflux with toluene at 190^{o}C. The reaction continued until no water was brought out. Toluene was then evaporated off and the reaction mixture was cooled to room temperature. MDI (0.048 mol, 12.012 g) was added to the reaction mixture. The temperature was slowly raised to 190^{o}C and the reaction was preformed at this temperature for 2 hours. The oligomer of polyamideimide (OPAI) was obtained.

Example2 Followed the example1 used TPA (0.02 mol, 3.32334 g) and PMDA (0.064 mol, 13.95968 g)

Example3 Followed the example1 used TPA (0.03 mol, 4.98501 g) and PMDA (0.054 mol, 11.77848 g)

Example4 A solution of ODA (0.04 mol, 8.0092 g) and PMDA (0.03 mol, 6.5436 g) in NMP (49.14 g) was charged into a 3-neck flask equipped with a stirrer. A solution of TPA (0.054 mol, 8.97318 g) in NMP (40.95 g) was charged into a 3-neck flask and the reaction mixture was heated at a temperature of 80^{o}C for an hour. The 3-neck flask was equipped with Dean Stark Apparatus and toluene (30 g) was added to the flask. The byproduct, water was brought out by azeotropic reflux with toluene at 190^{o}C. The reaction continued until no water was brought out. Toluene was then evaporated off and the reaction mixture was cooled to room temperature. MDI (0.048 mol, 12 g) was added to the reaction mixture. The temperature was slowly raised to 190^{o}C and the reaction was preformed at this temperature for 2 hours. The Oligomer of polyamideimide (OPAI) was obtained.

Example5 Followed the example4 used PMDA (0.02 mol, 4.3624 g) and TPA (0.064 mol, 10.63459 g)

Example6 Followed the example4 used PMDA (0.01 mol, 2.1812 g) and TPA (0.074 mol, 12.29658 g)

Example7 Followed the example1 changed MDI to TDI (0.048 mol, 8.35968 g)

Example8 Followed the example2 changed MDI to TDI (0.048 mol, 8.35968 g)

Example9 Followed the example3 changed MDI to TDI (0.048 mol, 8.35968 g)

Example10 Followed the example4 changed MDI to TDI (0.048 mol, 8.35968 g)

Example11 Followed the example5 changed MDI to TDI (0.048 mol, 8.35968 g)

Example12 Followed the example6 changed MDI to TDI (0.048 mol, 8.35968 g)

4.4 Preparation of amide-imide-epoxy adhesives

The ratio of oligomer amideimide and DGEBA showed

Divide2 ; amine EEW = 7467.72/2 = 3733.895
% = 3733.895*100/170 = 2169.409
Epoxy 100 : OPAI 2169.409

Divide3 ; amine EEW = 7467.72/3 = 2489.263
% = 2489.263*100/170 = 1464.273
Epoxy 100 : OPAI 1464.273

Divide4 ; amine EEW = 7467.72/4 = 1866.948
% = 1866.948*100/170 = 1098.204
Epoxy 100 : OPAI 1098.204

Divide5 ; amine EEW = 7467.72/5 = 1493.558
% = 1493.558*100/170 = 878.5635
Epoxy 100 : OPAI 878.5635

The amide-imide-epoxy adhesives were prepared two groups. Group1 prepared the adhesive without the rubber (NBR) but group2 prepared the adhesive with 5 %wt rubber (NBR) and all of sample stirred 1 day.

4.5 Preparation of adhesion peel test

The prepared adhesion peel tests were drop to the stud test. Sample thickness was 1 mm and baked at 230˚C for 90 min to cure then cooled to room temperature.

4.6 Characterization Instruments

4.6.1 Infrared Spectroscopy (FTIR)

Infrared survey spectra were recorded with Nicolet 6700 FTIR spectrometer. The scanning ranged from 400 to 4000 cm^{-1} with scanning 64 times. Background was gold and sample was solution.

Figure 4.7 Fourier transform infrared spectroscopy (FTIR) Equipment

4.6.2 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) thermograms were performed using a Diamond TG/DTA Thermogravimetric/Differrential Thermal Analyzer. The sample weights were 3-10 mg. The temperature range of 50-900^{o}C at a heating rate of 10^{o}C/min with nitrogen purge flow rate 100 ml/min were used.

Figure 4.8 Thermogravimetric analysis (TGA) Equipment

4.6.3 Differential Scanning Calorimetry (DSC)

The curing temperature of oligomer polyamideimide polymer products determined with a Perkin-Elmer diamond DSC from MEKTEC, at the Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Chulalongkorn University as shown in Figure 4.9. The analyses were performed at the heating rate of 20^{o}C min^{-1} in the temperature range of 50-250°C.

The heating cycle was run twice. In the first scan, samples were heated and the cooled to room temperature. In the second, samples were reheated at the same rate.

Figure 4.9 Perkin-Elmer Diamond DSC

4.6.4 Tensile testing machine

Tensile properties were characterized using an Instron universal testing machine with a test speed of 0.1 mm/min. The tensile testing machine of a constant-rate-of-crosshead movement is used. It has a fixed or essentially stationary member carrying one grip, and a moveable member carrying a second grip. Self-aligning grips employed for holding the test specimen between the fixed member and moveable member to prevent the alignment problem. An extension indicator is used to determine the tensile stress within the constant length of the test specimen.

Figure 4.10 Tensile testing machine Equipment

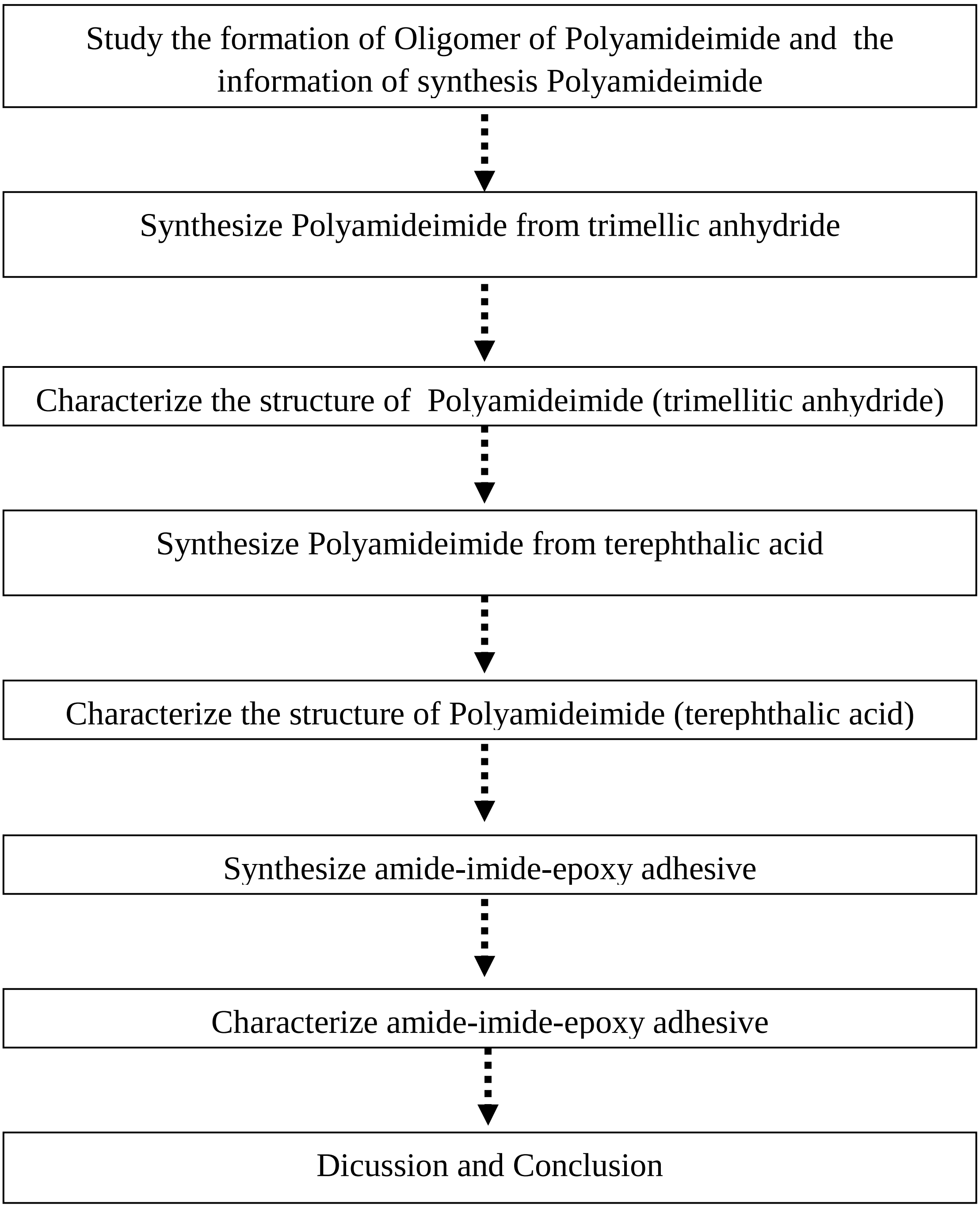

Figure 4.11 Flow diagram of research methodology

CHAPTER V

RESULTS AND DISCUSSION

This chapter provides the information about the properties of oligomer amideimide (OAI) from trimellitic anhydride (tri-carboxylic acid) / terephthalic acid (di-carboxylic acid), and the properties of the synthesized amide-imide-epoxy adhesive.

5.1 Oligomer amideimide

5.1.1 Preparation of OAI

All synthesized conditions and name definitions of synthesized oligomer amideimide are shown as below.

Table 5.1 Formulation and definition of OAI (tri-carboxylic)

Code	ODA(g)	TMA(g)	MDI(g)	OAI (g)	Bond		DGEBA (g)	NBR (g)
					amide	imide		
EODA	0.2942	-	-	-	-	-	1	-
EOAI(3)2	8.0092	16.1297	12.0120	21.9647	105[a]	105[a]	1	-
EOAI(3)3	8.0092	16.1297	12.0120	14.6431	105	105	1	-
EOAI(3)4	8.0092	16.1297	12.0120	10.9824	105	105	1	-
EOAI(3)5	8.0092	16.1297	12.0120	8.7859	105	105	1	-
EOAI(3)2R5	8.0092	16.1297	12.0120	21.9647	105	105	1	1.2086
EOAI(3)3R5	8.0092	16.1297	12.0120	14.6431	105	105	1	0.8233
EOAI(3)4R5	8.0092	16.1297	12.0120	10.9824	105	105	1	0.6306
EOAI(3)5R5	8.0092	16.1297	12.0120	8.7859	105	105	1	0.5150

[a] the amide and imide bond are 105 from TMA 0.084 mol : ODA 0.04 mol converse to percent bond (0.084/2) / 0.04 *100 = 105% because chemical reaction use TMA 2 mol : ODA 1 mol.

Table 5.2 Formulation and definition of OAI (di-carboxylic)

Code	ODA (g)	TPA (g)	PMDA (g)	MDI (g)	TDI (g)
EOAI(2M)4R5-1	8.0092	1.6617	16.1409	12.0120	-
EOAI(2M)4R5-2	8.0092	3.3233	13.9597	12.0120	-
EOAI(2M)4R5-3	8.0092	4.9850	11.7785	12.0120	-
EOAI(2M)4R5-4	8.0092	8.9732	6.5436	12.0120	-
EOAI(2M)4R5-5	8.0092	10.6346	4.3624	12.0120	-
EOAI(2M)4R5-6	8.0092	12.2966	2.1812	12.0120	-
EOAI(2T)4R5-1	8.0092	1.6617	16.1409	-	8.3597
EOAI(2T)4R5-2	8.0092	3.3233	13.9597	-	8.3597
EOAI(2T)4R5-3	8.0092	4.9850	11.7785	-	8.3597
EOAI(2T)4R5-4	8.0092	8.9732	6.5436	-	8.3597
EOAI(2T)4R5-5	8.0092	10.6346	4.3624	-	8.3597
EOAI(2T)4R5-6	8.0092	12.2966	2.1812	-	8.3597

From Table 5.2 shows the amount of chemical ; EOAI(2-)4R5-1, 2, and 3 are ODA and TPA mixed before mixed with PMDA. The EOAI(2-)4R5-4, 5, and 6 are ODA and PMDA mixed before mixed with TPA.

Table 5.3 Formulation and definition of OAI (di-carboxylic)2

Code	OAI (g)	Bond		DGEBA (g)	NBR (g)
		Amide	imide		
EOAI(2M)4R5-1	11.3984	25[b]	185[c]	1	0.6526
EOAI(2M)4R5-2	11.2736	50	160	1	0.6460
EOAI(2M)4R5-3	11.1488	75	135	1	0.6394
EOAI(2M)4R5-4	10.6904	135	75	1	0.6153
EOAI(2M)4R5-5	10.4333	160	50	1	0.6018
EOAI(2M)4R5-6	10.1761	185	25	1	0.5882
EOAI(2T)4R5-1	9.7436	25	185	1	0.5819
EOAI(2T)4R5-2	9.9309	50	160	1	0.5753
EOAI(2T)4R5-3	9.8061	75	135	1	0.5687
EOAI(2T)4R5-4	9.3477	135	75	1	0.5446
EOAI(2T)4R5-5	9.6392	160	50	1	0.5311
EOAI(2T)4R5-6	9.4762	185	25	1	0.5175

[b] the amide bond is 25 from TPA 0.01 mol : ODA 0.04 mol converse to percent bond

(0.01*2) / (0.04/2) *100 = 25%

[c] the imide bond is 185 from PMDA 0.074 mol : ODA 0.04 mol converse to percent bond

(0.074) / (0.04) *100 = 185%

5.1.2 Definition of OAI

EODA	(epoxy + ODA)
EOAI(3)-	(epoxy + OAI from tri-carboxylic)
EOAI(3)2	(epoxy + OAI from tri-carboxylic; Divide2)
EOAI(3)3	(epoxy + OAI from tri-carboxylic; Divide3)
EOAI(3)4	(epoxy + OAI from tri-carboxylic; Divide4)
EOAI(3)5	(epoxy + OAI from tri-carboxylic; Divide5)
EOAI(3)-R5	(epoxy + OAI from tri-carboxylic + NBR5%)
EOAI(2-)4R5	(epoxy + OAI from di-carboxylic; Divide4 + NBR5%)
EOAI(2M)4R5-	(epoxy + OAI from di-carboxylic and MDI; Divide4 + NBR 5%)
EOAI(2T)4R5-	(epoxy + OAI from di-carboxylic and TDI; Divide4 + NBR 5%)

5.1.3 The characteristic IR of OAI

The functional groups of OAI were investigated and confirmed by FT-IR spectra. Figure 5.1 shows a typical FT-IR spectrum of OI and Figure 5.2 shows a typical FT-IR spectrum of OAI. The OI are different from OAI because OI have not complete amide bond.

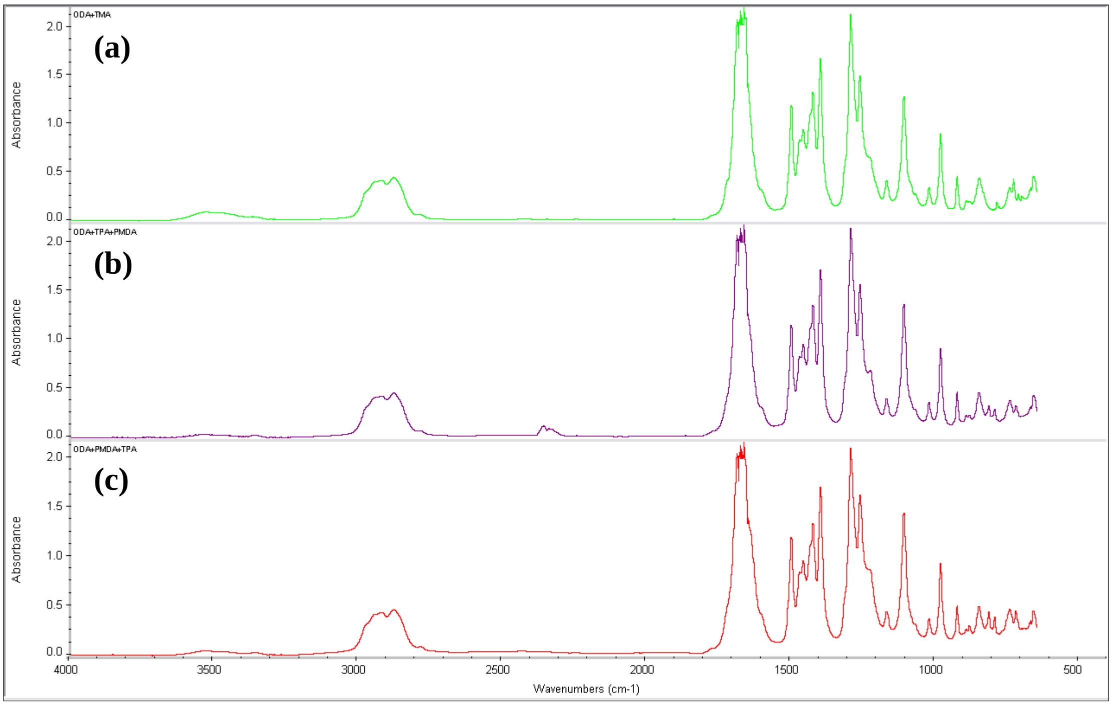

Figure 5.1 FT-IR spectra of OI (a) ODA+TMA (b) ODA+PMDA+TPA and (c) ODA+TPA+PMDA

From Figure 5.1, the FT-IR spectra of OI shows the poly(amic acid) are synthesized by (a) ODA+TMA (b) ODA+PMDA+TPA and (c) ODA+TPA+PMDA The characteristic IR adsorption of OI presents the characteristic imide adsorption peaks at 1779 cm^{-1} (imide C=O sysmetric), 1700 cm^{-1} (imide C=O asysmetric), 1400 cm^{-1} (imide C-N), and 731 cm^{-1} (imide ring deformation) that the ring closed.

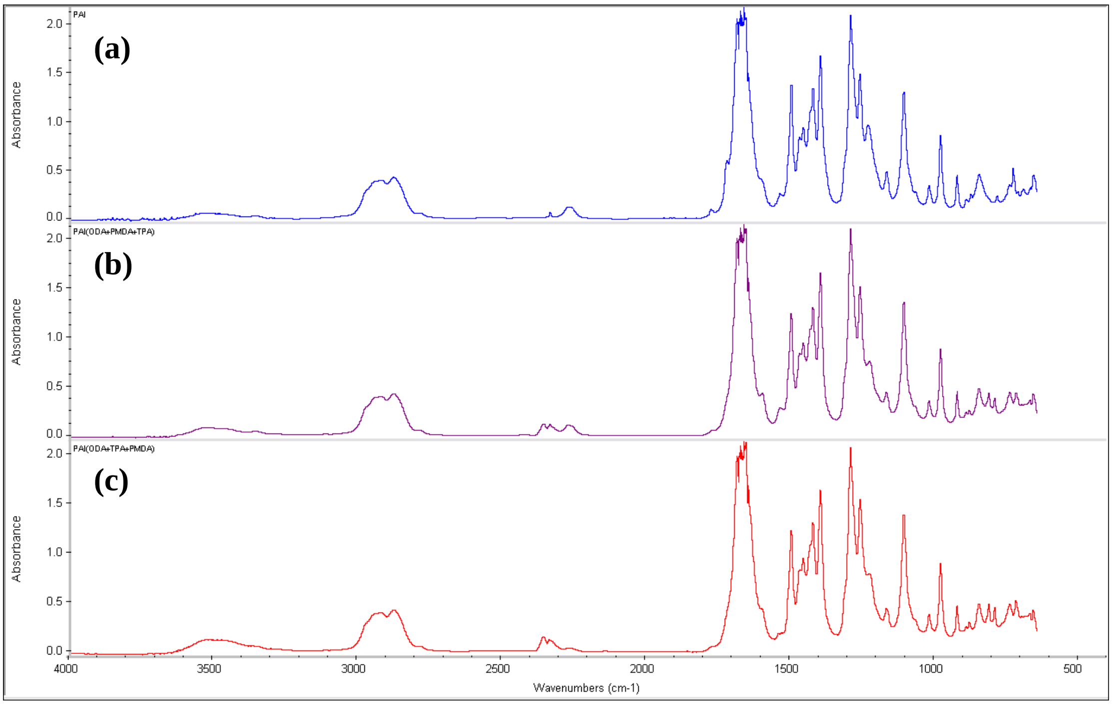

Figure 5.2 FT-IR spectra of OAI (a) [DA+TMA]+MDI

(b) [ODA+PMDA+TPA]+MDI and (c) [ODA+TPA+PMDA]+MDI

From Figure 5.2 shows the characteristic IR adsorption of OAI presents the characteristic imide adsorption peaks at 1779 cm^{-1} (imide C=O symetric), 1700 cm^{-1} (imide C=O asymetric), 1400 cm^{-1} (imide C-N), and 731 cm^{-1} (imide ring deformation). The characteristic amide adsorption peaks were at 1650 and 1501 cm^{-1}. It confirmed the functional group of oligomer amideimide that completeted reaction and amide-imide bone in main chain.

5.2 Thermal properties of amide-imide-epoxy adhesive

5.2.1 The curing temperature

The curing temperature was characterized by Differential Scanning Calorimetry (DSC) in order to get the appropriate temperature for curing the adhesive. The sample was heated at the rate of 20°C/min from 50°C to 250°C and then cooled down at the same rate. The second heating was perform in order to observe whether the reaction of curing has complete in the first heating or not.

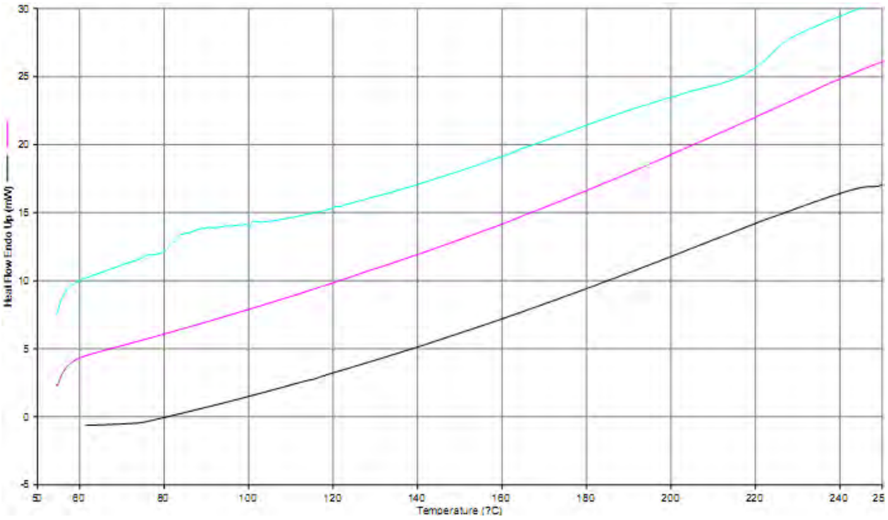

Figure 5.3 The DSC curve of amide-imide-epoxy adhesive in N_2 at heating rate 20 ^{o}c/min ; blue line was heated from 50 to 250^{o}c ,black line was cooled from 250 to 50^{o}c and magenta line was second heated from 50 to 250^{o}c.

From Figure 5.3, the endothermic peak at 230°C corresponded to the absorption of heat during the cure reaction of the epoxy that we used in this experiment from the first heating of the adhesive represented by the blue line. The second heating showed no peaks corresponded to all the reaction was complete during the first heating peak. Thus, the curing temperature of amide-imide-epoxy adhesive was set at 230^{o}c for the whole experiments.

5.2.2 Degradation temperature and char yield of amide-imide-epoxy adhesive from tri-carboxylic acid

The degradation temperature at 5% weight loss, degradation temperature at 10% weight loss and char yield can be shown in Table 5.4.

Table 5.4 The degradation temperature of amide-imide-epoxy adhesive.

Code	No.	Td 5% (^{o}c)	Td 10% (^{o}c)	Char yield (%)
EODA	1	350	365	14.83
EOAI(3)2	2	270	345	38.35
EOAI(3)3	3	272	354	36.07
EOAI(3)4	4	252	326	31.31
EOAI(3)5	5	281	350	30.38
EOAI(3)2R5	2	293	367	40.54
EOAI(3)3R5	3	302	361	40.63
EOAI(3)4R5	4	319	353	39.65
EOAI(3)5R5	5	308	357	33.32
EOAI(2M)4R5-1	1	343	368	35.06
EOAI(2M)4R5-2	2	343	374	35.38
EOAI(2M)4R5-3	3	325	363	33.73
EOAI(2M)4R5-4	4	336	370	38.16
EOAI(2M)4R5-5	5	355	374	30.05
EOAI(2M)4R5-6	6	355	372	32.31
EOAI(2T)4R5-1	1	339	361	32.68
EOAI(2T)4R5-2	2	349	367	35.81
EOAI(2T)4R5-3	3	348	365	32.07
EOAI(2T)4R5-4	4	348	366	32.15
EOAI(2T)4R5-5	5	342	361	30.12
EOAI(2T)4R5-6	6	246	327	21.77

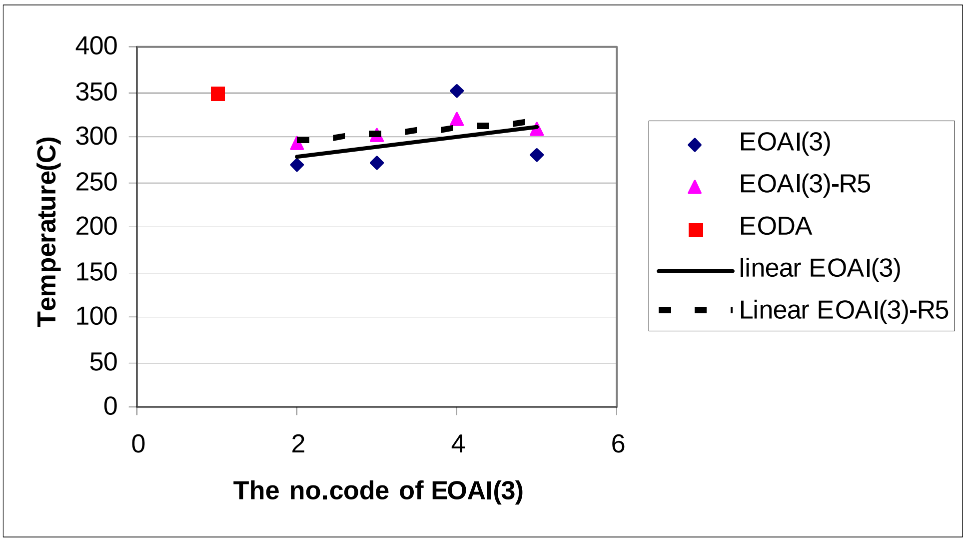

Figure 5.4 Degradation temperature at 5% weight loss of amide-imide-epoxy adhesive from tri-carboxylic acid

The x-axis of the curve showed the increase amount of epoxy ratio in the adhesive. The calculate on for the EOAI(3) number come from the number of reactive hydrogen that assume to be exist in the OAI corresponded with the amount of epoxide group in epoxy that combine to be the adhesives. The calculation for the appropriate amount of epoxy that mixed within the adhesive come from the stoichiometric balance between the reactive hydrogen and the EEW (epoxy equivalent weight) of the DGEBA. The calculation can be explain as follows,

Divide2 ; amine EEW = 7467.72/2 = 3733.895
% = 3733.895*100/170 = 2169.409
Epoxy 100 : OAI 2169.409
Divide3 ; amine EEW = 7467.72/3 = 2489.263
% = 2489.263*100/170 = 1464.273
Epoxy 100 : OAI 1464.273
Divide4 ; amine EEW = 7467.72/4 = 1866.948
% = 1866.948*100/170 = 1098.204
Epoxy 100 : OAI 1098.204
Divide5 ; amine EEW = 7467.72/5 = 1493.558
% = 1493.558*100/170 = 878.564
Epoxy 100 : OAI 878.564

The degradation temperature at 5% weight loss of amide-imide-epoxy adhesive with NBR rubber was almost higher than amide-imide-epoxy adhesive without NBR rubber. The maximum degradation temperature at 5% weight loss of amide-imide-epoxy adhesive without NBR rubber is EOAI(3)4 and amide-imide-epoxy adhesive with NBR rubber is EOAI(3)4R5. From Figure 5.4, the increase in the amount of crosslinked resulted from the increase weight ratio of epoxy in the adhesives concluded in the slightly increase in the degradation temperatures. The maximum occurred at EOAI(3)4 might be because of the optimum balance between the hydrogen that can react of the OAI and the number of the epoxide that can react of the epoxy created the highest crosslinked that specially increase in the degradation temperature. The EODA has very high degradation temperature equivalent with the best value of the EOAI because the EODA also has the high crosslink balance between epoxide group of DGEBA and reactive hydrogen of ODA.

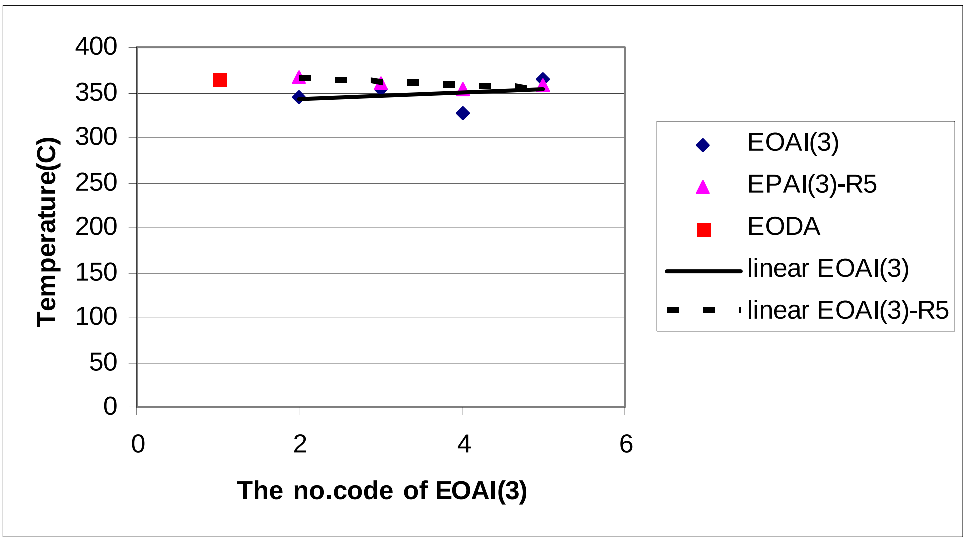

Figure 5.5 Degradation temperature at 10% weight loss of amide-imide-epoxy adhesive from tri-carboxylic acid

The degradation temperature at 10% weight loss of amide-imide-epoxy adhesive with NBR rubber was higher than amide-imide-epoxy adhesive without NBR rubber. However, from the data, the rate of losing weight of NBR might be higher than the normal OAI because if we reduce the amount of OAI in the adhesive, the adhesive loss weight faster than the non-rubber-toughening samples. Moreover, the Td10% of EOAI(3) without the rubber-toughening showed the same tendency as the Td5%. This might be because of the decrease amount of OAI in the samples. In Figure 5.5, the maximum degradation temperature at 10% weight loss of amide-imide-epoxy adhesive without NBR rubber is EOAI(3)5 and amide-imide-epoxy adhesive with NBR rubber is EOAI(3)2R5. The both the lowest Td10% were EOAI(3)4 which show the maxima in the Td5%. This might be because of the rate of burning of the crosslink might be higher than the normal EOAI(3). Thus, the most highest crosslinked samples showed the highest Td5% but the lowest Td10%.

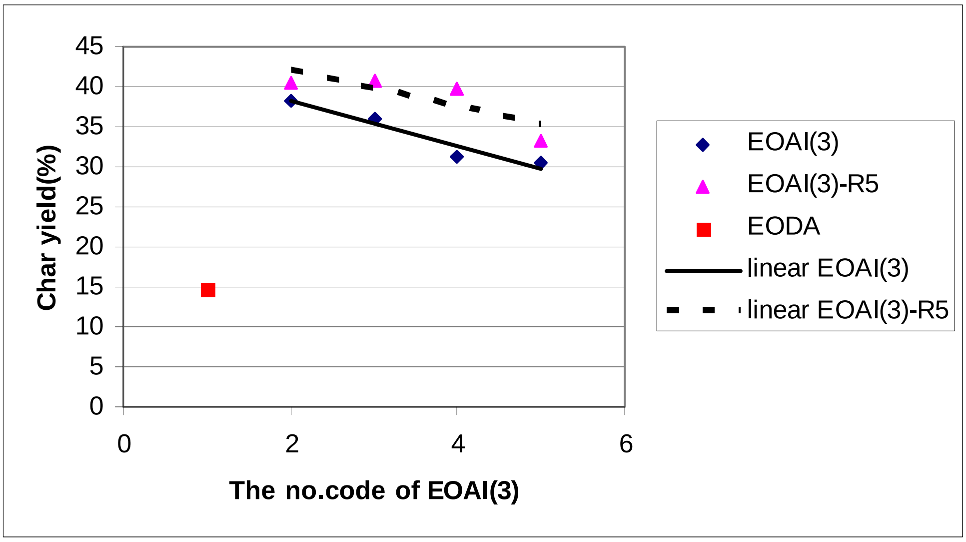

Figure 5.6 Char yield at 800^{o}c of amide-imide-epoxy adhesive from tri-carboxylic acid

Char yield at 800^{o}C of amide-imide-epoxy adhesive with NBR rubber was higher than amide-imide-epoxy adhesive without NBR rubber because the NBR leave more char than the normal EOAI(3). The maximum char yield of amide-imide-epoxy adhesive without NBR rubber is EOAI(3)2 and amide-imide-epoxy adhesive with NBR rubber is EOAI(3)4R5. (Figure 5.6)

The benzene ring normally are difficult to degrade than the normal aliphatic organic, thus, the benzene ring will leave more char than the normal aliphatic organic. The amide-imide-epoxy adhesives degraded at higher temperature than EODA because the amide-imide-epoxy adhesives have more benzene ring in the polymer chain than EODA. The amount of char from the amide-imide-epoxy adhesives decreased when the OAI content decreased, because the OAI will leave most of the char in the adhesives. The amide-imide-epoxy adhesives with NBR rubber are degraded at higher temperature than amide-imide-epoxy adhesive without NBR rubber because of the characteristic of the degradation of NBR.

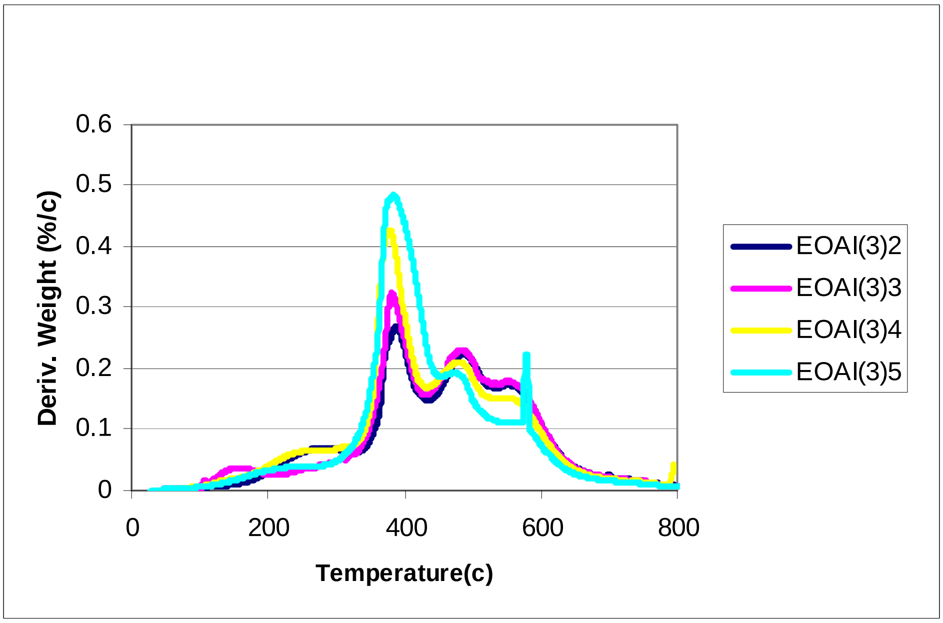

Figure 5.7 The derivative weight from TGA curve of amide-imide-epoxy adhesive without NBR rubber in N_2 at heating rate 10 ^{o}c/min

Derivative weight will show the starting point of the degradation by losing weight abruptly from the normal condition. From Figure 5.7 shows the four steps degradation of the amide-imide-epoxy adhesives. It's expected that the first step corresponded to the aliphatic C-C degradation at 200^{o}C, while the second step benzene ring started to decompose at 400^{o}C. Moreover, the third step C-N bonds were more durable and degraded at 500^{o}C and the final step every organic were degraded completely at 600^{o}c.

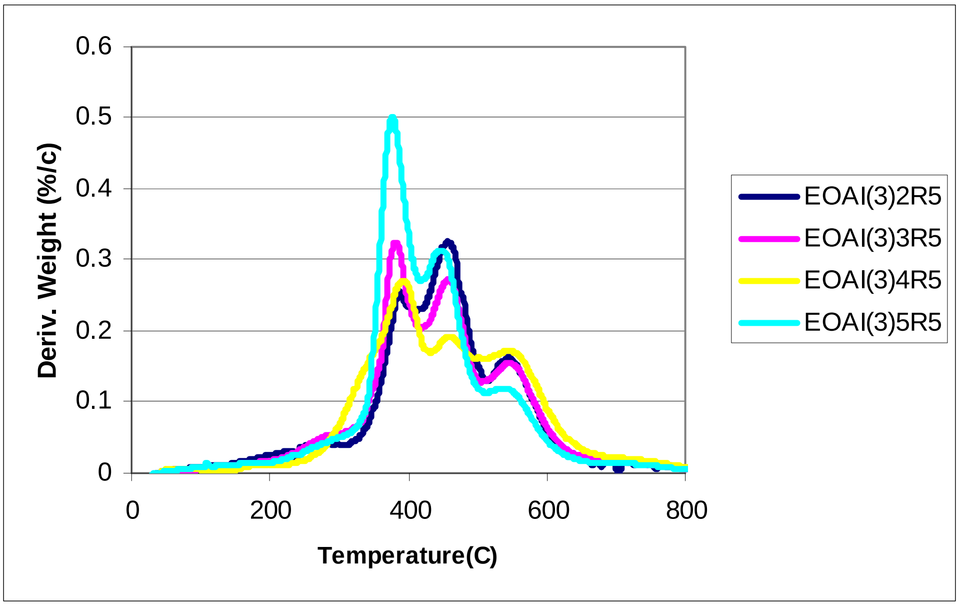

Figure 5.8 The derivative weight from TGA curve of amide-imide-epoxy adhesive with NBR rubber in N_2 at heating rate 10 ^{o}c/min

From Figure 5.8, there were four steps of degradation of the amide-imide-epoxy adhesive with NBR rubber. The first step C-C degraded at 250^{o}C, the second step benzene degraded at 380^{o}C, the third step C-N degraded at 450^{o}C and the final step all organic degraded completely at 550^{o}C. From the derivative weight, show the similar step of degradation but the different temperature and different amount of the degradation in processes. The C-C bond was harder to break (showed higher temperature), while the C-N bond was easier to break (showed lower temperature). This might be because of the more complex morphology of the rubber-toughening and the degradation of the nitrile (C-N) bond in the rubber that was easier than the C-N bond in the EOAI(3). The rate of degradation of rubber-toughening samples are higher than the non-toughening because the more deplete of the bond in the final step of the toughening come before the non-toughening.

5.2.3 Degradation temperature and char yield of amide-imide-epoxy adhesive from di-carboxylic acid

The degradation temperature at 5% weight loss, degradation temperature at 10% weight loss and char yield of the MDI samples are shown in Table 5.4.

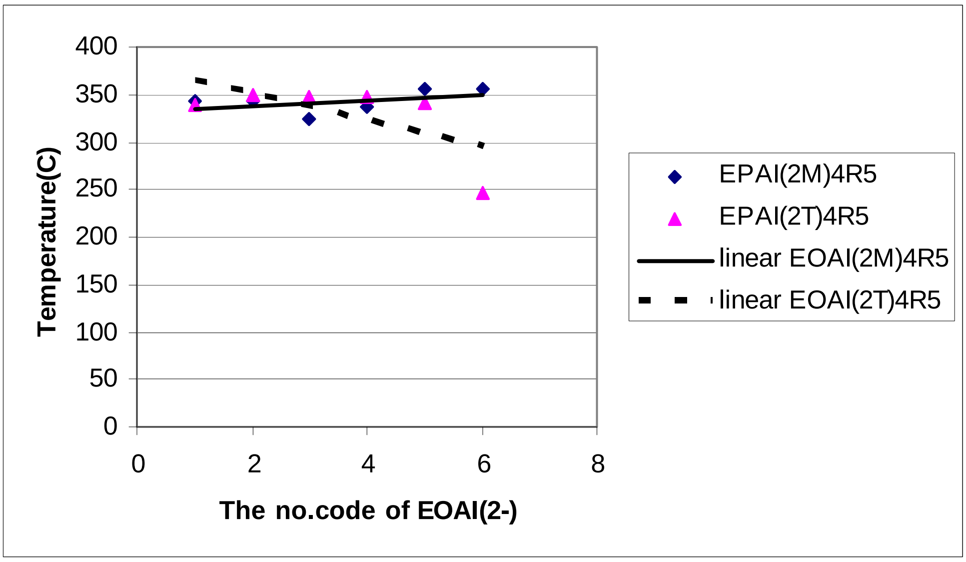

Figure 5.9 Degradation temperature at 5% weight loss of amide-imide-epoxy adhesive from di-carboxylic acid

The degradation at 5% weight loss of amide-imide-epoxy adhesive from TDI were slightly higher than from MDI. However, the Td5% were in the same vicinity with showed the similar effect of the isocyanate on the Td5%. The TDI did not have the aliphatic ring inside the molecules, so the degradation temperature were only slightly higher. The maximum degradation temperature at 5% weight loss of amide-imide-epoxy adhesive from MDI is EOAI(2M)4R5-5 and amide-imide-epoxy adhesive from TDI is EOAI(2T)4R5-2. (Figure 5.9)

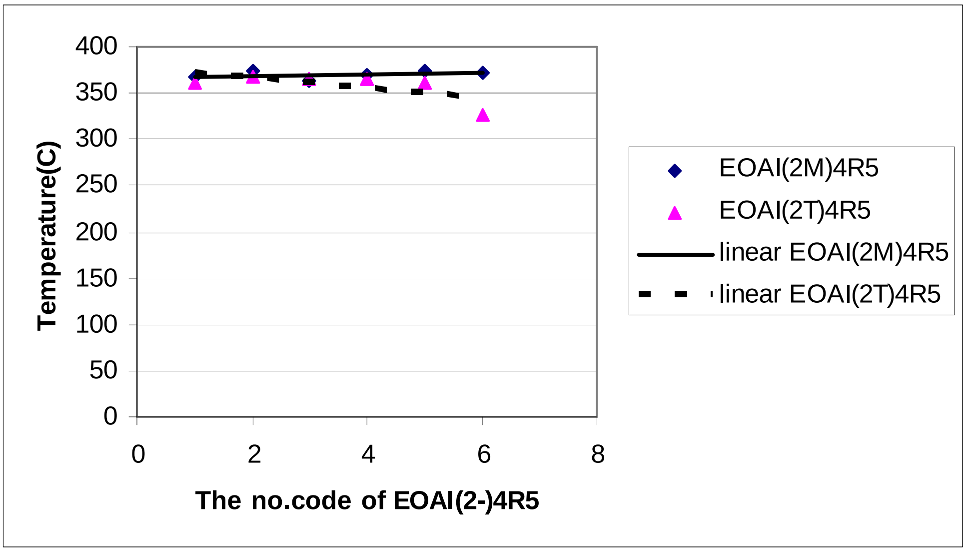

Figure 5.10 Degradation temperature at 10% weight loss of amide-imide-epoxy adhesive from di-carboxylic acid

The degradation at 10% weight loss of amide-imide-epoxy adhesive from MDI were in the same vicinity as the TDI. However, after losing the aliphatic chain of MDI from Td5%, the degradation mechanism for MDI is the same as TDI. The maximum degradation temperature at 10% weight loss of amide-imide-epoxy adhesive from MDI is EOAI(2M)4R5-5 and amide-imide-epoxy adhesive from TDI is EOAI(2T)4R5-2. (Figure 5.10)

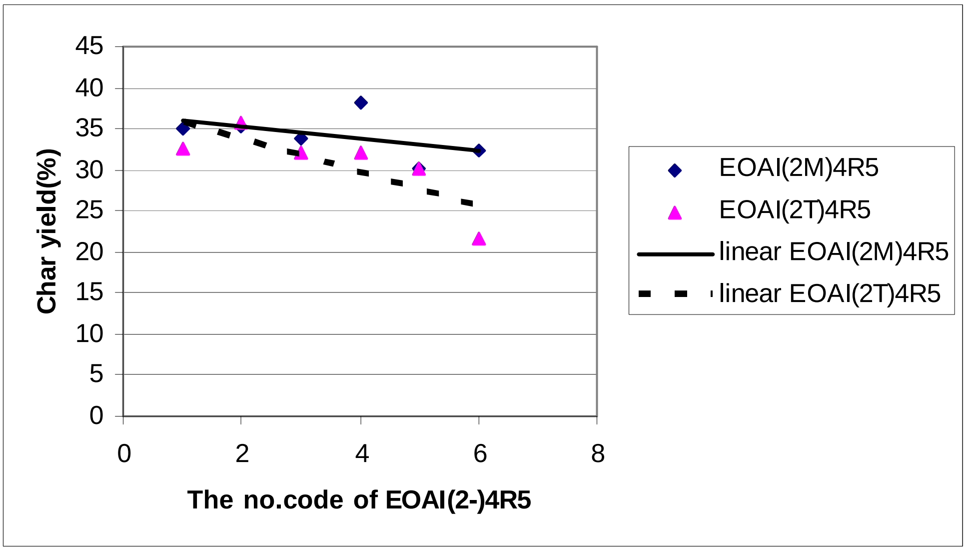

Figure 5.11 Char yield at 800^{o}c of amide-imide-epoxy adhesive from di-carboxylic acid

The char yields of amide-imide-epoxy adhesive from MDI were higher than from TDI, because the MDI has one more benzene ring than the TDI. If the concentration of the imide in EOAI(2-) decrease (more last number of EOAI(2-)4R5-6), the samples tend to have less char yield. The maximum char yield of amide-imide-epoxy adhesive from MDI is EOAI(2M)4R5-4 and amide-imide-epoxy adhesive from TDI is EOAI(2T)4R5-2. (Figure 5.11)

5.3 Adhesion peel test

The amide-imide-epoxy adhesives test the mechanical properties by adhesion peel test that report the elongation at break and tensile strebgth at break but don’t report the modulus.

5.3.1 Elongation at break

The elongation of the stud test will show the stiffness of the samples. If the samples were more flexible, the elongations at break tend to be higher. If the samples were stiffer, the elongations at break tend to be lower. The elongations of amide-imide-epoxy adhesive are shown in Table 5.5.

Table5.5 The elongation at break of amide-imide-epoxy adhesive

Code	No.	Elongation at break (mm)
EODA	1	1.244
EOAI(3)2	2	0.313
EOAI(3)3	3	0.500
EOAI(3)4	4	0.350
EOAI(3)5	5	0.150
EOAI(3)2R5	2	0.436
EOAI(3)3R5	3	0.413
EOAI(3)4R5	4	0.518
EOAI(3)5R5	5	0.508
EOAI(2M)4R5-1	1	0.486
EOAI(2M)4R5-2	2	0.508

EOAI(2M)4R5-3	3	0.492
EOAI(2M)4R5-4	4	0.263
EOAI(2M)4R5-5	5	0.730
EOAI(2M)4R5-6	6	0.457
EOAI(2T)4R5-1	1	0.441
EOAI(2T)4R5-2	2	0.643
EOAI(2T)4R5-3	3	0.514
EOAI(2T)4R5-4	4	0.882
EOAI(2T)4R5-5	5	0.730
EOAI(2T)4R5-6	6	0.742

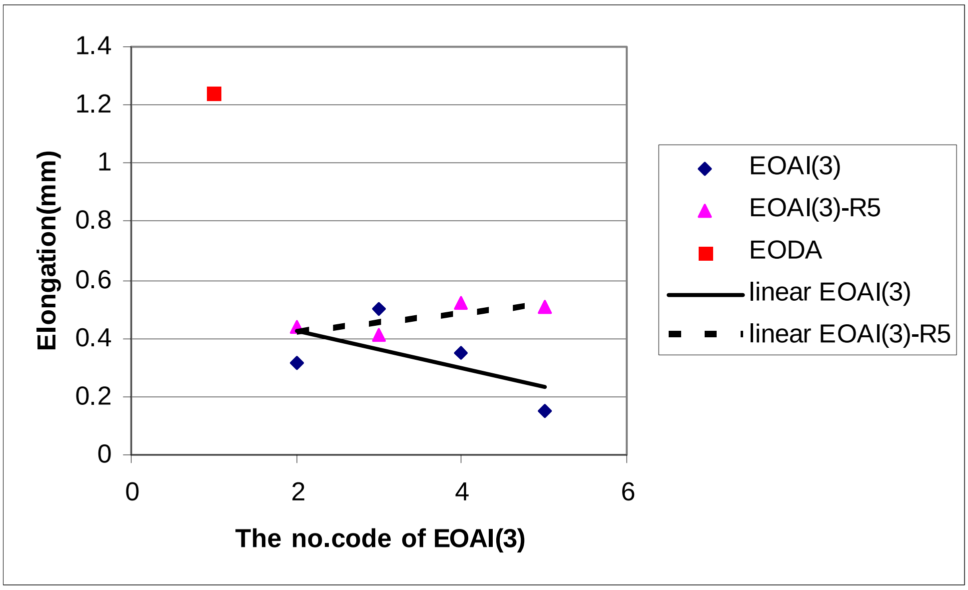

Figure 5.12 Elongation at break of amide-imide-epoxy adhesive from tri-carboxylic acid

The elongations of amide-imide-epoxy adhesives with NBR rubber were generally higher than amide-imide-epoxy adhesives without NBR rubber, because the rubber will make the composite more flexible. However, the rubber toughening samples still have lower elongation than the ODA adhesive without the rubber. This might be because the EODA can generate more crosslink within the equal volume more than the OAI even toughen with rubber. The elongation of amide-imide-epoxy adhesive without NBR rubber decreased when the OAI decreased because the more crosslink in the sample make the composite stiffer. However, the EODA expected to have more crosslink per g than the OAI, but the elongation was very good due to the characteristic of the amine in the ODA. The elongation of amide-imide-epoxy adhesive with NBR rubber increased when the OAI decreased, which show the effect of rubber toughening and the increase in the crosslink together. The maximum elongation of amide-imide-epoxy adhesive without NBR rubber is EOAI(3)2 and amide-imide-epoxy adhesive with NBR rubber is EOAI(3)3R5. (Figure 5.12)

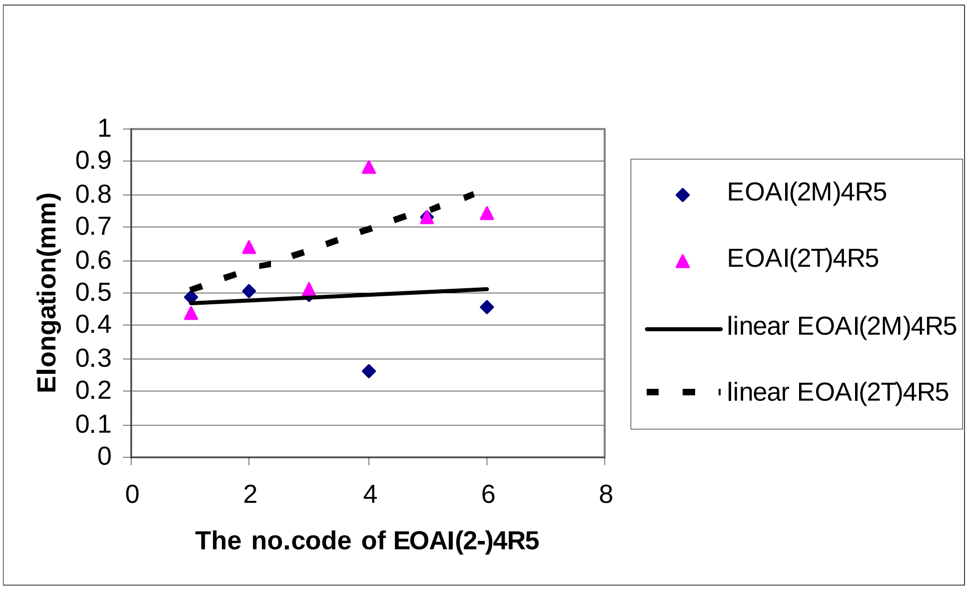

Figure 5.13 Elongation at break of amide-imide-epoxy adhesive from di-carboxylic acid

The elongations of amide-imide-epoxy adhesives from TDI are higher than amide-imide-epoxy adhesives from MDI because TDI can generate more crosslink per g more than MDI which is double of the size. The maximum elongation of amide-imide-epoxy adhesive from MDI is EOAI(2M)4R5-5 and from TDI is EOAI(2T)4R5-4. (Figure 5.13) The sample with MDI have less elongation than the comparable three arm acid (EOAI(3)4R5). However, the sample with the TDI have larger elongation than the comparable three arm acid (EOAI(3)4R5, 0.518) if the amount of amine is exceed 135 and imide bond less than 75. Moreover the maximum elongation occurred, when the EOAI(2T)4R5 was used, but cannot be comparable to EODA sample because of the dense of the crosslink per g of adhesive that apply between stud.

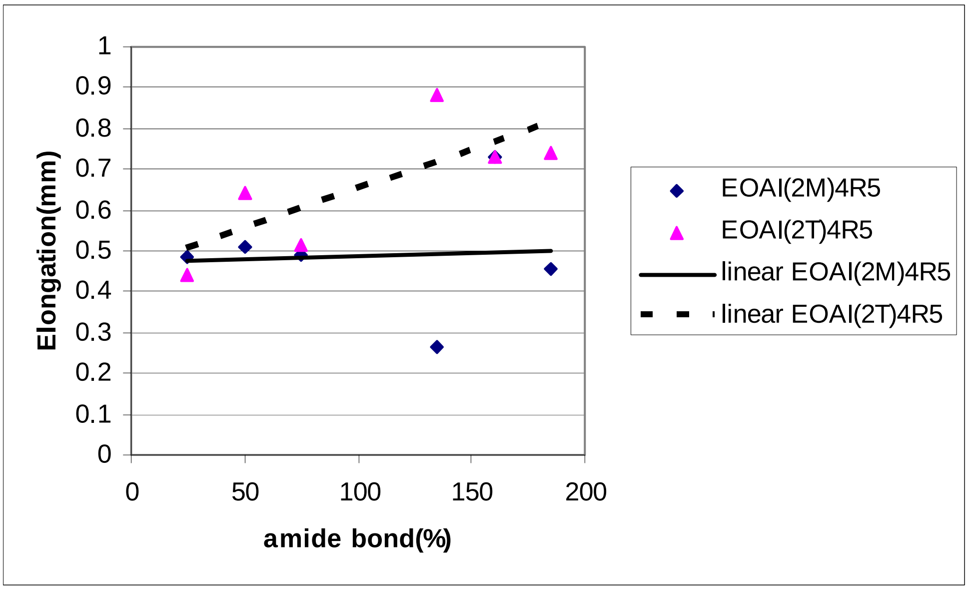

Figure 5.14 Elongation at break vs amide bond of amide-imide-epoxy adhesive from di-carboxylic acid

The elongations of amide-imide-epoxy adhesives from MDI have no trend when the amide bond increased. In other words, the variation in the elongation of the MDI sample of two arm acids is scattered. The elongation of amide-imide-epoxy adhesives from TDI increased when the amide bond increased and when the imide bond decreased. From Figure 5.14, the maximum elongation of amide-imide-epoxy adhesive from MDI at amide bond is 160 (EOAI(2M)4R5-5) and amide-imide-epoxy adhesive from TDI at amide bond is 135 (EOAI(2T)4R5-4). However, because of the characteristic of the reactant, the amide bond cannot be increase more than 200 (without imide bond) and the imide cannot be less than 10, so the appropriate ratio of the amine for the elongation is the EOAI(2T)4R5-4.

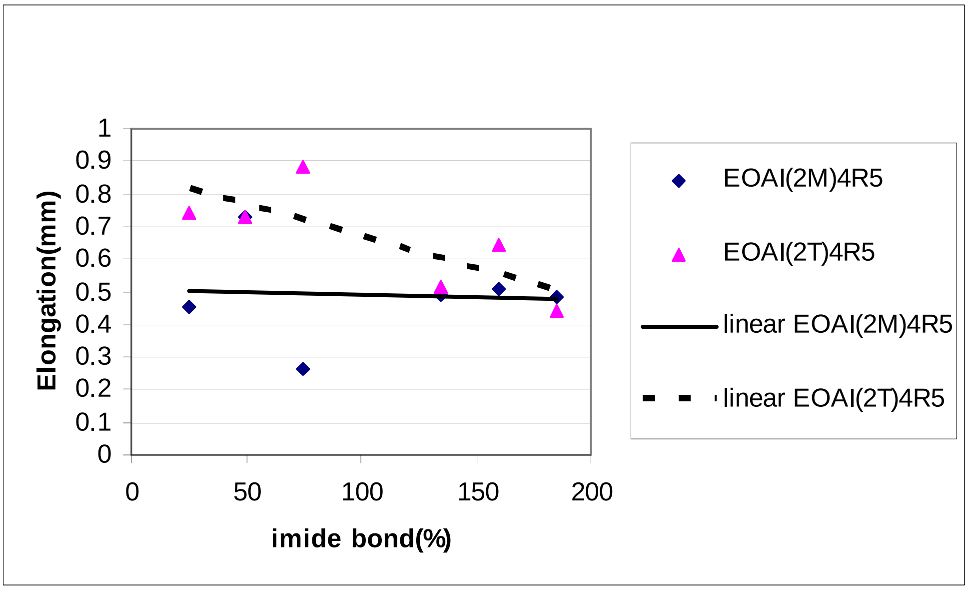

Figure 5.15 Elongation at break vs imide bond of amide-imide-epoxy adhesive from di-carboxylic acid

By the same characteristics, the elongations of amide-imide-epoxy adhesives from MDI have no trend when the imide bond increased and the variation of the elongation is scattered. The elongation of amide-imide-epoxy adhesives from TDI decreased when the imide bond increased by the same times as the amine bond increased. From Figure 5.15, the maximum elongation of amide-imide-epoxy adhesive from MDI at imide bond is 50 and amide-imide-epoxy adhesive from TDI at imide bond is 75. By the same reason as above, the same conclusion that EOAI(2T)4R5-4 is the best for the elongation can be found.

The elongation of amide-imide-epoxy adhesive from di-carboxylic was higher than amide-imide-epoxy adhesive from tri-carboxylic, if the amine ratio is more than the imide ratio.

5.3.2 Tensile strength at break

The tensile strength at break are summarized in Table 5.6.

Table5.6 The tensile strength at break of amide-imide-epoxy adhesive

Code	No.	Tensile strength at break (MPa)
EODA	1	22.938
EOAI(3)2	2	3.996
EOAI(3)3	3	3.585
EOAI(3)4	4	2.511
EOAI(3)5	5	2.480
EOAI(3)2R5	2	4.532
EOAI(3)3R5	3	5.661
EOAI(3)4R5	4	8.297
EOAI(3)5R5	5	7.589
EOAI(2M)4R5-1	1	8.270
EOAI(2M)4R5-2	2	4.230
EOAI(2M)4R5-3	3	4.518
EOAI(2M)4R5-4	4	2.132
EOAI(2M)4R5-5	5	4.635
EOAI(2M)4R5-6	6	3.317
EOAI(2T)4R5-1	1	5.384
EOAI(2T)4R5-2	2	7.269
EOAI(2T)4R5-3	3	5.989
EOAI(2T)4R5-4	4	9.836
EOAI(2T)4R5-5	5	10.510
EOAI(2T)4R5-6	6	8.076

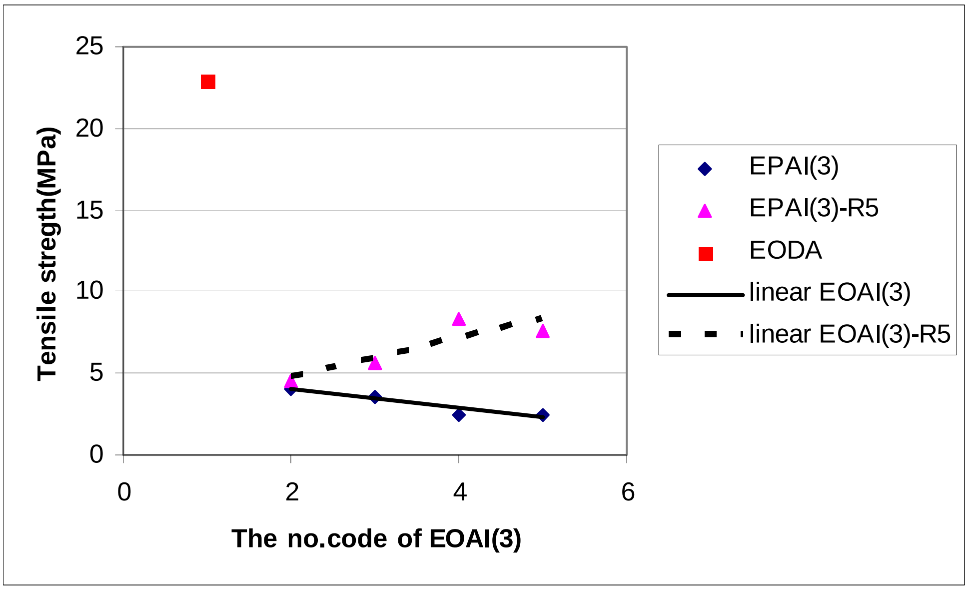

Figure 5.16 Tensile strength at break of amide-imide-epoxy adhesive from tri-carboxylic acid

The tensile strength of amide-imide-epoxy adhesives with NBR rubber are higher than amide-imide-epoxy adhesives without NBR rubber because the rubber will modify the crack characteristic of the samples, so the sample can received more load before yield. The tensile strength of amide-imide-epoxy adhesive without NBR rubber decreased when the OAI decreased which is contradicting to the increase in crosslink. However, more crosslink can make the sample stiff and fragile, so the sample can have less tensile strength. The tensile strength of amide-imide-epoxy adhesive with NBR rubber increased when the OAI decreased because the distribution of the crosslink within the sample by toughening rubber will increase the tensile strength. The maximum tensile strength of amide-imide-epoxy adhesive without NBR rubber is EOAI(3)2 and amide-imide-epoxy adhesive with NBR rubber is EOAI(3)4R5, from Figure 5.16. However, the tensile strength of EODA is very high, even more than any other rubber toughening EOAI(3). The reason might be because of the amine characteristic of ODA and denser crosslink per g of the sample that generate three time higher tensile strength.

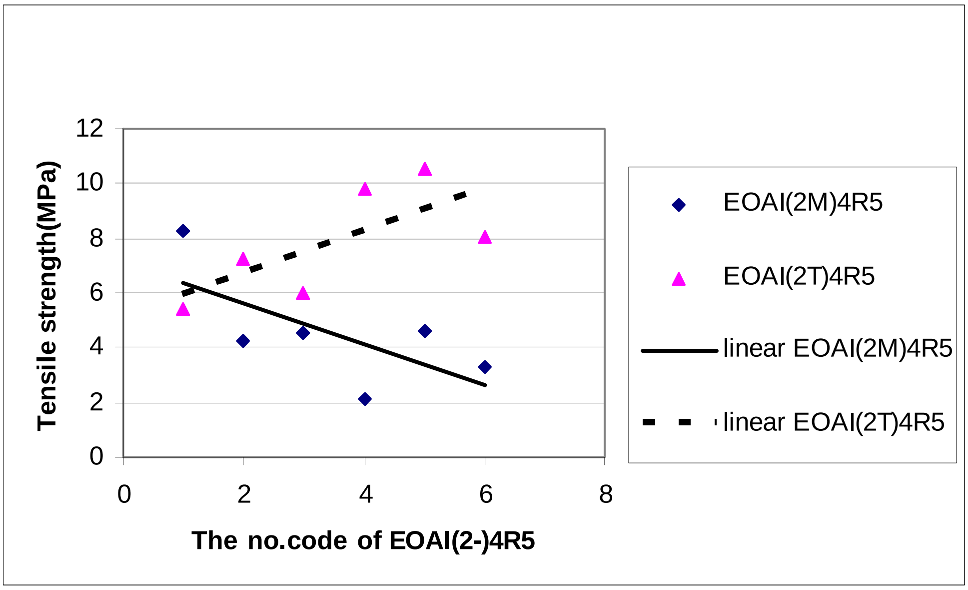

Figure 5.17 Tensile strength at break of amide-imide-epoxy adhesive from di-carboxylic acid

The tensile strength of amide-imide-epoxy adhesives from TDI are higher than amide-imide-epoxy adhesives from MDI, because the TDI samples have more dense crosslink per g than the MDI which the molecule is double size. The maximum tensile strength of amide-imide-epoxy adhesive from MDI is EOAI(2M)4R5-1 and from TDI is EOAI(2T)4R5-5, from Figure 5.17. When compare the three arm acid system with two arm acid system, the two arm acid sample have higher tensile strength if the amount of the amide is higher than 135 and the amount of imide is below 75. However, this still cannot be comparable to the EODA which have the double tensile strength than the best of two arm acid with TDI (EOAI(2T)4-R5-5), because of the small special characteristic amine of dense crosslink ODA.

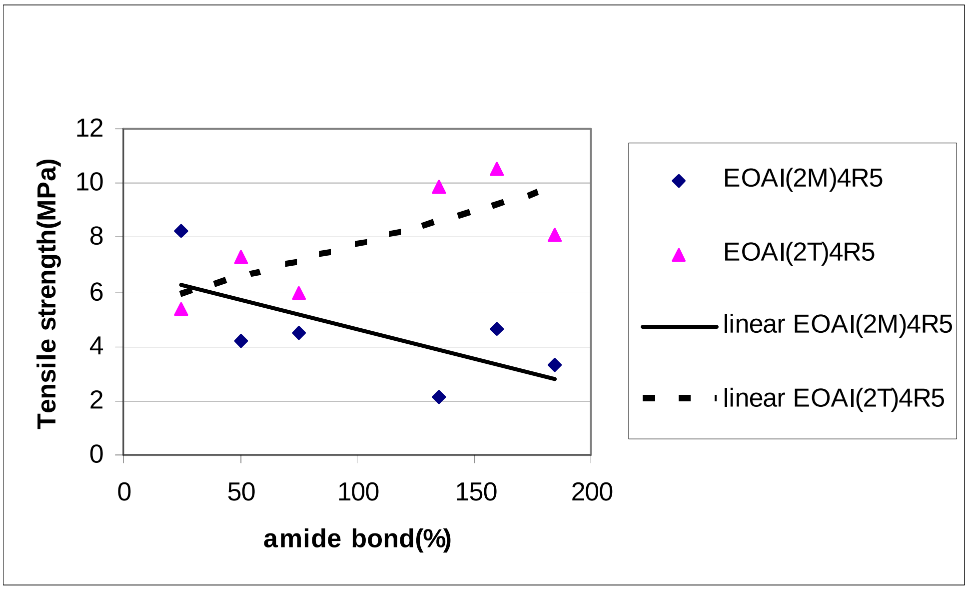

Figure 5.18 Tensile strength at break vs amide bond of amide-imide-epoxy adhesive from di-carboxylic acid

The tensile strength of amide-imide-epoxy adhesives from MDI decreased when the amide bond increased. This might be because of the stiffening of the samples of MDI when the crosslink according to amide was increased. The tensile strength of amide-imide-epoxy adhesives from TDI increased when the amide bond increased which is the same trend as the elongation and might be explain by the more crosslink from amide groups. The maximum tensile strength of amide-imide-epoxy adhesive from MDI at amide bond is 25 and amide-imide-epoxy adhesive from TDI at amide bond is 160, from Figure 5.18. However, the gain in tensile strength has to balance with the gain in elongation to get the most ductile adhesive.

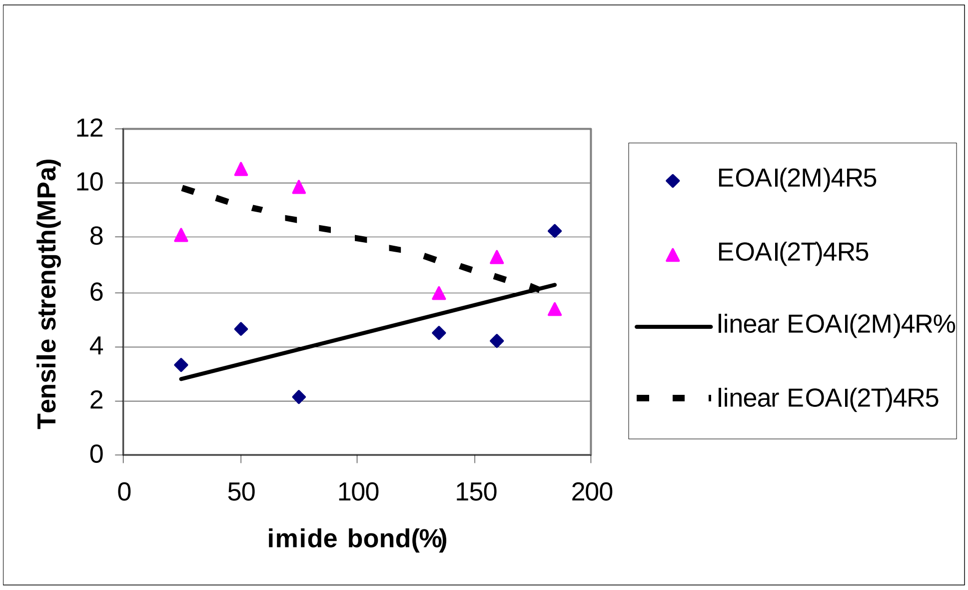

Figure 5.19 Tensile strength at break vs imide bond of amide-imide-epoxy adhesive from di-carboxylic acid

Contradict to the amide bond, the tensile strength of amide-imide-epoxy adhesives from MDI increased when the imide bond increased. However, this increase came from the less stiff sample from amide. Both amide and imide have to be together because of the characteristics of the reactant, so the reverse contribution was obviously found. The tensile strength of amide-imide-epoxy adhesives from TDI decreased when the imide bond increased which is also the opposite for what we found from amide bond. The maximum tensile strength of amide-imide-epoxy adhesive from MDI at imide bond is 185 and amide-imide-epoxy adhesive from TDI at imide bond is 50, from Figure 5.19.

The tensile strength of amide-imide-epoxy adhesive from di-carboxylic was higher than amide-imide-epoxy adhesive from tri-carboxylic, if the TDI was used and the amount of amide is above 135.

5.3.3 Toughness

Toughness is the product of tensile strength at break and elongation at break. By definition, it means the energy that can be absorbed by the sample before failure. By geometry, it defines as the area under the tensile stress and elongation curve. By mathematics, it approximately defines by the half of the multiplication product of tensile strength and elongation. To explain the durable of the materials, both tensile strength and elongation have to be considered. Toughness is one of the key parameter to numeric measure the durability of materials. The toughness can be approximated in Table 5.7.

Table5.7 The toughness of amide-imide-epoxy adhesive

Code	No.	Toughness
EODA	1	14.271
EOAI(3)2	2	0.625
EOAI(3)3	3	0.897
EOAI(3)4	4	0.439
EOAI(3)5	5	0.186
EOAI(3)2R5	2	0.988
EOAI(3)3R5	3	1.170
EOAI(3)4R5	4	2.150
EOAI(3)5R5	5	1.927
EOAI(2M)4R5-1	1	2.008
EOAI(2M)4R5-2	2	1.074
EOAI(2M)4R5-3	3	1.112
EOAI(2M)4R5-4	4	0.281
EOAI(2M)4R5-5	5	1.692
EOAI(2M)4R5-6	6	0.757
EOAI(2T)4R5-1	1	1.188
EOAI(2T)4R5-2	2	2.338
EOAI(2T)4R5-3	3	1.538
EOAI(2T)4R5-4	4	4.340
EOAI(2T)4R5-5	5	3.836
EOAI(2T)4R5-6	6	2.995

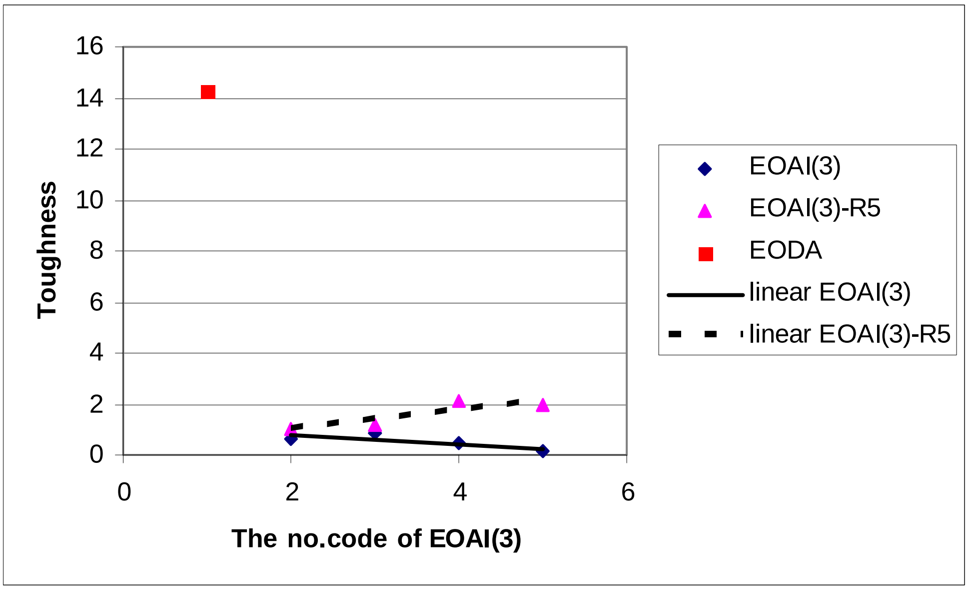

Figure 5.20 Toughness of amide-imide-epoxy adhesive from tri-carboxylic acid

The toughness of amide-imide-epoxy adhesives with NBR rubber are higher than amide-imide-epoxy adhesives without NBR rubber, because the toughening effects from the rubber that increase the absorbed failure energy in the materials. The toughness of amide-imide-epoxy adhesive without NBR rubber decreased when the OAI decreased, while the toughness of amide-imide-epoxy adhesive with NBR rubber increased when the OAI decreased. The reasons can be considered to be as same as previous reasons. When concerning the non rubber-toughening adhesive toughness, the increase in crosslink will stiffen the materials. When concerning the rubber-toughening adhesive toughness, the increase in crosslink together with the rubber-toughening will increase the ductility of the samples. The maximum toughness of amide-imide-epoxy adhesive without NBR rubber is EOAI(3)3 and amide-imide-epoxy adhesive with NBR rubber is EOAI(3)4R5, from Figure 5.20. However, the toughness of the EODA was farer above the best of rubber-toughening three arms acid material (EOAI(3)4R5) due to the amine specialty and the denser crosslink per g of adhesive.

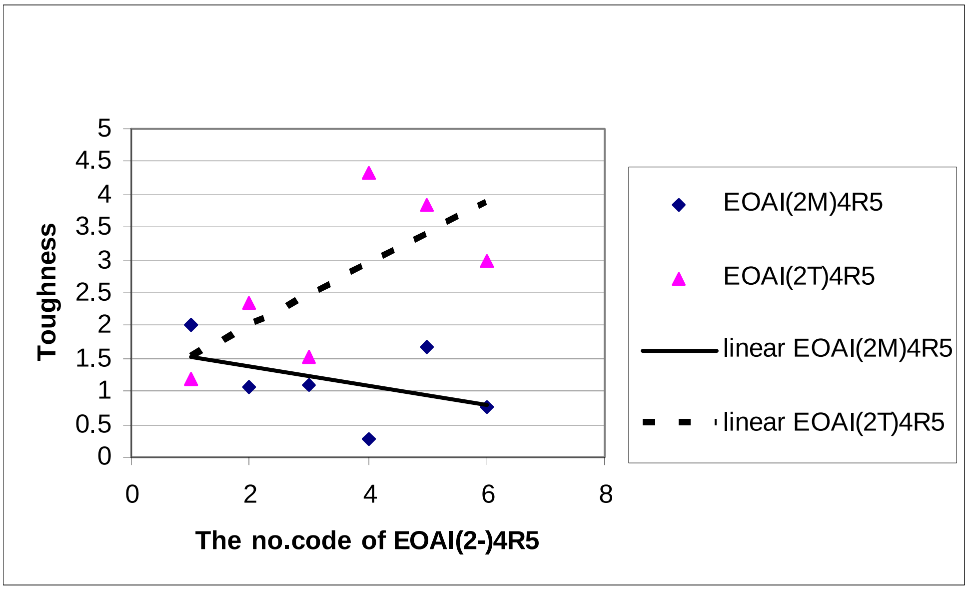

Figure 5.21 Toughness of amide-imide-epoxy adhesive from di-carboxylic acid

Most of the toughness of amide-imide-epoxy adhesives from TDI are higher than amide-imide-epoxy adhesives from MDI because of the denser crosslink per g of TDI. The maximum toughness of amide-imide-epoxy adhesive from MDI is EOAI(2M)4R5-1 and from TDI is EOAI(2T)4R5-4, from Figure 5.21. The toughness of the maximum two arms acid material (EOAI(2T)4R5-4) was about double larger than the comparable three arms acid material (EOAI(3)4R5) and triple less tough than the EODA.

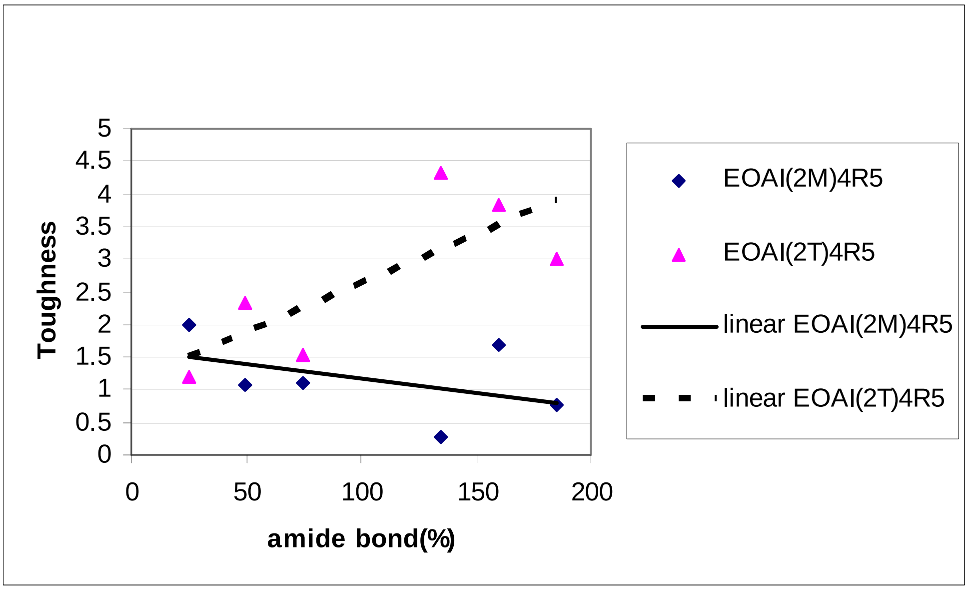

Figure 5.22 Toughness vs amide bond of amide-imide-epoxy adhesive from di-carboxylic acid

The toughness of amide-imide-epoxy adhesives from MDI decreased when the amide bond increased, while the toughness of amide-imide-epoxy adhesives from TDI increased when the amide bond increased. This phenomenon was the same as the tensile strength and the reasons to explain the situation might be the same. The maximum toughness of amide-imide-epoxy adhesive from MDI at amide bond is 25 and amide-imide-epoxy adhesive from TDI at amide bond is 135, from Figure 5.22. Because of the characteristic of the reactants, the best combination of amide and imide bond was 135:75 that will give the highest toughness. However, the other properties have to be considered if the materials might be preferred than the EODA.

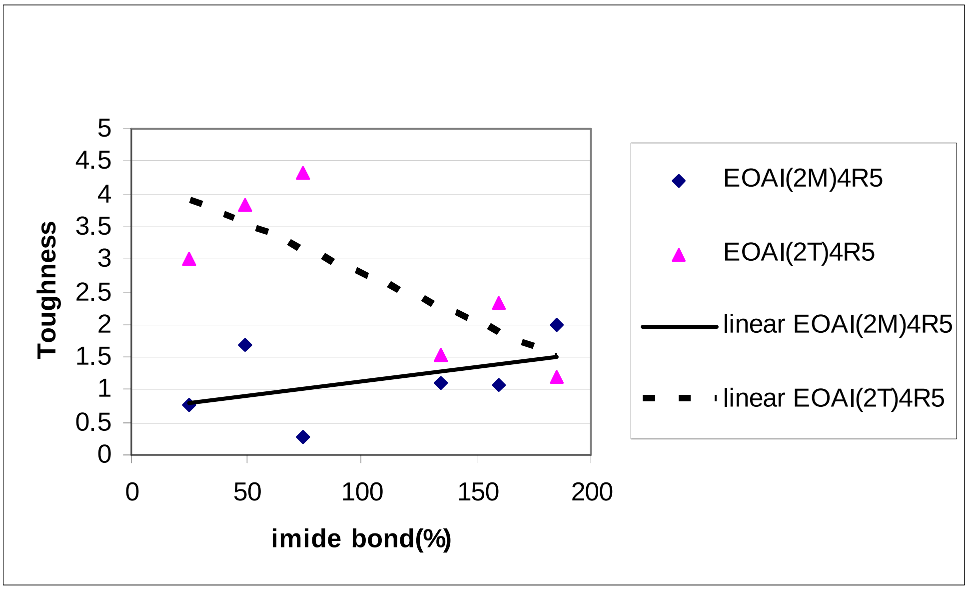

Figure 5.23 Toughness vs imide bond of amide-imide-epoxy adhesive from di-carboxylic acid

The toughness of amide-imide-epoxy adhesives from MDI increased when the imide bond increased, while the toughness of amide-imide-epoxy adhesives from TDI decreased when the imide bond increased. The opposite characteristics from amide bond were found and the reasons might be the same. The maximum toughness of amide-imide-epoxy adhesive from MDI at imide bond is 185 and amide-imide-epoxy adhesive from TDI at imide bond is 75, from Figure 5.23.

The toughness of amide-imide-epoxy adhesive from di-carboxylic was higher than amide-imide-epoxy adhesive from tri-carboxylic, if the amide bond is higher than 135. The most durable di-carboxylic adhesive is EOAI(2T)4R5-4 which give the best toughness and comparable tensile strength with the best elongation.

In general, the mechanical properties of amide-imide-epoxy adhesive from di-carboxylic was higher than amide-imide-epoxy adhesive from tri-carboxylic, if the amide bond is higher than 135. The toughening by rubber will increase the toughness when increase the crosslink and decrease the OAI in the adhesives. Moreover, the higher crosslink in non-rubber-toughening adhesives or the lower OAI will result in lower the toughness. The TDI samples tend to have more toughness than the MDI because of the smaller size of TDI per g of the samples. The MDI will lower the toughness when increase the amide bond, while the TDI will increase the toughness when increase the amide bond. The crosslink and the density of the crosslink might be the cause of these phenomena.

CHAPTER VI

CONCLUSIONS & RECOMMENDATIONS

6.1 Conclusions

In this research, the synthesis oligomer amideimide and amide-imide-epoxy adhesive properties were investigated.

6.1.1 Synthesis of oligomer amideimide

The polyamideimide was synthesized by trimellitic anhydride and can be synthesized by terphthalic acid. A number of conclusions may be summarized as follows:

1. From FT-IR spectrum, it confirmed the functional group of oligomer amideimide.

6.1.2 Amide-imide-epoxy adhesive

The conclusion of this research can be summarized as follows,

1. From DSC, the curing temperature of the amide-imide-epoxy adhesives are 230^{o}C.

2. From TGA, the degradation temperature of the amide-imide-epoxy adhesives decreased when the OAI content decreased. The amide-imide-epoxy adhesives with NBR rubber are degraded at higher temperature than amide-imide-epoxy adhesive without NBR rubber. The amide-imide-epoxy adhesive from MDI are degraded at higher temperature than the amide-imide-epoxy adhesive from TDI.

3. From Universal tensile testing machine

3.1 The elongation of amide-imide-epoxy adhesives with NBR rubber are higher than amide-imide-epoxy adhesives without NBR rubber. The elongation of amide-imide-epoxy adhesives from TDI are higher than amide-imide-epoxy adhesives from MDI. The elongation of amide-imide-epoxy adhesive from di-carboxylic was higher than amide-imide-epoxy adhesive from tri-carboxylic, if the amine ratio is more than the imide ratio.

3.2 The tensile stress of amide-imide-epoxy adhesives with NBR rubber are higher than amide-imide-epoxy adhesives without NBR rubber. The tensile stress of amide-imide-epoxy adhesives from TDI are higher than amide-imide-epoxy adhesives from MDI. The tensile stress of amide-imide-epoxy adhesive from di-carboxylic was higher than amide-imide-epoxy adhesive from tri-carboxylic, if the TDI was used and the amount of amide is above 135.

3.3 The toughness of amide-imide-epoxy adhesives with NBR rubber are higher than amide-imide-epoxy adhesives without NBR rubber. The toughness of amide-imide-epoxy adhesives from TDI are higher than amide-imide-epoxy adhesives from MDI. The toughness of amide-imide-epoxy adhesive from di-carboxylic was higher than amide-imide-epoxy adhesive from tri-carboxylic, if the amide bond is higher than 135.

The mechanical properties of amide-imide-epoxy adhesives with NBR rubber are higher than amide-imide-epoxy adhesives without NBR rubber. The mechanical properties of amide-imide-epoxy adhesives from TDI are higher than amide-imide-epoxy adhesives from MDI. The mechanical properties of amide-imide-epoxy adhesive from di-carboxylic was higher than amide-imide-epoxy adhesive from tri-carboxylic if the amide bond is higher than 135.

6.2 Recommendations

6.2.1 There should be more investigation in the properties of the amide-imide-epoxy adhesive such as dieletic constant, storage modulus etc.

6.2.2 There should be synthesize the OAI open ring to prepare with OAI closed ring.

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APPENDICES

APPENDICES A

THERMOGRAVIMETRIC ANLYSIS (TGA) CHARACTERIZATION

APPENDIX A

THERMOGRAVIMETRIC ANLYSIS (TGA)
CHARACTERIZATION

A-1 TGA diagrams of amide-imide-epoxy adhesive

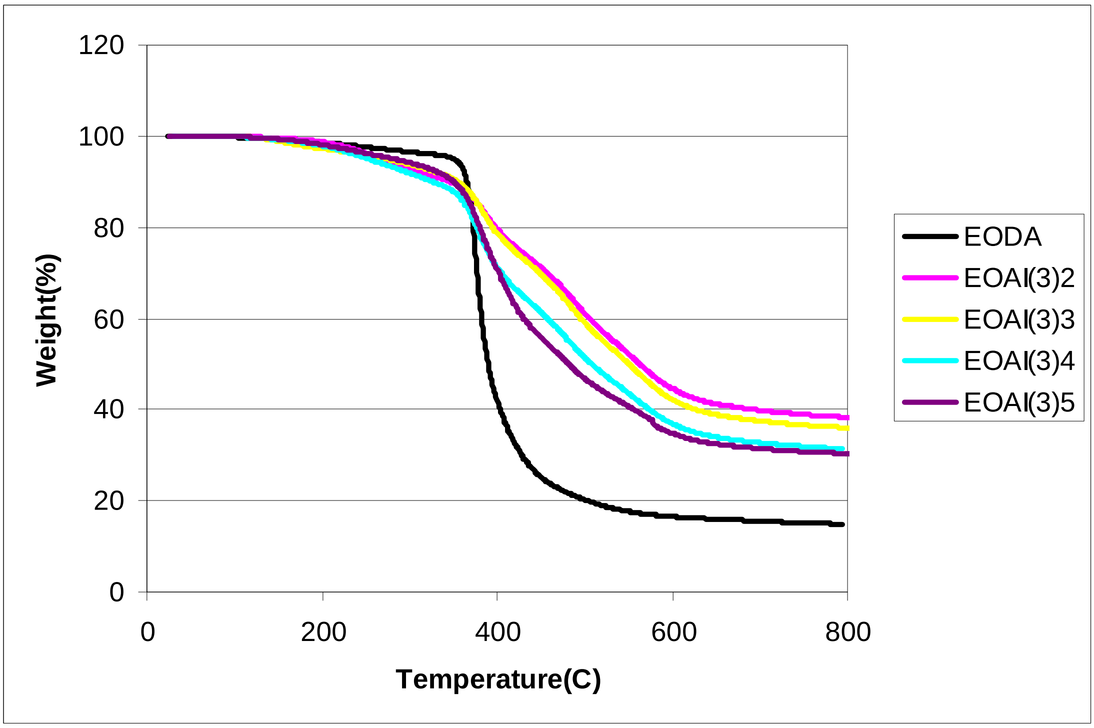

Figure A-1 The weight loss from TGA curve of the amide-imide-epoxy adhesive in N_2 at heating rate 10^{o}c/min

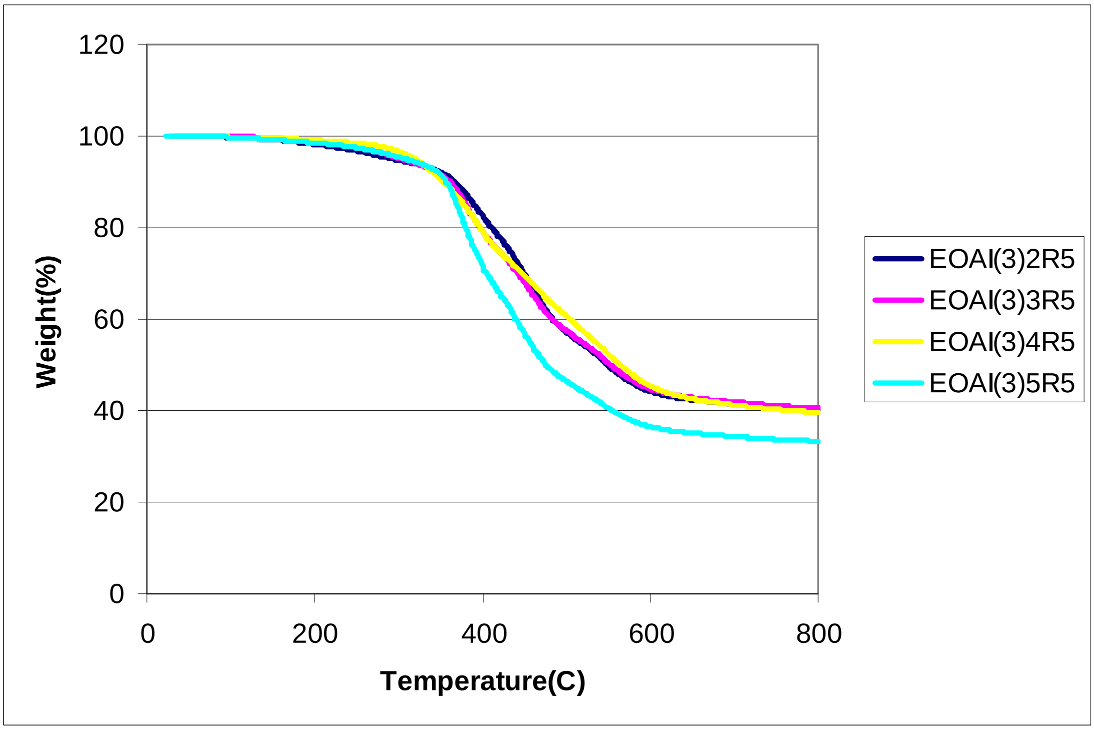

Figure A-2 The weight loss from TGA curve of the amide-imide-epoxy adhesive content NBR rubber in N_2 at heating rate 10^{o}c/min

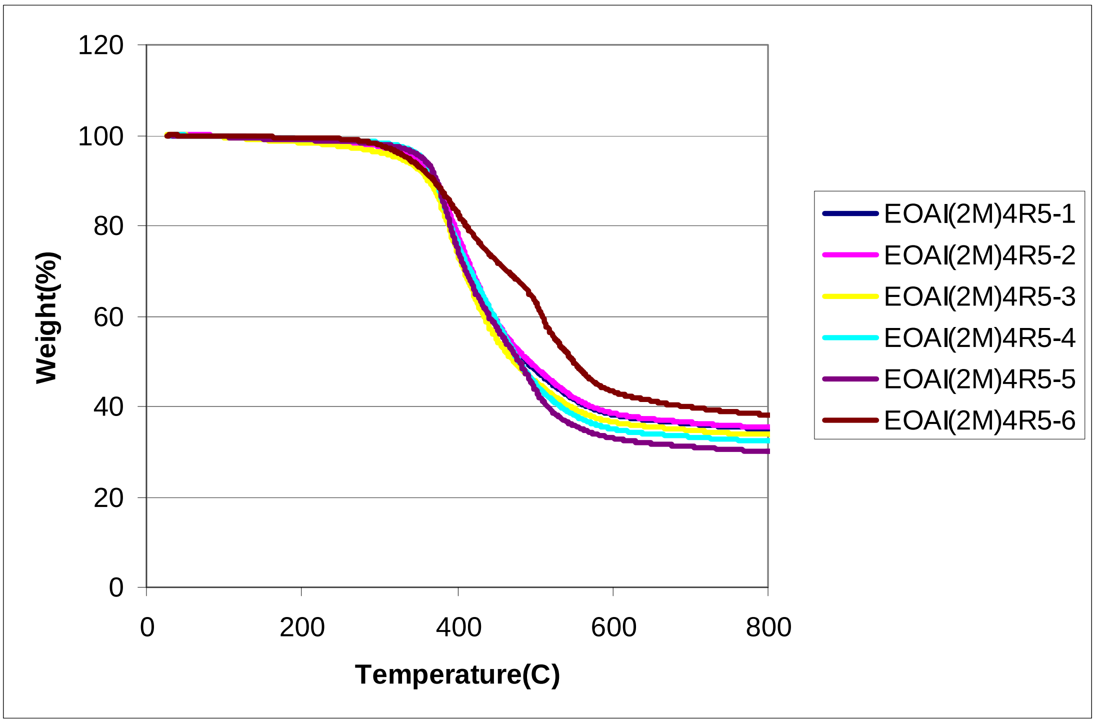

Figure A-3 The weight loss from TGA curve of the amide-imide-epoxy adhesive (from TPA and MDI)content NBR rubber in N_2 at heating rate 10^{o}c/min

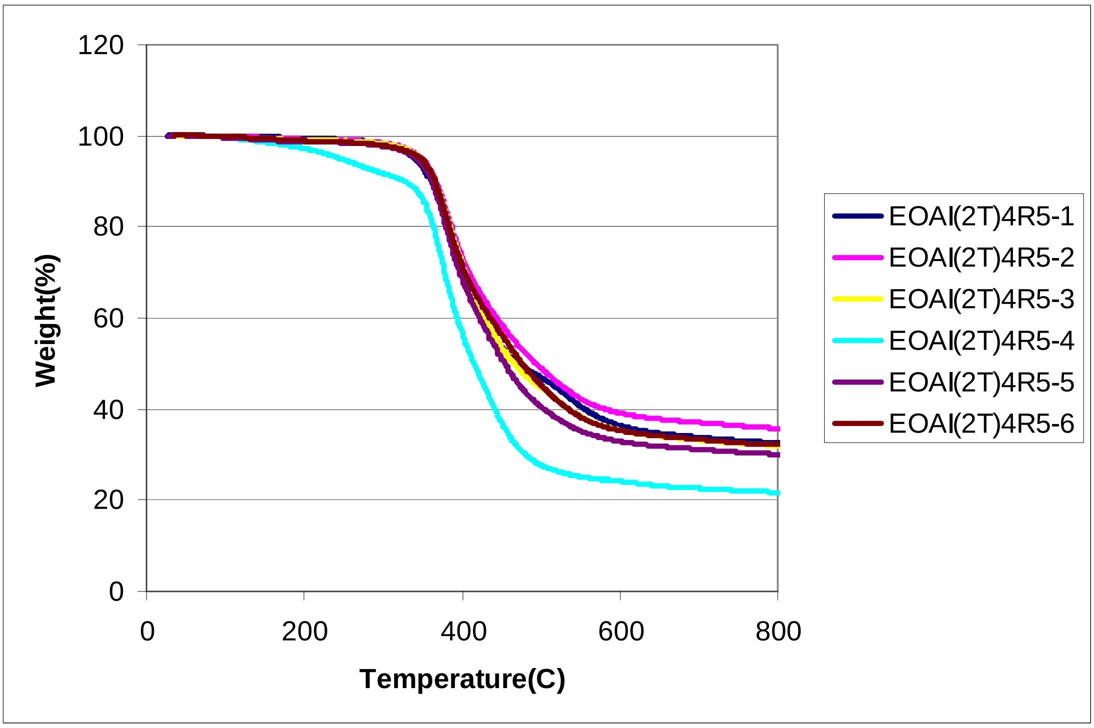

Figure A-4 The weight loss from TGA curve of the amide-imide-epoxy adhesive (from TPA and TDI)content NBR rubber in N_2 at heating rate 10^{o}c/min

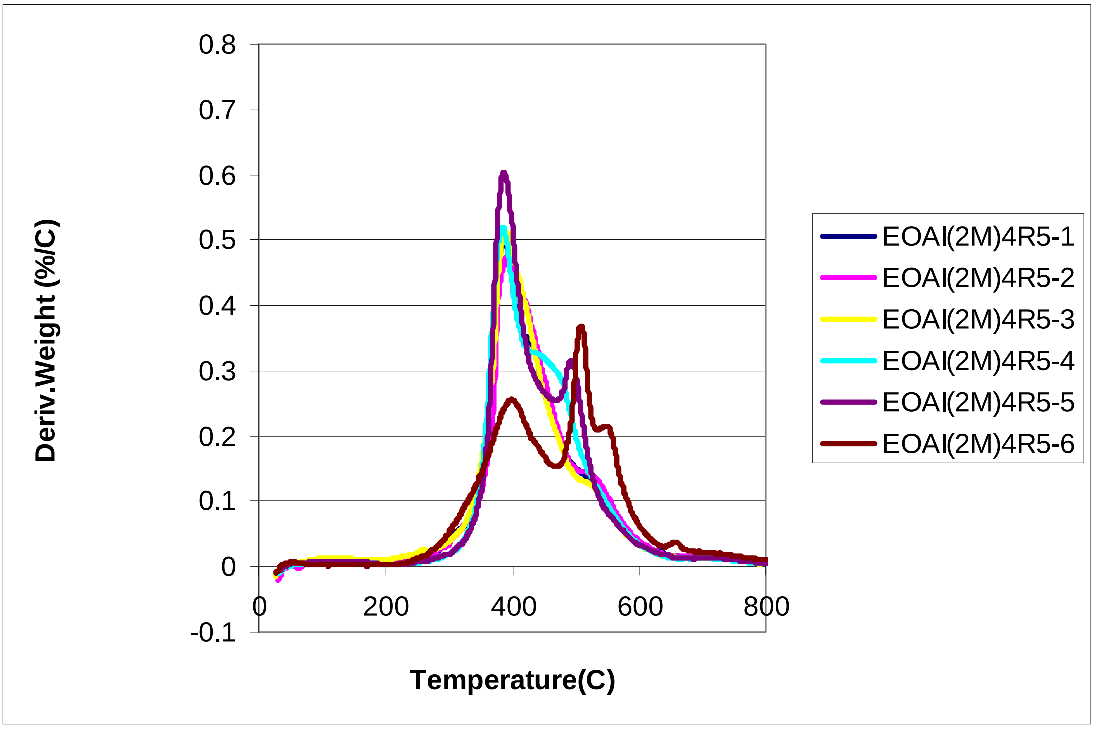

Figure A-5 The derivative weight from TGA curve of amide-imide-epoxy adhesive (from TPA and MDI) content NBR rubber in N_2 at heating rate 10 ^{o}c/min

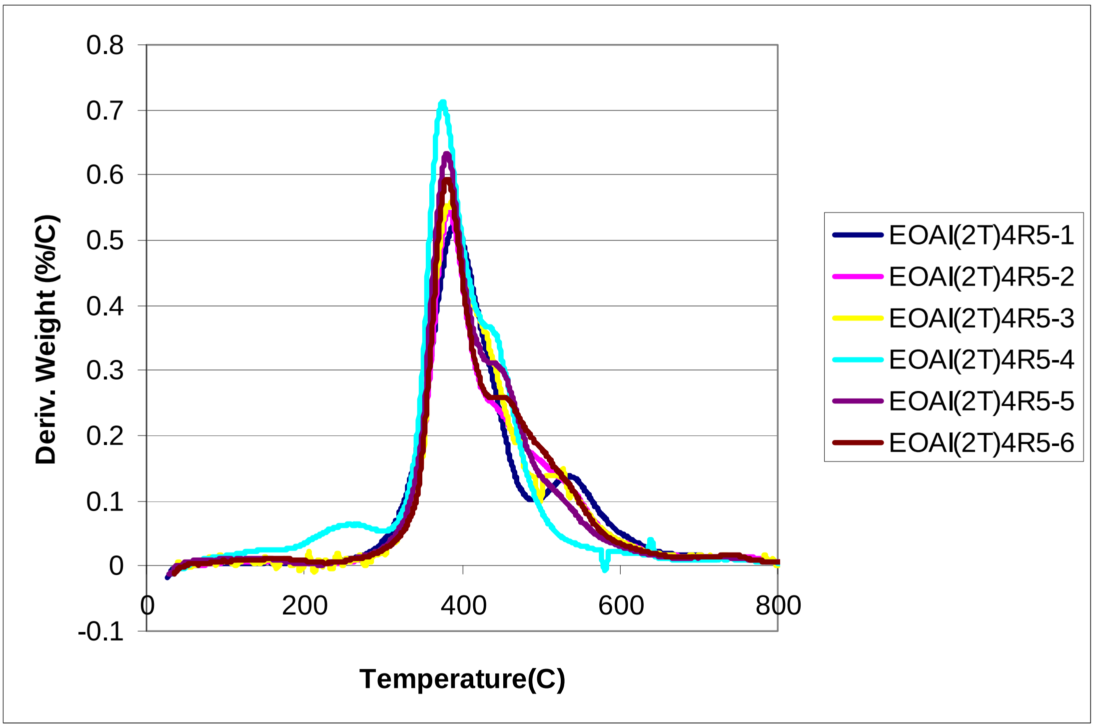

Figure A-6 The weight loss from TGA curve of the amide-imide-epoxy adhesive (from TPA and TDI)content NBR rubber in N_2 at heating rate 10^{o}c/min

APPENDICES B

TENSILE TESTING MACHINE CHARACTERIZATION

APPENDIX B

TENSILE TESTING MACHINE CHARACTERIZATION

B-1 Adhesion peel test of amide-imide-epoxy adhesive

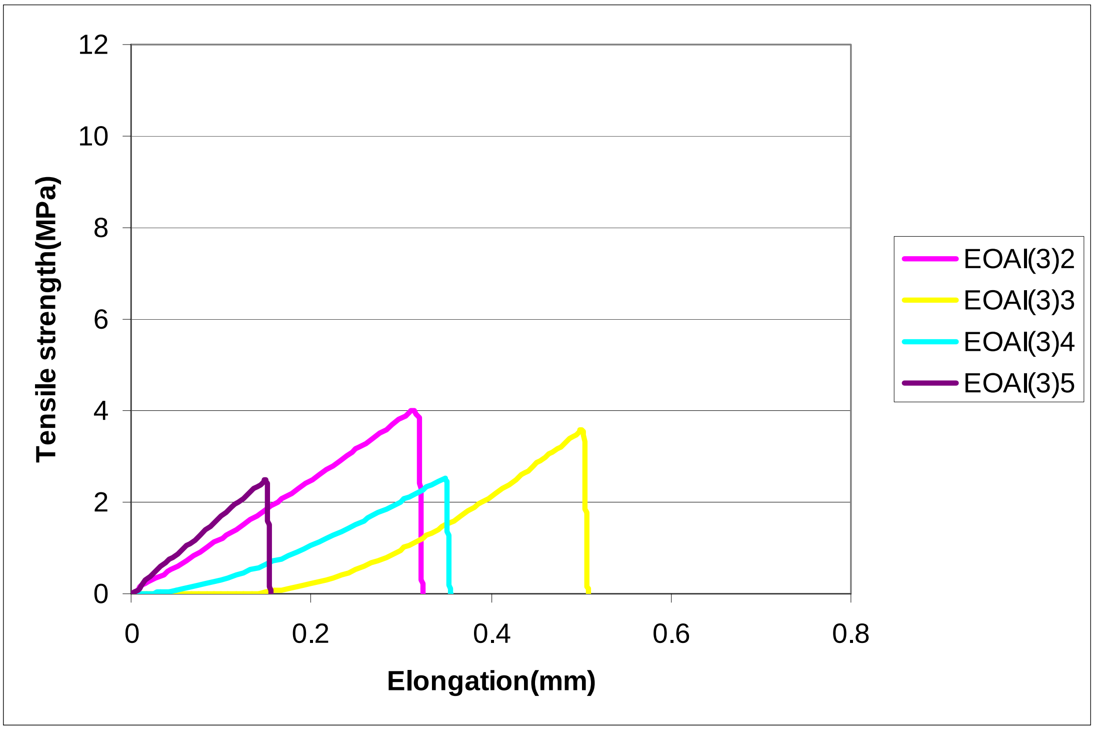

Figure B-1 The adhesion peel test of the amide-imide-epoxy adhesive

at rate 5 mm/min

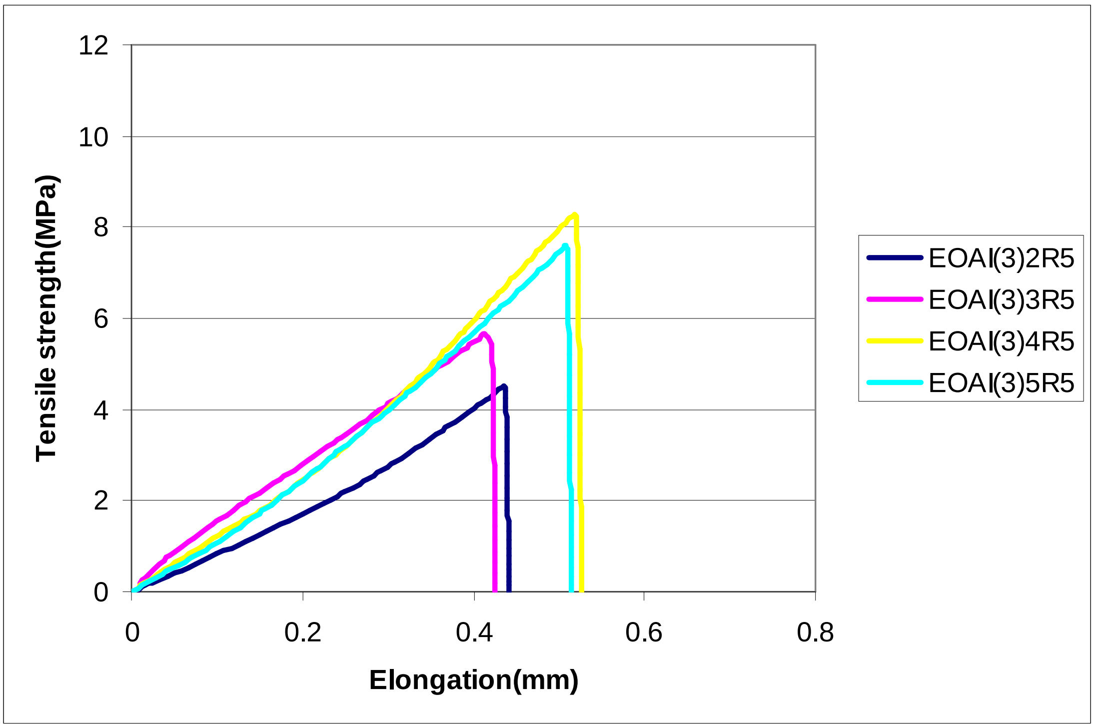

Figure B-2 The adhesion peel test of the amide-imide-epoxy adhesive content NBR rubber at rate 5 mm/min

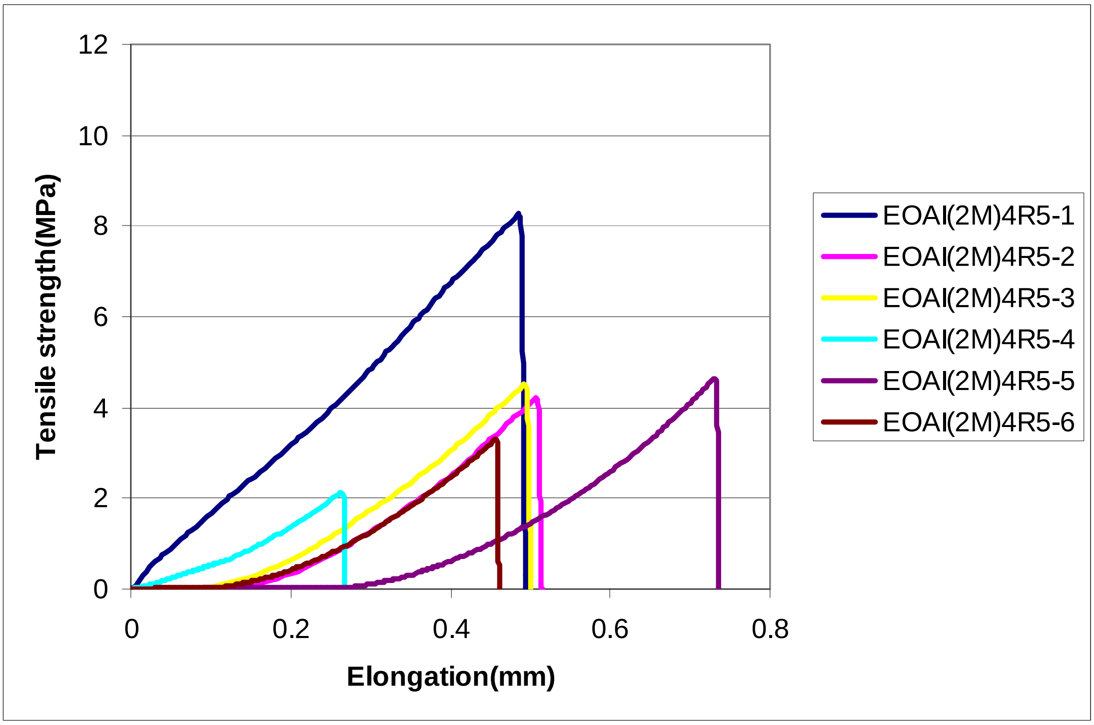

Figure B-3 The adhesion peel test of the amide-imide-epoxy adhesive (from TPA and MDI)content NBR rubber at rate 0.1 mm/min

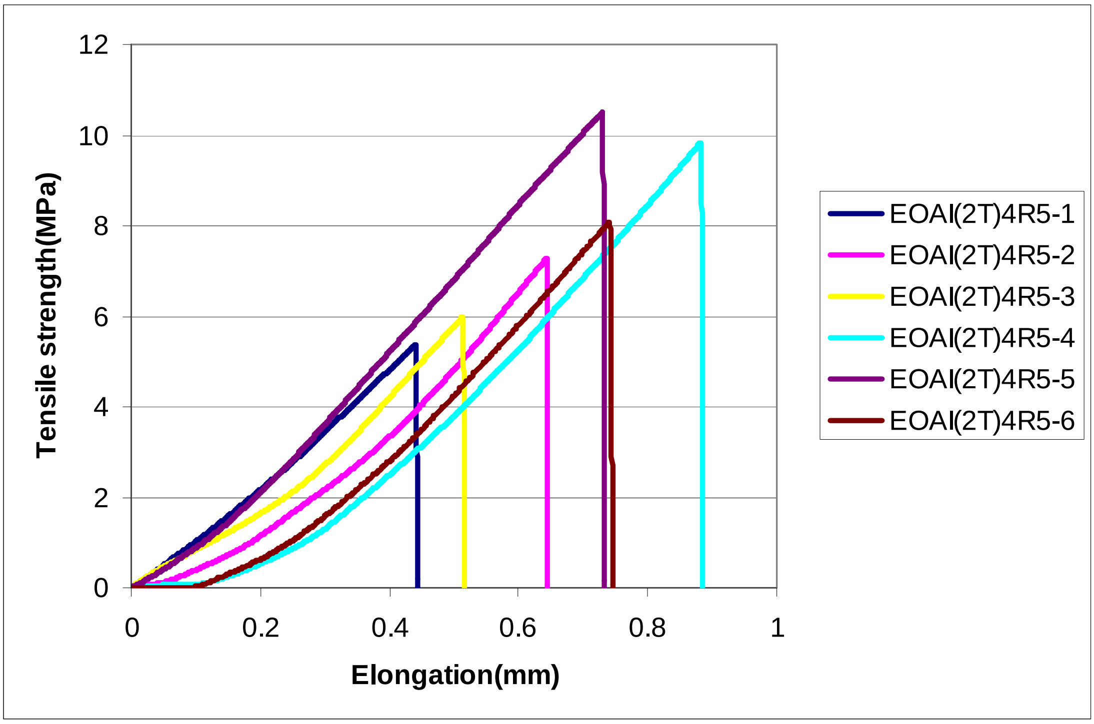

Figure B-4 The adhesion peel test of the amide-imide-epoxy adhesive (from TPA and TDI)content NBR rubber at rate 0.1 mm/min

APPENDICES C

CALCULATION

APPENDIX C

CALCULATION

C.1 Calculation of Molecular weight of OAI

C.1.1 OAI from tri-carboxylic (OAI(3))

ODA (MW 200.23) 0.04 mol TMA (MW 192.02) 0.084 mol
MDI (MW 250.25) 0.048 mol

DP1 = (1+(0.04/0.084))/(1-(0.04/0.084))
= 2.818182
OPI mol = (0.04+0.084)/2.818182
= 0.044
OPI MW = ((0.04*200.23)+(0.084*192.02))/(0.044-(18*2.818182))
= 497.8836
DP2 = (1+(0.044/0.048))/(1-(0.044/0.048))
= 23
OPAI mol = (0.044+0.048)/23
= 0.004
OPAI MW = ((0.044*497.8836)+(0.048*250.25))/(0.004-(44*23))
= 7467.72

C.1.2 OAI from di-carboxylic (OAI(2M)1)

ODA (MW 200.23) 0.04 mol TPA (MW 166.17) 0.01 mol
PMDA (MW 218.12) 0.074 mol MDI (MW 250.25) 0.048 mol

DP1 = (1+(0.01/0.04))/(1-(0.01/0.04))
= 1.666667
OPI1 mol = (0.04+0.01)/1.666667
= 0.03
OPI1 MW = ((0.04*200.23)+(0.01*166.17))/(0.03-(18*1.666667))
= 292.3633
DP2 = (1+(0.03/0.074))/(1-(0.03/0.074))
= 2.363636
OPI2 mol = (0.03+0.074)/2.363636
= 0.044
OPI2 MW = ((0.03*292.3633)+(0.074*218.12))/(0.044-(18*2.363636))

= 523.6314

DP3 = (1+(0.044/0.048))/(1-(0.044/0.048))

= 23

OPI2 mol = (0.044+0.048)/23

= 0.004

OPI2 MW = ((0.044*523.6314)+(0.048*250.25))/(0.004-(44*23))

= 7750.945

C.1.3 OAI from di-carboxylic (OAI(2M)2)

ODA (MW 200.23) 0.04 mol TPA (MW 166.17) 0.02 mol

PMDA (MW 218.12) 0.064 mol MDI (MW 250.25) 0.048 mol

DP1 = (1+(0.02/0.04))/(1-(0.02/0.04))

= 3

OPI1 mol = (0.04+0.01)/3

= 0.02

OPI1 MW = ((0.04*200.23)+(0.02*166.17))/(0.02-(18*3))

= 512.63

DP2 = (1+(0.02/0.064))/(1-(0.02/0.064))

= 1.909091

OPI2 mol = (0.02+0.064)/1.909091

= 0.044

OPI2 MW = ((0.02*512.63)+(0.064*218.12))/(0.044-(18*1.909091))

= 515.9155

DP3 = (1+(0.044/0.048))/(1-(0.044/0.048))

= 23

OPI2 mol = (0.044+0.048)/23

= 0.004

OPI2 MW = ((0.044*515.9155)+(0.048*250.25))/(0.004-(44*23))

= 7666.07

C.1.4 OAI from di-carboxylic (OAI(2M)3)

ODA (MW 200.23) 0.04 mol TPA (MW 166.17) 0.03 mol

PMDA (MW 218.12) 0.054 mol MDI (MW 250.25) 0.048 mol

DP1 = (1+(0.03/0.04))/(1-(0.03/0.04))

= 7

OPI1 mol = (0.04+0.03)/7

= 0.01

OPI1 MW = ((0.04*200.23)+(0.03*166.17))/(0.01-(18*7))

= 1173.43

DP2 = (1+(0.01/0.054))/(1-(0.01/0.054))

= 1.454545

OPI2 mol = (0.01+0.054)/1.454545

= 0.044

OPI2 MW = ((0.01*1173.43)+(0.054*218.12))/(0.044-(18*1.454545))

= 508.1995

DP3 = (1+(0.044/0.048))/(1-(0.044/0.048))

= 23

OPI2 mol = (0.044+0.048)/23

= 0.004

OPI2 MW = ((0.044*5081995)+(0.048*250.25))/(0.004-(44*23))

= 7581.195

C.1.5 OAI from di-carboxylic (OAI(2M)4)

ODA (MW 200.23) 0.04 mol PMDA (MW 218.12) 0.03 mol

TPA (MW 166.17) 0.054 mol MDI (MW 250.25) 0.048 mol

DP1 = (1+(0.03/0.04))/(1-(0.03/0.04))

= 7

OPI1 mol = (0.04+0.03)/7

= 0.01

OPI1 MW = ((0.04*200.23)+(0.03*218.12))/(0.01-(18*3))

= 1329.28

DP2 = (1+(0.01/0.054))/(1-(0.01/0.054))

= 1.454545

OPI2 mol = (0.01+0.054)/1.454545

= 0.044

OPI2 MW = ((0.01*1329.28)+(0.054*166.17))/(0.044-(18*1.454545))

= 479.8632

DP3 = (1+(0.044/0.048))/(1-(0.044/0.048))

= 23

OPI2 mol = (0.044+0.048)/23

= 0.004

OPI2 MW = ((0.044*479.8632)+(0.048*250.25))/(0.004-(44*23))

= 7269.495

C.1.6 OAI from di-carboxylic (OAI(2M)5)

ODA (MW 200.23) 0.04 mol PMDA (MW 218.12) 0.02 mol

TPA (MW 166.17) 0.064 mol MDI (MW 250.25) 0.048 mol

DP1 = (1+(0.02/0.04))/(1-(0.02/0.04))

= 3

OPI1 mol = (0.04+0.02)/3

= 0.02

OPI1 MW = ((0.04*200.23)+(0.02*218.12))/(0.23-(18*3))

= 564.58

DP2 = (1+(0.02/0.064))/(1-(0.02/0.064))

= 1.909091

OPI2 mol = (0.02+0.064)/1.909091

= 0.044

OPI2 MW = ((0.02*564.59)+(0.064*166.17))/(0.044-(18*1.909091))

= 463.9655

DP3 = (1+(0.044/0.048))/(1-(0.044/0.048))

= 23

OPI2 mol = (0.044+0.048)/23

= 0.004

OPI2 MW = ((0.044*463.9655)+(0.048*250.25))/(0.004-(44*23))

= 7094.62

C.1.7 OAI from di-carboxylic (OAI(2M)6)

ODA (MW 200.23) 0.04 mol PMDA (MW 218.12) 0.01 mol

TPA (MW 166.17) 0.074 mol MDI (MW 250.25) 0.048 mol

DP1 = (1+(0.01/0.04))/(1-(0.01/0.04))

= 1.666667

OPI1 mol = (0.04+0.01)/1.666667

= 0.03

OPI1 MW = ((0.04*200.23)+(0.01*218.12))/(0.03-(18*1.666667))

= 309.68

DP2 = (1+(0.03/0.074))/(1-(0.03/0.074))

= 2.363636

OPI2 mol = (0.03+0.074)/2.363636

= 0.044

OPI2 MW = ((0.03*309.68)+(0.074*166.17))/(0.044-(18*2.363636))

= 448.0677

DP3 = (1+(0.044/0.048))/(1-(0.044/0.048))

= 23

OPI2 mol = (0.044+0.048)/23

= 0.004

OPI2 MW = ((0.044*448.0677)+(0.048*250.25))/(0.004-(44*23))

= 6919.745

VITA

Mr. Vayo Malithong was born on January 19, 1985 in Singburi, Thailand. He received the Bachelor’s Degree in Chemical Engineering from Department of Chemical Engineering, Faculty of Engineering, Thammasat University in February 2007, He entered the Master of Engineering in Chemical Engineering at Chulalongkorn University in June, 2007.