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SYNTHESIS OF PHOSPHORODIAMIDATES AS CROSSLINKING AGENT

FOR EPOXY RESIN

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science

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ได้สังเคราะห์ฟอสโฟโรไดอะมิเดตสองชนิด คือฟีนิลฟอสฟอนิกเอทิลีนไดเอมีนไดเอไมด์ และฟีนิลฟอสฟอนิกพาราฟีนิลลีนไดเอมีนไดเอไมด์ เพื่อใช้เป็นสารเชื่อมขวางสำหรับการเตรียมพอลิเมอร์อีพ็อกซีที่มีฟอสฟอรัสและไนโตรเจนเป็นส่วนประกอบ จากผลการศึกษาดนศาสตร์พบว่าพลังงานก่อกัมมันต์สำหรับปฏิกิริยาเชื่อมขวางของเรซินอีพ็อกซีเชื่อมขวางกับฟอสโฟโรไดอะมิเดตสูงกว่าปฏิกิริยาเชื่อมขวางของเรซินอีพ็อกซีเชื่อมขวางกับเอทิลีนไดเอมีนและเชื่อมขวางกับพาราฟีนิลลีนไดเอมีนซึ่งใช้เป็นสารอ้างอิง ผลจากการทดสอบ TGA แสดงให้เห็นว่าอุณหภูมิเริ่มต้นของการสลายตัวเมื่อถูกความร้อนต่ำลงแต่ปริมาณเถ้าเพิ่มขึ้นเมื่อเรซินอีพ็อกซีเชื่อมขวางกับฟอสโฟโรไดอะมิเดต จากผลการทดสอบค่าดัชนีของปริมาณออกซิเจนพบว่าพอลิเมอร์อีพ็อกซีที่มีฟอสฟอรัสเป็นส่วนประกอบจะมีประสิทธิภาพในการหน่วงไฟได้ดีกว่าเรซินอีพ็อกซีที่เชื่อมขวางกับเอทิลีนไดเอมีนและเชื่อมขวางกับพาราฟีนิลลีนไดเอมีน อีกทั้งการเกิดควันก็ลดลง ผลที่ได้จากการทดสอบ UL-94 แสดงให้เห็นว่าพอลิเมอร์อีพ็อกซีที่มีฟอสฟอรัสเป็นส่วนประกอบผ่านระดับ V ตามมาตรฐาน UL-94 จากการศึกษาสมบัติเชิงกลของเรซินอีพ็อกซีเชื่อมขวางกับฟอสโฟโรไดอะมิเดต พบว่ามีค่าความทนต่อแรงดึงที่จุดขาดต่ำ ในขณะที่การยืดตัวที่จุดขาดสูงกว่าเรซินอีพ็อกซีที่เชื่อมขวางกับเอทิลีนไดเอมีนและเชื่อมขวางกับพาราฟีนิลลีนไดเอมีนซึ่งไม่มีฟอสฟอรัสเป็นองค์ประกอบ

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Two phosphorodiamidates including phenyl phosphonic ethylene diamine diamide (PPEDD) and phenyl phosphonic *p*-phenylene diamine diamide (PPPDD) have been synthesized and used as crosslinking agents for the preparation of phosphorus-nitrogen-containing epoxy polymers. The investigation of kinetics revealed that activation energy for crosslinking reaction of epoxy resins cured with phosphorodiamidates were higher than crosslinking reaction of epoxy resins cured with ethylenediamine and cured with *p*-phenylenediamine which were employed as references. The results from TGA experiments indicated that the onset temperature of thermal degradation decreased but char yield increased when epoxy resins were cured with phosphorodiamidates. Limiting Oxygen Index (LOI) results demonstrated that flame resistances of phosphorus-containing polymers are higher than those of ethylenediamine-cured and *p*-phenylenediamine-cured epoxy resins. Smoke evolution is also reduced. The results obtained from the UL-94 tests show that phosphorus-containing polymers passed flame retarding class V according to the UL-94 standard. The investigations of mechanical properties were that epoxy resins cured with phosphorodiamidates give lower tensile strength, but better elongation at break than epoxy resins cured with ethylenediamine and cured with *p*-phenylenediamine where no phosphorus were present.

Field of Study: Petrochemistry and Polymer Science Student's Signature.....

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LIST OF ABBREVIATIONS

E_a	activation energy
E_{α}	activation energy value at a given conversion deg
AHEW	amine hydrogen equivalent weight
δ	chemical shifts
α	conversion degree
J	coupling constants
$^{\circ}\text{C}$	degree celsius
D_2O	deuterium oxide
DGEBA	diglycidyl ether of bisphenol A
DSC	differential scanning calorimetry
EEW	epoxide equivalent weight
EDA	ethylenediamine
FT-IR	fourier transform-infrared spectroscopy
R	gas constant
T_g	glass transition temperature
β	heating rate
Hz	hertz
DMSO-d_6	hexadeuterio dimethylsulfoxide
LOI	limiting oxygen index
MALDI-TOF-MS	matrix assisted laser desorption ionization time-of-flight mass spectrometer
mg	milligram
<i>p</i> -	para

phr	part per hundred of resin
ppm	part per million
T _p	peak temperature
%	percent
PDA	<i>p</i> -phenylenediamine
PPDC	phenylphosphonic dichloride
PPEDD	phenyl phosphonic ethylene diamine diamide
PPPDD	phenyl phosphonic <i>p</i> -phenylene diamine diamide
T	temperature
THF	tetrahydrofuran
TGA	thermogravimetric analysis
t	time

CHAPTER I

INTRODUCTION

1.1 Statement of the problem

Epoxy resins belong to the thermosetting class of plastics. Most of epoxy resin can be synthesized by using bisphenol A with epichlorohydrin. The advantages of this type of resin are low viscosity, low shrinkage on cure, high adhesive properties of various materials, excellent chemical and moisture resistance, as well as superior electrical and mechanical properties. Because of their versatility, the epoxy resins are used in numerous industrial applications. Epoxy resins are also used in adhesives, laminates, surface coatings, polymer composites, encapsulation compounds and sealant compounds for electronic packages. However, limited flame retardancy is one of their major drawbacks, being an essential requirement of epoxy-based formulations, especially when they are used as one-part systems [1]. Several approaches have been used to enhance the flame retardancy of epoxies. For example, brominated reactive compounds, like tetrabromobisphenol A (TBBA) has been used for fire resistance. However, flame retardant epoxy resins containing bromine release hydrogen bromide during combustion, which causes corrosion and toxicity thus the use of brominated flame retardant, will be banned in the future [2]. Therefore, halogen-free flame retardants, especially organophosphorus, are thought to be environment-friendly flame retardants because their combustion products are less toxic and less corrosive. Two main approaches to achieve an incorporation of organophosphorus flame retardant into epoxy resins include the additive and the reactive approaches. However, flame retardants of the reactive type are of interest recently because they exhibit several advantages over those of the additive type [3, 4].

Imparting flame retardant into epoxy resins can be achieved through the utilization of phosphorus-containing epoxides, which are reported to be effective flame retardants. In addition, flame retardant of epoxy resin can be achieved by using phosphorus-containing amine as crosslinking agents. Some studies indicated that a significant improvement of flame retardant efficiency was observed when phosphorus

and nitrogen were both used as the crosslinking agent mainly act as intumescent flame retardants. Phosphorus element was acid source to break down to produce an inorganic acid under heat, and then it takes part in the dehydration of the carbonization agent to yield the char. In the meantime nitrogen element was the blowing agent to decompose to yield gaseous products which can not flame in air. The gas causes char to swell insulating protective layer over the surface of the material. This shield limits the heat transfer from the heat source to the substrate [5, 6].

Therefore, the main purpose of this research is to improve inherent flame retardant properties of epoxy resin (Epon828) *via* a novel phosphorodiamidates synthesized as curing agent, these flame retardants which possess both phosphorus and nitrogen and one anticipated to exhibit synergistic effect on flame retarding properties. Its effect on the curing process was to be evaluated by differential scanning calorimetry, while the effect on thermal degradation was estimated by thermogravimetric measurements. In addition, the effect on the mechanical properties was measured in tensile test. Limiting oxygen index and UL-94 were measured to characterize the flame retardant performance.

1.2 Research objectives

The objectives of this research are as follows

1. To synthesize phosphorodiamidates as both crosslinking agent and flame retardant for epoxy resin.
2. To study kinetics of the curing reaction of diglycidyl ether of bisphenol A with a variety of crosslinking agent.
3. To investigate the thermal properties, flame retardant properties, and mechanical properties of cured epoxy resins.

1.3 Scope of the investigation

The stepwise investigation was carried out as follows:

1. Literature survey for method to synthesize phosphorodiamidates.
2. Literature survey for method to prepare epoxy polymer using diamines as crosslinking agents.
3. Synthesis of phosphorodiamidates.

- phenyl phosphonic ethylene diamine diamide
- phenyl phosphonic *p*-phenylene diamine diamide

4. Preparation of epoxy polymers using diamines as crosslinking agent. The crosslinking temperature and crosslinking time were determined.
5. Investigation kinetics of the curing reaction of diglycidyl ether of bisphenol A with a variety of crosslinking agent.
6. Characterization of the thermal properties, flame retardant properties, and mechanical properties of cured epoxy resins.
7. Result interpretation and summary.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Epoxy resin

The term epoxy resin refers to a broad group of reactive compounds that are characterized by the presence of one or more oxirane (also called epoxy ring or ethoxyline ring, shown in **Figure 2.1**). This is represented by a three-member ring consisting of one oxygen atom and two carbon atoms.

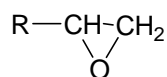


Figure 2.1 The epoxy or oxirane ring structure [7].

The commercial epoxy resins were marketed for the first time in the late 1940's, they can be formed from the reaction of bisphenol A with an excess of epichlorohydrin in the presence of sodium hydroxide. The reaction occurred by the formation of chlorohydrin followed by dehydrohalogenation. The general reaction produces diglycidyl ether of bisphenol A (DGEBA) as shown in **Figure 2.2** [7, 8].

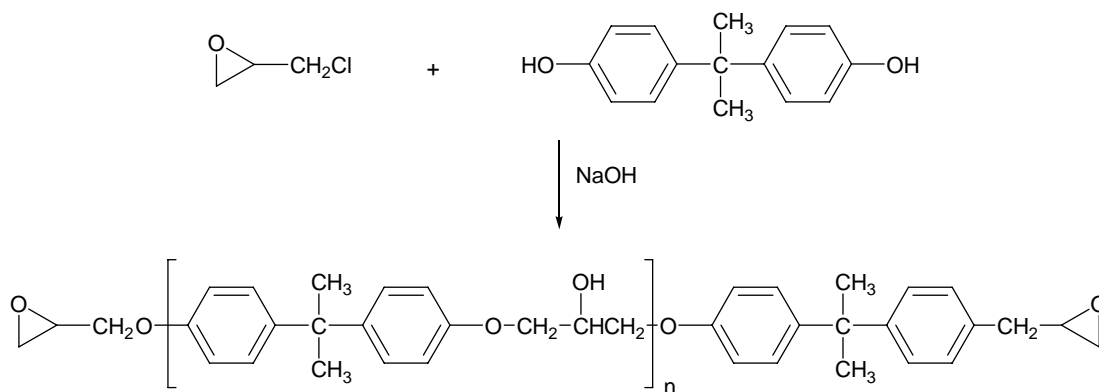


Figure 2.2 Synthesis of DGEBA epoxy resin from bisphenol A and epichlorohydrin [8].

DGEBA is not only the oldest type of epoxy resins but it is the most valuable in many applications. The primary reasons for their popularity have been [9]

1. The raw materials used to synthesize these resins are relatively low cost;

2. The resins can be cured by a large number of different crosslinking agents at both room and elevated temperatures; and
3. The cured resins have relatively good mechanical and chemical properties.

The conversion of epoxy resins into useful products network must be cured or crosslinked by chemical reaction into a three-dimensional network by the use of crosslinking agents or curing agents. Crosslinking agents function by reacting with or causing the reaction of epoxide or the hydroxyl groups in the epoxy resin. In general, crosslinking agents suitable for DGEBA are three major chemical types such as amines (**Figure 2.3**, a), phenol-novolacs (HO-Nov, b) and acid anhydrides (c) [10].

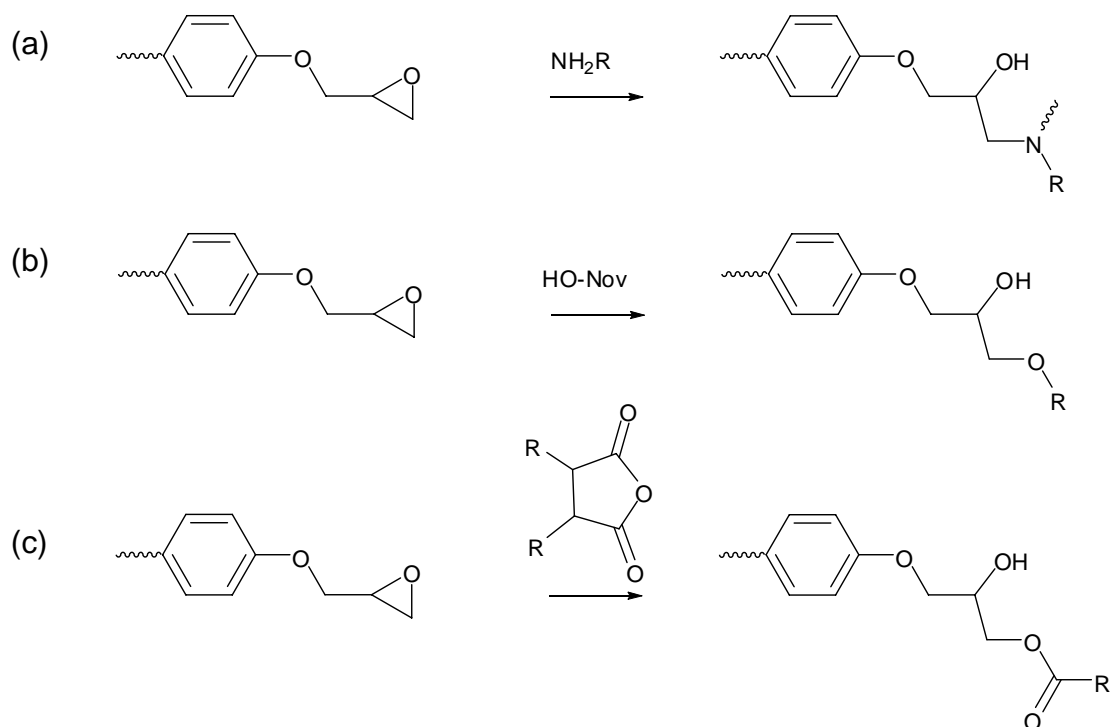


Figure 2.3 Newly formed bonds during curing of epoxy resins using: (a) amine, (b) phenol-novolac and (c) anhydride as curing agents [10].

The amines comprise well over half volume of the total crosslinking agent market. The amines can be divided into aliphatic, cycloaliphatic, aromatic and tertiary amines. In the basic crosslinking reaction of epoxides based on DGEBA with amines, the active hydrogen in primary amine reacts with an epoxy group to form secondary amine (**Figure 2.4**, a), and the secondary amine reacts with an epoxy group to cure

(b). Then, the resultant tertiary amine polymerizes epoxy groups (c). The crosslinking speed of individual amine depends on the type and loading of amine [11].

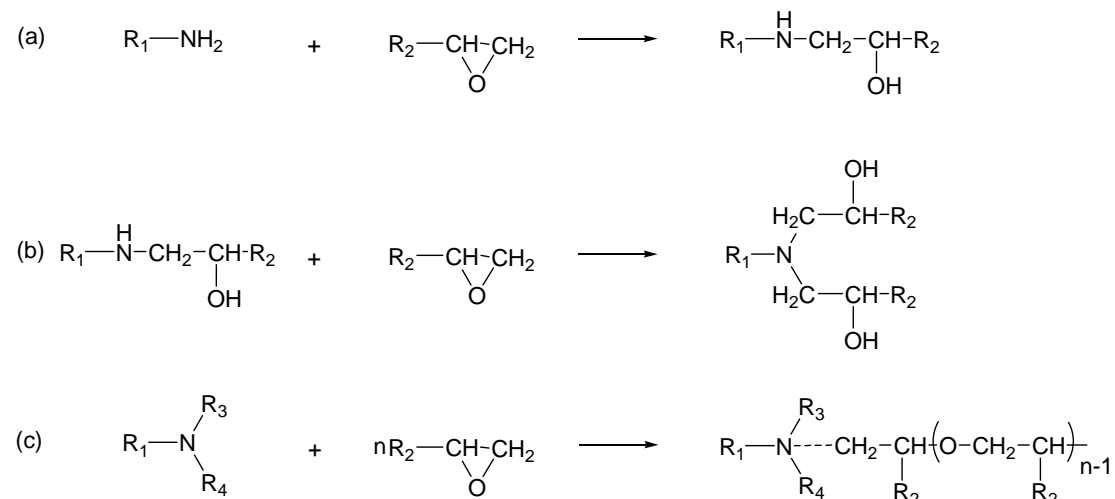


Figure 2.4 Crosslinking reaction of DGEBA with amine [11].

Crosslinked epoxy polymers have useful properties such as low cure shrinkage, no volatiles given off during cure, compatibility with a great number of materials, strength and durability, adhesion, corrosion and chemical resistance, and electrical insulation. Therefore, they offer wide applications in the areas of adhesive bonding, construction materials, coating, laminates, molding, printed circuit boards and aerospace.

2.2 Thermal degradation of epoxy resin

Like other thermosetting polymers, when exposed to high temperatures (300-400 °C), the cured epoxy decomposes releasing heat, smoke, soot and toxic volatiles. It has been proposed that in the thermal degradation of cured epoxy, generally four different reactions are taking place in the condensed phase. The main reactions are end-chain or random-chain scissions, which generate free radical species. Concurrently, various functional groups or atoms which are not part of polymer backbone can be stripped off. This reaction is known as chain stripping. The last reaction occurring is crosslinking of different radicals formed during the chain scission to form new thermally stable polymers or carbonaceous char. In the case of epoxy resins, the first step of amine cured epoxies is caused by dehydration due to

elimination of water molecule from oxypropylene group (-CH₂-CH(OH)-) and subsequent formation of allylic amides (**Figure 2.5**, a). The unsaturated moiety can then undergo isomerisation (c) followed by allylic-oxygen bond scission (d). In the case of amine hardeners the weak C-N bond produced during curing will then undergo allylic-nitrogen bond scission (b) to form volatile particles or contribute to charring. Another cause of scission can be hyperoxide degradation, which leads to the formation of carbonyl (e) followed by splitting of amine (C-N) or ether bonds (C-O) to yield light volatile products (f) [12, 13].

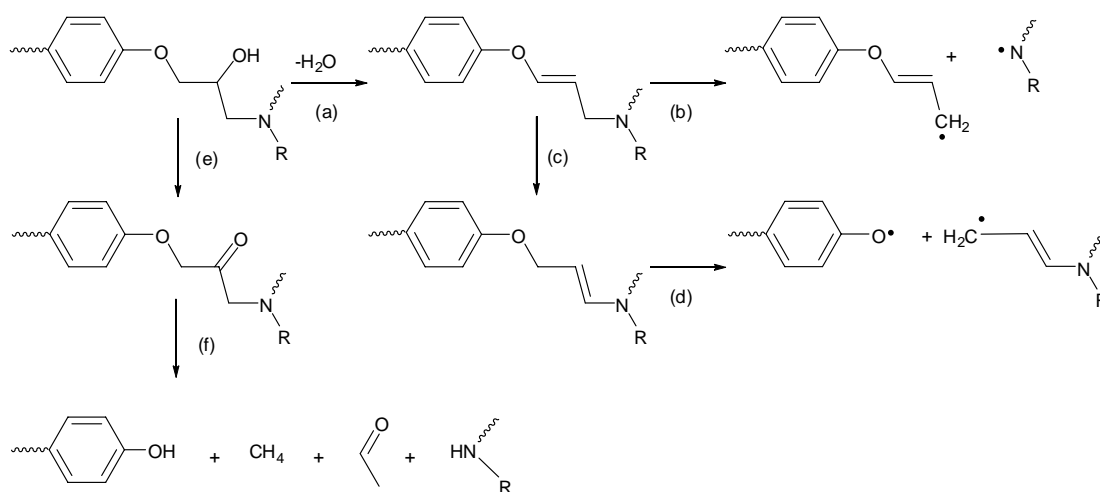
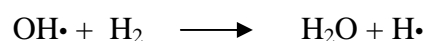
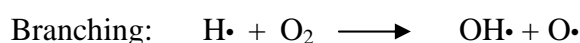


Figure 2.5 Thermal degradation paths of an amine cured epoxy resin [12].

2.3 Flame retardant systems for polymers

The combustion cycle of polymer is shown in **Figure 2.6**. When polymer is exposed to fire, polymer will thermally decompose with the release of heat, smoke and combustible gases. The combustible gases flow into the fire, where the combustible gases react with oxygen in air to produce highly reactive hydrogen (H•) and hydroxy (OH•) radicals. These radicals have role leading to the decomposition and sustained burning polymer. The exothermic reactions that generates of the thermal energy in the flame are



The $H\cdot$ radicals produced feed-back into reaction, and thereby the combustion reaction sequence a self-propagating process that continues as long as sufficient oxygen is available. The heat generated raises in the combustion zone that in turn accelerates the decomposition rate of polymer [14].

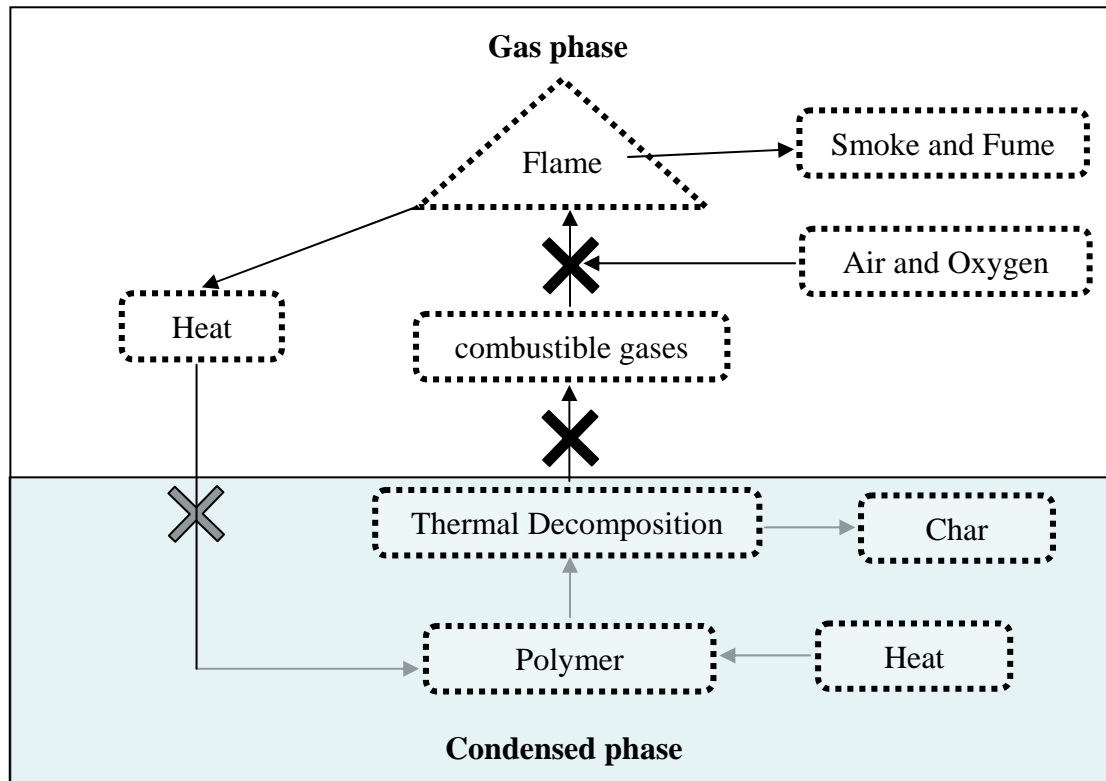


Figure 2.6 Combustion cycle of a polymer fire cross marks represent the main approaches to extinguish a fire scenario [15].

Flame retardant polymers work by disrupting the cycle in a number of possible ways for instance: by reducing amount of combustible gases reaching the flame which in turn leads to extinction; inhibition of the exothermic oxidation reaction in the flame via radical scavenging; and promote the formation of a thermal barrier (charring) at the surface of the condensed phase which blocks the release of gaseous fuel and prevents the transfer of heat back to the burning polymer.

The action of flame retardants are often classified as condense phase or gas phase, depending on whether they disrupt the decomposition of the polymer or combustion in the flame.

In the case of condensed phase, two types of reaction can take place. Firstly, the breakdown of the polymer occurs so it melts like a liquid and flows away from the flame. Second, the flame retardant can cause charring layer to form on the polymer surface. This can occur, for example, by the dehydrating action of the flame retardant generating double bonds in the polymer. Ultimately, these form a carbonaceous layer by cyclizing and crosslinking processes.

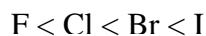
The flame retardant in the gas phase operates by interfering with the combustion reaction, thus reducing both flame propagation and the amount of heat returned from the fire to the polymer. Another mechanism is the release of non-combustible gases to dilute the concentration of H• and OH• radicals in the flame.

2.4 Types of flame retardants

Flame retardants are classified into two categories. Additive flame retardants are incorporated into the polymer either prior to, during, or following polymerization while reactive flame retardants are reactive components chemically built into a polymer molecule.

2.4.1 Halogenated flame retardants

The halogenated flame retardants can be classified as aliphatic, cycloaliphatic, and aromatic structures. The nature of the halogen atoms is varied in each type of structure. The effectiveness of halogen containing flame retardants increases in the order:



Fluorine- and iodine-based flame retardants are not used in practice because neither type interferes with the combustion process at the right point. Fluorine is not used due to its strong bond with carbon, while iodine is loosely attached to carbon. In addition, fluorine and iodine are more expensive than chlorine or bromine, which also limits development of flame retardants based on these two halogens. Bromine and chlorine are the only halogen compounds having commercial significance as flame-retardant chemicals. The bromine-based flame retardants are much more common than the chlorinated types because of their higher efficacy. As a function of

halogenated flame retardants either undergo pyrolysis inside the condensed phase or evaporate and are destroyed in the gas phase [16].

Among halogen-containing flame retardants, diglycidyl ether of bis(3,3',5,5'-tetrabromobisphenol) A (DGEBTBA, **Figure 2.7**) is the most widely used in epoxy resins.

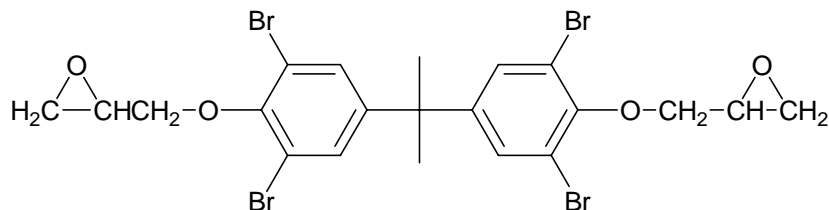


Figure 2.7 DGEBTBA flame retardant used for epoxy resins [17].

DGEBTBA is built into the backbone of the resin. When under thermal stress, the action of DGEBTBA appears to be effective in both the gas phase and condensed phase. In the gas phase, it acts as flame poisons in stage of ignition by blocking access of oxygen and heat, and in stage of combustion, by influencing the combustion reactions. It is necessary for the burning process to proceed through decomposition and release volatile bromine radicals that scavenge hydrogen radicals in the flame to form non-flammable hydrogen bromide gas (**Figure 2.8**). In the condensed phase, it redirects the chemical reactions involved in decomposition of polymer. The chemical reactions may involve halogenation followed by dehydrohalogenation to yield a polymeric residue rich in double bonds which can be converted to carbon [17, 18, 19].

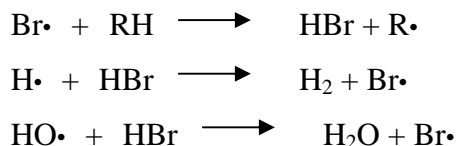


Figure 2.8 Gas phases reaction of DGEBTBA flame retardant [17].

However, flame retardant epoxy resins containing bromine release hydrogen bromide during a fire scenario, which are highly toxic for the people exposed to these gases, possibly resulting in death due to poisoning. Considerable environmental effects and health restrictions have been considered in regard to controlling the inherent flammability of epoxy resins by incorporation of flame retardant containing

bromine. These considerations have led to examination in terms of overall fire hazards of bromine containing epoxy resins and the search for bromine free and environmentally friendly flame retardant epoxy resins [20].

2.4.2 Metal hydroxides fillers

Metal hydroxides such as, Antimony oxides, Alumina trihydrate and magnesium hydroxide have several positive effects when applied as a flame retardant. They are very cheap, easy to use, non toxic, non corrosive and environmentally friendly.

Antimony oxides are the most common synergist with halogen containing flame retardants. Chemical transformations of antimony oxides in the condensed phase are an example of the formation of volatile metal-containing compounds during combustion. The synergistic effect on the system consists in antimony trioxide combination with an organic halogen compound, forms antimony trihalide and oxyhalide at flame temperatures. The antimony trihalide is the principal active agent and acts in both the gas phase and the condensed phase to suppress flame propagation. The volatile antimony halide acts as a source of halogen radicals that react with free radicals through a reaction that is less exothermic than the propagation reaction of chain scissions, thereby reducing the heat generated and as a consequence reducing the rate of thermal degradation of the polymer matrix. This mechanism is illustrated in **Figure 2.9**. In the condensed phase the antimony oxide promotes the formation of highly crosslinked carbonaceous char, which serves to insulate the substrate and to restrict the diffusion of volatiles in the flame.

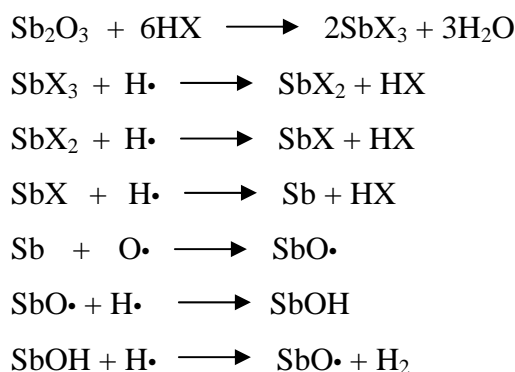
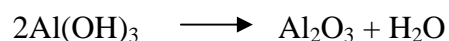
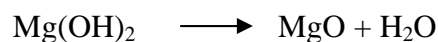


Figure 2.9 Gas phases reaction of antimony trihalide flame retardant [21].

Although generally known as alumina trihydrate (sometimes referred to as aluminium hydroxide), this has the chemical formula $\text{Al}(\text{OH})_3$ and its high proportion (34.6%) of chemically bound water. This water of hydration is stable and unreactive at the processing temperature exceeding $180\text{ }^\circ\text{C}$. When heated to approximately $220\text{ }^\circ\text{C}$ or higher by exposure to a flame zone, the hydrate decomposes into its constituents, with the absorption of a considerable amount of heat and dilutes the combustible gases.



Magnesium hydroxide ($\text{Mg}(\text{OH})_2$), like alumina trihydrate, act as a flame retardant and smoke suppressant, it functions by the release of water at around $330\text{ }^\circ\text{C}$, which absorbs heat and dilutes the combustible gases. However, the major advantage of magnesium hydroxide over alumina trihydrate is the higher decomposition temperature meaning that polymer containing magnesium hydroxide can be processed at higher temperatures than those using alumina trihydrate.



Metal hydroxides have one major drawback as flame retardants. High loading, typically in range 50-60%, are required to achieve desired levels of flame retardancy thus more typically because significant detrimental effects in the physical properties of the base resin [21].

2.4.3 Phosphorus Flame Retardants

Phosphorus-containing flame retardant is believed to perform most of its flame retardant function in the condensed phase, the gas phase, or concurrently in both phases.

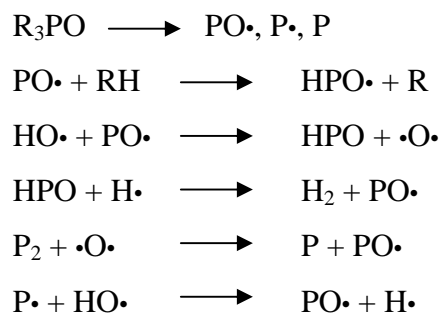


Figure 2.10 Gas phases reaction of phosphorus-containing flame retardant [21].

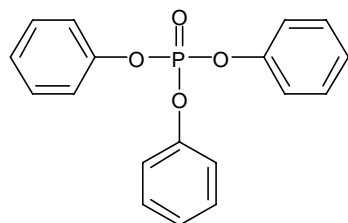
Some phosphorus compounds decompose in the condensed phase to form phosphoric or polyphosphoric acids. These can promote charring. The polyphosphoric acids also can form a thin glassy coating, which can shield the polymer substrate from the flame and oxygen. Moreover, intumescence system requires an acid such as phosphoric acid, results in dense char on polymer surface. In the gas phase by inhibition of the exothermic oxidation reaction in the flame by radical scavenging, thus reduces the energy feedback to the polymer surface, as illustrated in **Figure 2.10** [21, 22].

2.4.3.1 Additive phosphorus flame retardants

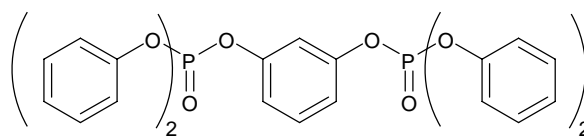
Additive phosphorus flame retardant has several positive effects when applied. The use of fillers has the great advantage that most additives are very cheap and widely applicable.

Red phosphorus has been suggested as flame retardant additive for epoxy resin. The flame retarding mechanism for red phosphorus and epoxy resin is believed to be through the formation of phosphorus-oxygen bonds, which catalyzes the dehydration of polymer and then promote charring. However, when used red phosphorus as flame retardant will give toxic phosphine gas during combustion [23].

Other phosphorus compounds can be used as additive flame for epoxy resin such as triphenylphosphate and resorcinol bis(diphenyl phosphate) as shown in **Figure 2.11**. The results indicate those phosphorus compounds are released in the gas phase during combustion to dilute oxygen concentration and inhibited of the oxidation of free radical chain reaction.



Triphenylphosphate



Resorcinol bis(diphenyl phosphate)

Figure 2.11 Commercially available phosphates [15].

Moreover, phosphorus compounds are mostly active by condensed phase mechanism. A strong char yield decreases fuel supply to the flame and hence reduces the rate of heat release during combustion to reach the desired flame retardant properties level, high loadings are necessary, which often has a negative impact on the physical and mechanical properties of cured polymer [15].

2.4.3.2 Reactive phosphorus flame retardants

A traditional technique for preparation of flame retardant epoxy materials is to blend the flame retardant additive with the polymer. There is no chemical bonding between the flame retardant additive and the substrate polymer, some defects, such as low efficiency of flame retardant, leaking out during processing and usage, and detrimental effects on thermal and mechanical properties of polymer. Therefore, the present trend is moving towards using reactive type flame retardants, which forms chemical bond to the polymer. Imparting reactive type flame retardant into epoxy resins can be achieved through phosphorus-containing epoxy resin or phosphorus-containing amine [24].

When compared to phosphorus additive, phosphorus-containing epoxy resins were found to show lower thermal stability, with a reduced initial decomposition temperature, but a higher char yield at high temperature. During the initial decomposition step, the thermally stable char is formed to protect layer against heat and oxygen diffusion on the polymer surface and prevent further degradation.

Wang *et al.* [25] reported the method for the synthesis bis-phenoxy (3-hydroxy) phenyl phosphine oxide (BPHPPO)-containing epoxy resin (**Figure 2.12**) from phosphorus-containing hydroquinone.

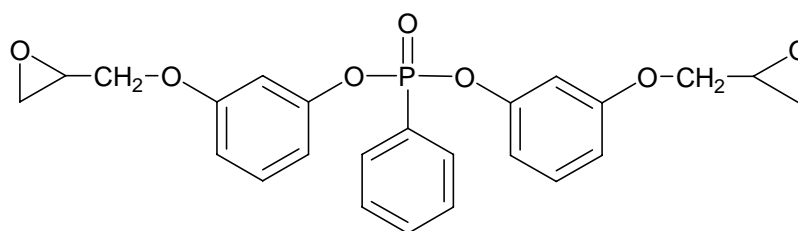


Figure 2.12 BPHPPO-containing epoxy resin [25].

When this epoxy was mixed with DGEBA, the limiting oxygen index (LOI) (the LOI test is shown in chapter III) increased from 22 to 28 with increasing phosphorus content from 0 to 1.4%, it reached a plateau when the phosphorus contents exceeded 2.1%.

Many research articles discuss the use of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) (**Figure 2.13**). DOPO can be either pre-reacted with epoxy resin or used as a reactive additive during curing.

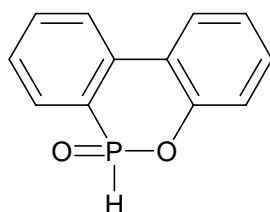


Figure 2.13 The structure of DOPO [26].

Wang *et al.* [26] synthesized phosphorus-containing epoxy resins (1–3% phosphorus content) (**Figure 2.14**) by the reaction of DOPO and the DGEBA. When phosphorus content increased from 0 to 1.6%, the LOI increased from 22 to 28.

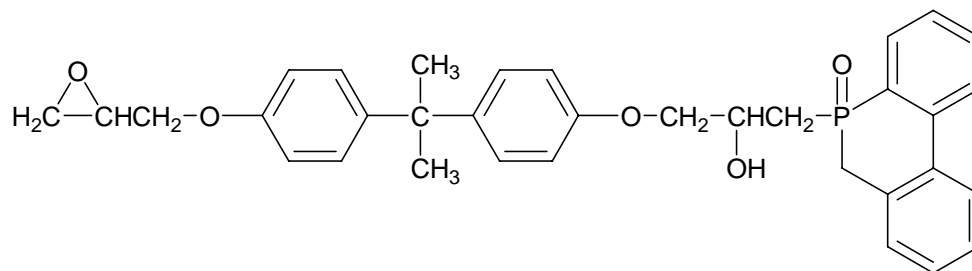


Figure 2.14 DOPO-containing epoxy resins [26].

Moreover, Wang *et al.* [27] synthesized a series of advanced epoxy resins with various epoxy equivalent weights from a reactive phosphorus-containing diol, 2-(6-oxido-6Hdibenz[c,e][1,2]oxaphosphorin-6-yl)-1,4-dihydroxy phenylene (**Figure 2.15**) and DGEBA. The cured advanced epoxy resins showed higher char yields (10-18%) than non-flame retardant system (1%). Higher LOI value is obtained with increase in phosphorus content. LOI increased from 22 to 28 when phosphorus content is increased from 0 to 1.41%.

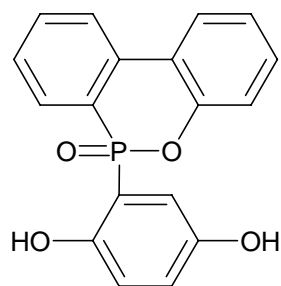


Figure 2.15 Phosphorus-containing diol [27].

In another study, Bhuniya *et al.* [28] synthesized phosphorus-containing epoxy resins (**Figure 2.16**) by phenylphosphonic dichloride was first reacted with bisphenol and then the dihydroxy compound was converted into an epoxy monomer by reaction with epichlorohydrin. The LOI values of these phosphorus-containing epoxy resins ranged from 33 to 40. The maximum LOI value was obtained for resorcinol-based flame retardant due to its highest phosphorus content.

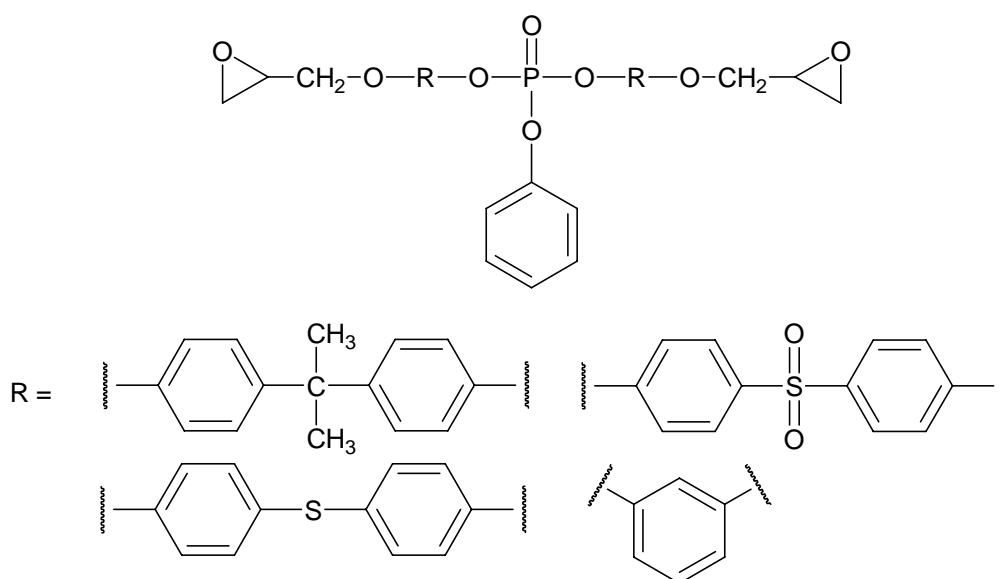


Figure 2.16 Phosphorus-containing epoxy resins [28].

Phosphorus containing crosslinking agents as shown in **Figure 2.17** have been used in the past to increase the flame resistance of cured epoxy. Synergistic combination of phosphorus and nitrogen in these crosslinking agents leads to significant improvement in flame resistance of cured epoxy. The phosphorus-nitrogen

synergism is probably due to the formation of intermediates containing P–N bonded, which are better phosphorylating agents than are related phosphorus compounds without nitrogen and thus lead to an increase in char yield and greater phosphorus retention in the char.

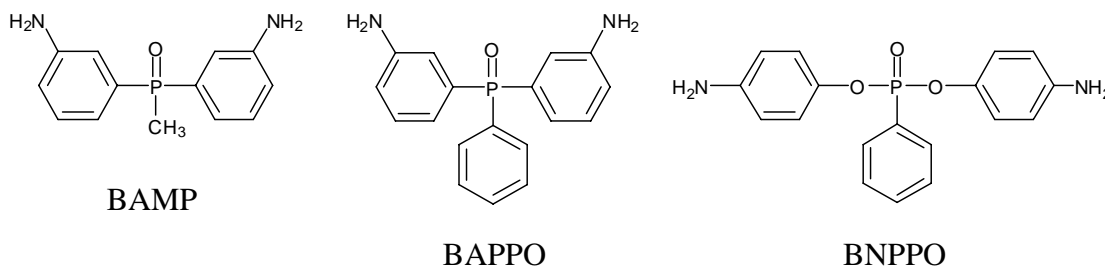


Figure 2.17 Phosphorus-containing diamines [29, 30].

Wang *et al.* [29] have compared bis(3-aminophenyl)methylphosphine oxide (BAMP) with 4,4'-diaminodiphenylmethane (DDM) and 4,4'-diaminodiphenylsulfone (DDS) in DGEBA. Cured epoxy resin with BAMP showed higher LOI than non-phosphorus-containing polymers. However, the phosphorus-containing polymer decompose at lower thermal temperature than non-phosphorus-containing polymer because of phosphoric acid species were formed upon thermal decomposition, which catalyze dehydration of epoxy at lower temperature. This was attributed char-forming flame retardant action.

Liu *et al.* [30] prepared two phosphorus-containing diamine compounds, bis(4-aminophenoxy) phenyl phosphine oxide (BAPPO) and bis(3-nitrophenyl) phenyl phosphine oxide (BNPPO). When curing with DGEBA, the cured epoxy showed higher char yield and LOI values comparison with DGEBA cured with DDM, DDS and dicyanodiamide.

2.4.3.3 Intumescent phosphorus-based flame retardants

The word intumescence comes from the Latin *intumescere*, which means to swell up. An intumescent material, which when heated beyond a critical temperature begins to swell to form foamed cellular charred layers on the surface of the burning material. This layer acts as a physical barrier to heat and fuel transfer, protecting the underlying material from the action of the heat flux or flame.

Intumescent flame retardants have aroused a great deal of attention in the recent years in the flame retardant for epoxy resins. To make an intumescent system, three kinds of components are incorporated into formulations to obtain intumescent flame retardancy:

1. an acid source which is inorganic salt or inorganic acid ester
2. a carbonization agent which is polyhydric compound currently
3. a blowing agent which can bring noncombustible gas in air

The mechanism of intumescent in flame retardant polymer is usually described as follows: first, the acid source breaks down to produce an inorganic acid under heat, then it takes part in the dehydration of the carbonization agent to yield the carbon char, while the blowing agent decomposes to yield gaseous products which can not flame in air. The gas causes the char to swell and finally an insulating multicellular protective layer yields at the surface of the material. This protective char limits both the heat transfer from the heat source to the substrate and the mass transfer from the substrate to the heat source resulting in a conservation of the underlying material as illustrated in **Figure 2.18** [31, 32].

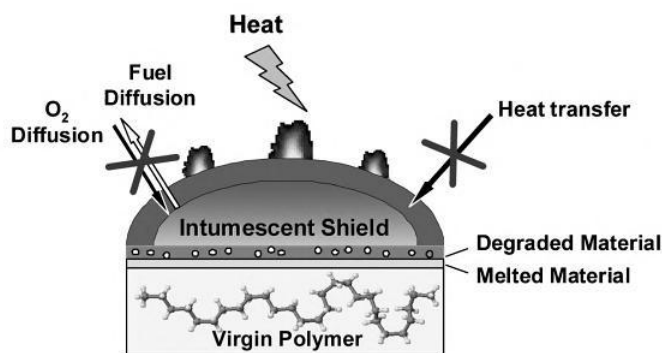


Figure 2.18 Schematic action of an intumescent polymeric formulation [31].

Wang *et al.* [33] prepared intumescent flame retardant epoxy system from epoxy resin (diglycidyl ether of bisphenol A), low molecular weight polyamide (cure agent, LWPA), and ammonium polyphosphate (APP). The results of LOI and UL-94 (the UL-94 test is shown in chapter III) indicate that APP can improve the flame retardancy of LWPA-cured epoxy resins. Only 5 wt % of APP can increase the LOI value of epoxy resins from 19.6 to 27.1, and improve the UL-94 ratings, can reach V-0 rating of UL-94 and non-dripping with the content of APP over 5 wt %.

Toldy *et al.* [34] synthesized efficient phosphorus-containing crosslinking agents $P(O)(NHCH_2CH_2NH_2)_3$ and $P(O)(OCH_2CH_2NH_2)_3$ and used them in epoxy resins. The results exhibited those the limiting oxygen index (LOI) values are increased by addition of the organophosphorous compounds. The peak of heat release were reduced compared to non-flame retarded resin, furthermore a shift in time were observed, which increases the time to escape in case of fire. When compared to flame retardant containing P-O bonded ($P(O)(OCH_2CH_2NH_2)_3$), flame retardant containing P-N bonded ($P(O)(NHCH_2CH_2NH_2)_3$) was found to show higher LOI value and was achieved UL-94 V-0 rating, while flame retardant containing P-O bonded resulted in HB rating.

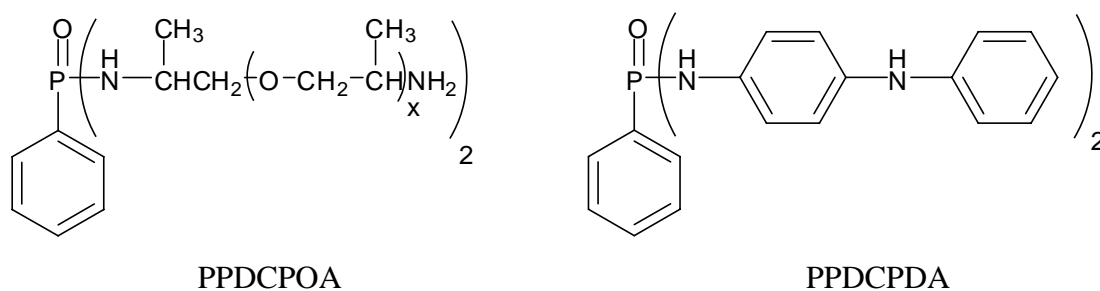


Figure 2.19 Phosphorus-containing amine curing agents [35].

Jeng *et al.* [35] have compared PPDCPOA and PPDCPDA (**Figure 2.19**) with polyoxyalkylene amines (POA) and *p*-phenylenediamine (PDA) in DGEBA. The LOI measurement showed that the cured epoxy resins with phosphorus-containing amine (PPDCPOA and PPDCPDA) had a pronounced improvement in flame-retardant properties when compared with non phosphorus-containing amines (POA and PDA). Furthermore, the weight retention in TGA for all epoxy polymers were increased with increasing phosphorus and aromatic contents in nitrogen at temperature up to 850 °C (PPDCPDA>PPDCPOA>PDA>POA). However, this trend was not so distinct in air due to the complicated thermal oxidation.

2.5 Analytical methods for polymers characterization

2.5.1 Differential scanning calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is the dominant technique for the thermal analytical investigation of polymer materials. It measures change in energy input into a substance and a reference material as they are subjected to a controlled temperature program. Furthermore, all practically physical and chemical processes relate to the changes in enthalpy or specific heat, and the applicability of DSC to condensed-phase systems is almost universal. The measurement process is quantitative and the change of enthalpy is usually a linear function of the reaction coordinate. A DSC endothermic or exothermic peak is shown in **Figure 2.20**.

A DSC measurement gives the rate of change of enthalpy, so that the area between a DSC curve and its extrapolated baseline indicates the total heat of reaction. The conversion reacted is obtained from division of the fractional area by the total area. The amplitude between the baseline and the DSC curve measures the rate of reaction [36].

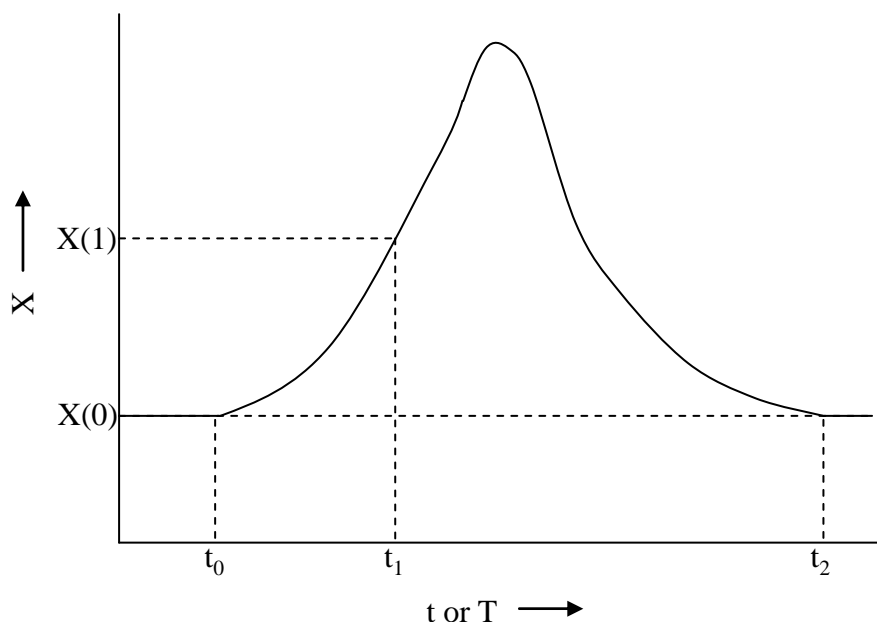


Figure 2.20 First-order transition peak for DTA: $X = \Delta T$; for DSC: $X = J/s$, peak area = enthalpy of transition, fractional area/total area = fraction conversion, peak amplitude/total area = rate of conversion [37].

The glass transition (T_g) is the temperature where the polymer goes from a hard, glass like state to a rubber like state. In DSC experiments, T_g is usually reported as the temperature at the half-height of the heat capacity increase. T_g can also be taken as the inflection point, which is slightly different and corresponds to the peak in the derivative of the heat flow or heat capacity versus temperature as shown in **Figure 2.21**. [38].

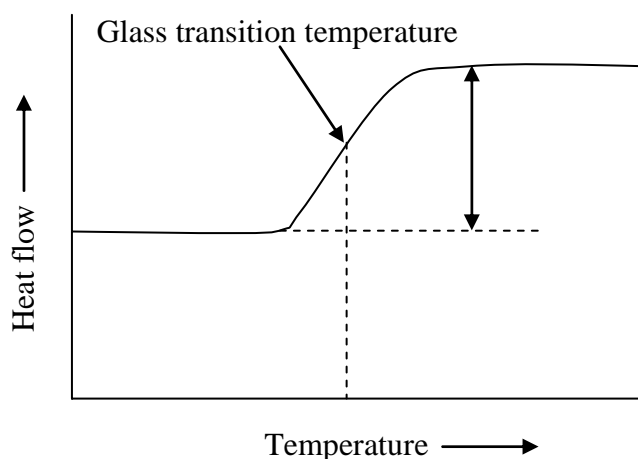


Figure 2.21 Characterization of glass transition during recording of a DSC curve [38].

2.5.2 Thermogravimetric analysis (TGA)

Thermogravimetry is the branch of thermal analysis which examines the change in mass of a sample as a function of temperature in the scanning mode or as a function of time in the isothermal mode. Not all thermal events bring about a change in the mass of the sample such as melting, crystallization or glass transitions, but important exceptions, obtained which include desorption, absorption, sublimation, vaporization, oxidation, reduction and decomposition. Generally, it is used to characterize the decomposition and thermal stability of polymers under a variety of conditions, and to examine the kinetics of the physicochemical processes occurring in the sample. The mass change characteristics of a material are dependent on the experimental conditions employed. The Instrumental factors such as sample mass, volume and physical form, the shape and nature of the sample holder, the nature and pressure of the atmosphere in the sample chamber and the scanning rate all have significant influences on the characteristics of the recorded TG curve.

TG curves are plotted with the mass change (Δm) expressed as a percentage on the vertical axis and temperature (T) or time (t) on the horizontal axis. A TG curve representation of a one-stage reaction process observed in the scanning mode is shown in **Figure 2.22**.

The reaction is characterized by two temperatures, T_i and T_f which are called the initial decomposition temperature and the final temperature, respectively. T_i is the lowest temperature at which the onset of a mass change can be detected for a given set of experimental conditions. Similarly, T_f is the lowest temperature by which the process responsible for the mass change has been completed. The values of T_i and T_f are not the absolute value significance as both the reaction temperature and the reaction intervals ($T_i - T_f$) have no definitive value but depend on the experimental conditions [39].

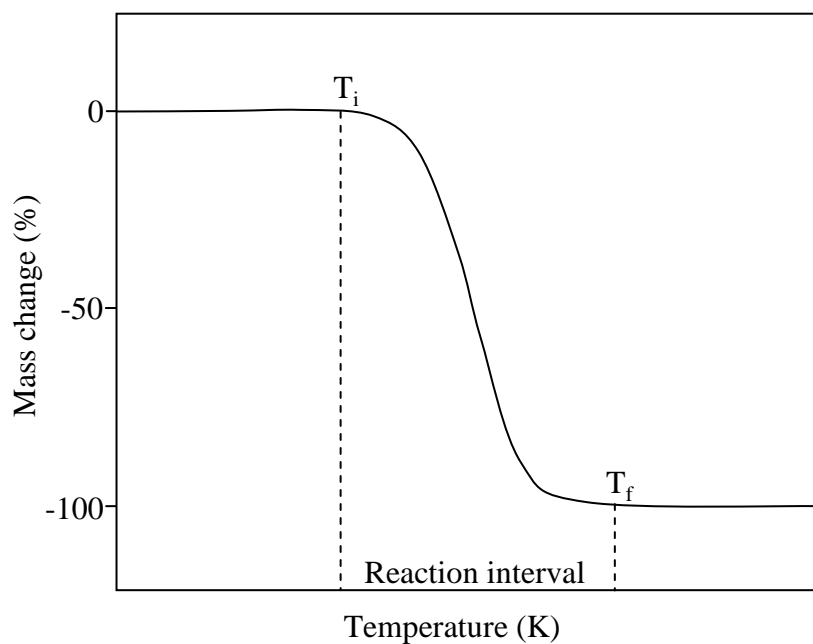


Figure 2.22 Schematic single stage TGA curve [39].

2.5.3 Limiting oxygen index (LOI) test

ASTM D2863 is used to determine the oxygen index, which is the minimum oxygen concentration (in a flowing mixture of oxygen and nitrogen) that will just support candle-like downward flaming combustion of a material initially at room temperature. It serves as a measure of the ease of extinction of the material. The

specimen size depends on the application. The specimen is placed vertically inside the test column and ignited at the top with a small gas flame to find the minimum oxygen concentration required in the mixture with nitrogen to support marginal combustion in the sample. The rating or LOI is expressed in terms of this volume percent oxygen concentration. A high LOI is demonstrative of a less easily ignited and less flammable material. LOI apparatus will be shown in Chapter III [16].

2.5.4 Tensile properties

The tensile test is popular because of the properties obtained could be applied to design different components. The test is also used to measure the resistance of a material to a static or slowly applied tensile force. A setup is shown in **Figure 2.23**. The standard specimen is placed in a tensile test machine and a force (F), called the load, is applied. A strain gages are intended for the measure the amount that the specimen stretches between the gage marks when the force is applied. Thus, what is measured is the change in length of tensile specimen (Δl) over a particular original gage length (l_o). Information concerning the strength, Young's modulus, failure strength, stiffness and ductility of a material can be obtained from such a tensile test.

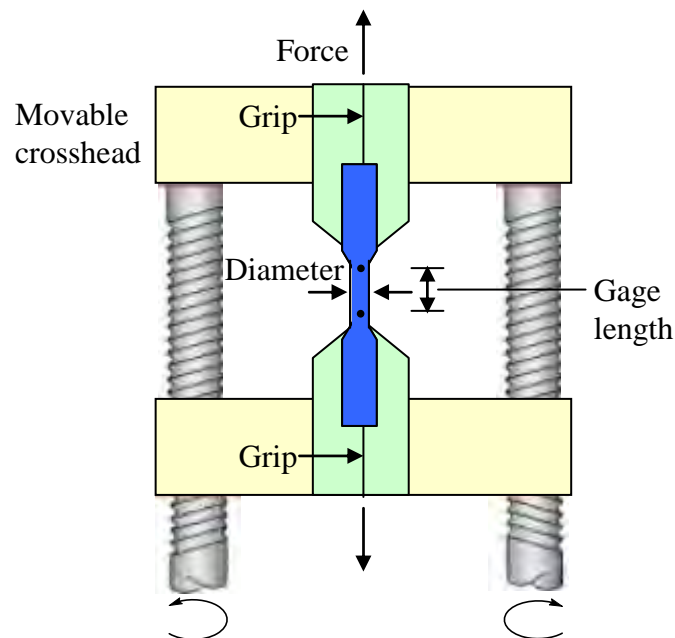


Figure 2.23 A unidirectional force is applied to a specimen in the tensile test by means of the moveable crosshead [40].

The results of a single test apply to all sizes and cross-sectional area of the specimen for a given material if converts the force to stress and the distance between gage marks to strain.

$$\text{Stress } (\sigma) = \frac{F}{A_o}$$

$$\text{Strain } (\epsilon) = \frac{\Delta l}{l_o}$$

Where A_o is the original cross-sectional area of the specimen before any load is applied, l_o is the original distance between the gage marks, and Δl is the change in length after force (F) is applied at any time. [40]. A stress-stain curve is shown in **Figure 2.24**.

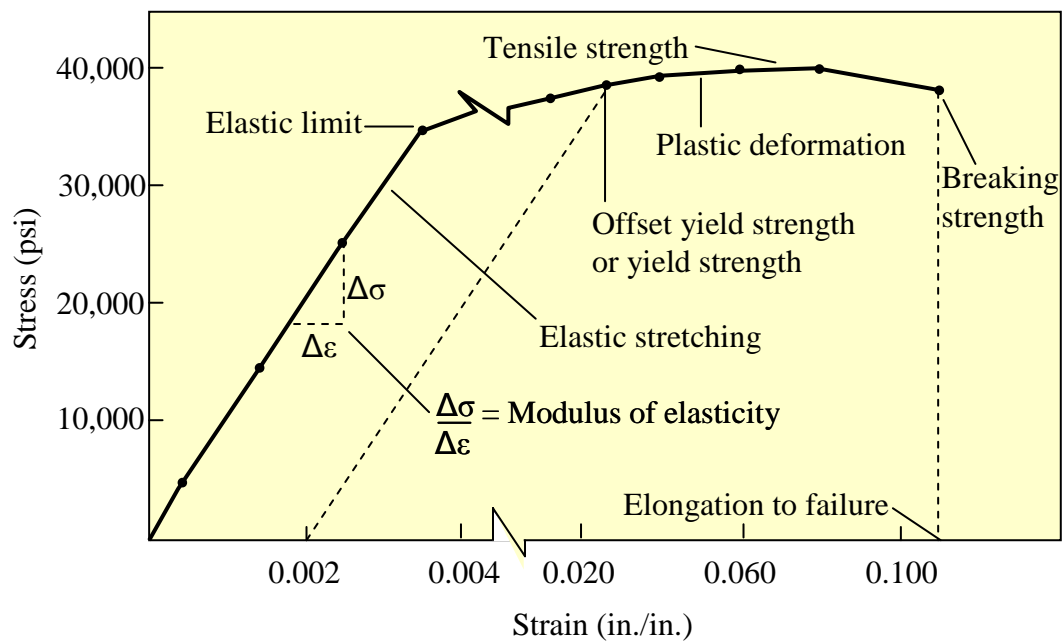


Figure 2.24 The stress-strain curve [40].

CHAPTER III

METHOD AND MATERIALS

3.1 Chemicals

Chemicals were reagent grade and were used without further purification.

They were purchased from the following vendors:

- Aldrich Chemical Co., Inc.: phenylphosphonic dichloride (PPDC)
- Fluka Chemical Corp.: ethylenediamine (EDA), *p*-phenylenediamine (PDA), sodium methoxide
- Carlo Erba Reagent: triethylamine (TEA)
- Merck Co., Ltd.: methanol

Tetrahydrofuran (THF) was purchased from Labscan Asia Co., Ltd. as solvent for the synthesis was reagent grade and was purified by standard method prior to use. Solvents for chromatography including dichloromethane, hexanes, ethyl acetate and methanol were commercial grade and were distilled before use. Diglycidyl ether of bisphenol-A (DGEBA, Grade Epon 828; epoxy equivalent 187) was received by East Asiatic (Thailand) Public Co., Ltd..

3.2 Instruments and equipments

3.2.1 Nuclear magnetic resonance (NMR) spectroscopy

All reported proton (^1H) and carbon (^{13}C) NMR were recorded using a Varian Mercury plus 400 NMR spectrometer operating at 400 MHz for ^1H and 100 MHz for ^{13}C nuclei. The samples were analyzed in hexadeuterio dimethylsulfoxide (DMSO-d_6) and deuterium oxide (D_2O). The chemical shifts (δ) are reported in parts per million (ppm) and are relative to that of tetramethylsilane (TMS) or relative to the reference peak of the deuterated solvent. Coupling constants (J) are given in Hertz (Hz). Phosphorus (^{31}P) NMR spectra were obtained on a Varian Unity Inova 500 MHz NMR spectrometer at the Scientific and Technology Research Equipment Center, Chulalongkorn University. Phosphoric acid was used as an external standard.

3.2.2 Fourier transform-infrared (FT-IR) spectroscopy

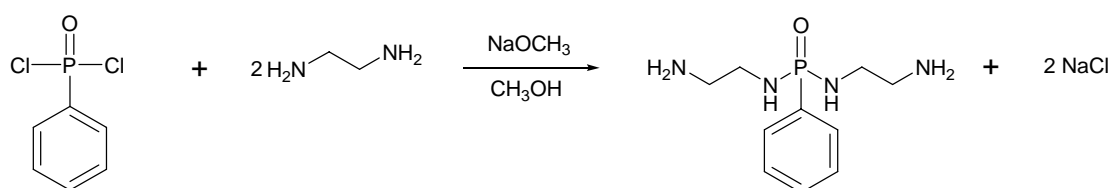
The FT-IR spectra were recorded on a Perkin Elmer: Spectrum RX-1 spectrometer with over 32 scans at a resolution of 4 cm^{-1} . The samples were prepared by mixing dried sample with KBr and compressing into disks or casting as films on NaCl cell. The spectra were acquired by using the Omnic ESP by plotting of the relative transmitted or reflected energy intensity as a function of frequency, normally in cm^{-1} in a range of $4000\text{-}500\text{ cm}^{-1}$.

3.2.3 Matrix assisted laser desorption ionization time-of-flight mass spectrometer (MALDI-TOF-MS)

Mass spectra were determined on a Bruker Microflex Matrix Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometer (MALDI-TOF-MS). The instrument was equipped with a nitrogen laser to desorb and ionize the samples. A stainless steel target was used as the substrate on which the samples were deposited. Sample was prepared in methanol when dithranol was used as the matrix and in water when α -cyano-4-hydroxy cinnamic acid (CCA) was used as the matrix.

3.3 Methods

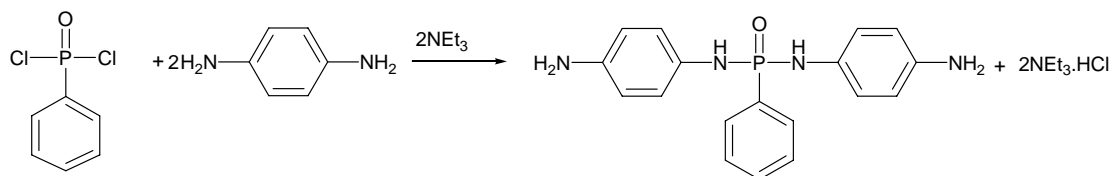
3.3.1 Synthesis of phenyl phosphonic ethylene diamine diamide



The synthesis of phenyl phosphonic ethylene diamine diamide was carried out analogously to the literature procedure by Toldy *et al.* [34] with a slight modification. Phenyl phosphonic ethylene diamine diamide was synthesized in a one-step route. The solution of ethylenediamine (10 mL, 0.15 mol) in dried tetrahydrofuran (THF) (30 mL) was placed in a 500 mL three neck round-bottom flask equipped with a magnetic stirrer. A solution of phenylphosphonic dichloride (7 mL, 0.05 mol) in dried THF (20 mL) was added dropwise into the solution with continuous stirring at $0\text{ }^\circ\text{C}$

under a nitrogen atmosphere over a period of 30 minutes. After addition of PPDC solution, the mixture was stirred for 2 h and then heated up to 60 °C with stirring under reflux cooler for 2 h. After that a solution of NaOCH₃ (5.40 g, 0.10 mol) in methanol (10 mL) was added and the mixture was stirred at 60 °C for 2 h. After the reaction was complete, the formed salt was filtered off. The filtrate was placed in a rotary evaporator to remove THF and methanol. Finally, the crude mixture was purified by flash silica gel chromatography (eluent: dichloromethane/ methanol, 9:1 v/v and 1 %v/v TEA in mixed solvents). The product was obtained as a white solid in 24% yield. ¹H NMR (D₂O): δ 2.84 (s, -NH- and -NH₂), 3.20-3.18 (m, 8H, -CH₂-), 7.35-7.56 ppm (m, 5H, aromatic protons); ¹³C NMR (D₂O): δ 38.2 (CH₂-NH₂), 40.6 (CH₂-NH), 128.3, 130.5 (CH=C(PO)-) 135.3, 137.2 ppm (C(PO)=CH-); ³¹P (D₂O): δ 18.73 ppm (s); FT-IR (KBr): 3100-3500 cm⁻¹ (-NH- and -NH₂ stretching), 1582 cm⁻¹ (P-Ph stretching), 1206 cm⁻¹ (P=O stretching), 945 cm⁻¹ (P-N stretching); MALDI-TOF-MS (CCA): *m/z* Calcd for C₁₀H₁₉N₄OP : 242.13. Found 242.69.

3.3.2 Synthesis of phenyl phosphonic *p*-phenylene diamine diamide



The synthesis of phenyl phosphonic *p*-phenylene diamine diamide was carried out analogously to the reaction described above. Phenyl phosphonic *p*-phenylene diamine diamide was synthesized by a one-step route. The solution of *p*-phenylenediamine (19 g, 0.18 mol) in dried THF (80 mL) was placed in a 1000 mL three neck round-bottom flask equipped with magnetic stirrer. Triethylamine (17 mL, 0.12 mol) was added to the solution. A solution of phenylphosphonic dichloride (8 mL, 0.06 mol) in dried THF (40 mL) was added dropwise into the solution with continuous stirring at 0 °C under a nitrogen over a period of 1 h. After addition of PPDC solution, the mixture was stirred for 3 h and then heated up to 60 °C for 4 h. After the reaction was complete, the solvent was evaporated off. The resulting solid product was slurried in 200 mL of water to remove triethylamine hydrochloride and the resultant solid was filtered off and dried. The mixture was purified by flash silica

gel chromatography (eluent: hexanes/ ethyl acetate, 7:3 v/v and 1 %v/v TEA in mixed solvents). The product was obtained as a reddish white solid in 35% yield. ^1H NMR (DMSO- d_6) δ 4.16 (s, -NH- and -NH $_2$), 6.84 (s, 8H, CH=C(NH)-, CH=C(NH $_2$)-), 7.38-7.57 ppm (m, 5H, aromatic protons); ^{13}C NMR (DMSO- d_6): δ 118.5 (CH=C(NH)-), (CH=C(NH $_2$)-), 125.4 (C-NH $_2$), 128.3, 133.3, 135.1 (CH=C(PO)-), 138.2 (C(PO)=CH), 145. 2 ppm (C-NH); ^{31}P (DMSO- d_6): δ 10.02 ppm (s); FT-IR (KBr): 2800-3300 cm^{-1} (-NH- and -NH $_2$ stretching), 1612 cm^{-1} (P-Ph stretching), 1209 cm^{-1} (P=O stretching), 1524 cm^{-1} (C=C in phenyl stretching), 965 cm^{-1} (P-N stretching), 690 cm^{-1} (para-disubstituted aromatic C-H bending); MALDI-TOF-MS (dithranol): m/z Calcd for C $_{18}$ H $_{19}$ N $_4$ OP : 338.13. Found 338.57.

3.3.3 Preparation of epoxy polymers using diamines as crosslinking agents.

The epoxy polymers were prepared analogously to the method by Chantarasiri *et al.* [41]. DGEBA epoxy resin was mixed with each diamine curing agent in a stoichiometric amount between the number of hydrogens of the amines and the number of the epoxy groups. The amounts of curing agent and epoxy resin used in order to obtain effective curing stoichiometric required were calculated as follows:

$$\text{phr} = \frac{\text{AHEW} \times 100}{\text{EEW}} \quad (3.1)$$

where phr is parts by weight of amine to be used with 100 parts by weight of epoxy resin. AHEW is weight of the amine molecule over the number of hydrogen atoms that are attached to the nitrogen atoms that was calculated as follows:

$$\text{AHEW} = \frac{\text{molecular weight of amine}}{\text{number of available amine hydrogens per molecule}} \quad (3.2)$$

EEW is calculated by dividing the molecular mass of the epoxy molecule by the number of epoxy groups in molecule.

DGEBA epoxy resin was mixed with each diamine curing agent and mechanically stirred at room temperature. The stirred mixtures become homogeneous then were degassed under vacuum until gas bubbles were no longer observed. The degassed mixture was put into a mold and cured in a vacuum oven at different isothermal temperatures. The sample was characterized by DSC and the progress of

the reaction was followed by FT-IR spectroscopy. The disappearance of the IR band of the epoxide group at 917 cm^{-1} was observed when the reaction was complete.

3.4 Investigation of thermal properties

3.4.1 Investigation by differential scanning calorimetry (DSC)

A differential scanning calorimeter (DSC) model Netzch 204 F1 Phoenix Instrument from the Scientific and Technology Research Equipment Center, Chulalongkorn University was used to study the curing behaviors. The mixture of DGEBA and diamine was put in aluminum pans and then scans were conducted at 5, 10, 15, and 20 °C/min heating rates in the temperature ranging from room temperature to 250 °C under a nitrogen atmosphere.

The temperature of the peak position of exotherm with heating rate of 5 °C/min was chosen as the curing temperature. The glass transition temperature of cured epoxy resins was determined at the heating rate of 10 °C/min under nitrogen atmosphere. The sample was heated to 200 °C for 17.5 min, then cooled down to room temperature and kept at this temperature for 5 min to remove polymer history. The sample was then heated again to 200 °C for 17.5 min. The DSC thermograms are shown in chapter IV.

3.4.2 Investigation by thermogravimetric analysis (TGA)

A thermogravimetric analyzer model Mettler Toledo TGA/SDTA851° at the Scientific Instruments Service Centre, King Mongkut's Institute of Technology Ladkrabang was used to study thermal stability and the decomposition of the cured epoxy resin. The experiment was done using the heating rate of 10 °C/min, both in nitrogen and air atmosphere. The temperature was ramped from room temperature to 800 °C using the sample mass of about 10 mg. The weight-loss profile, TGA thermograms are shown in chapter IV.

3.5 Investigation of flame retardant properties

3.5.1 Investigation by limiting oxygen index (LOI) test

The tests were carried out according to ASTM D2863-06a standard [42]. The specimen dimensions were $120 \times 12 \times 2\text{ mm}^3$ and they shall be marked at 10 mm and at 60 mm from the end to be ignited. The specimens were clamped vertically at the

center of the column. The flow valves were set to introduce the desired concentration of oxygen in the column. The relative flammability of the sample bar was determined by measuring the minimum concentration of oxygen needed to keep a sample burning from 10 mm to 60 mm. Limiting oxygen index apparatus is shown in **Figure 3.1**.

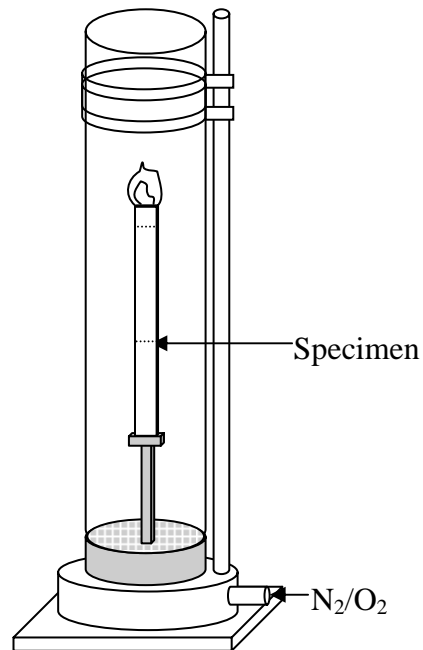


Figure 3.1 Limiting oxygen index apparatus [43].

3.5.2 Investigation by UL flame rating (UL-94)

The tests were carried out according to the UL-94 standard [44] which can be divided into two categories: horizontal and vertical testing. In the horizontal flame tests, the flame was applied to the free end of specimens held in a horizontal orientation for 30 seconds and the rate of burning was determined as the flame front progresses. To pass the test the specimen must not have a burning rate greater than 1.5 inches/minute or stop burning before the flame reaches the 4 inch mark as shown in **Figure 3.2**.

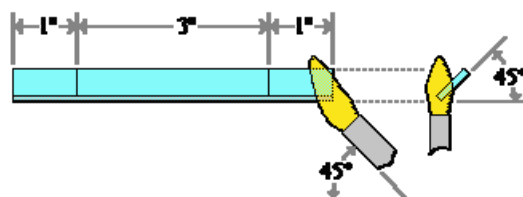


Figure 3.2 Horizontal flame test [45].

In the vertical flame test, a flame is applied to the base of the specimen held in the vertical position for 10 seconds. If the flame on the material is extinguished after the flame is removed, the flame is applied once again for 10 more seconds as shown in **Figure 3.3**. The following three grades of classifications are usually used to define the fire properties of the specimen:

Table 3.1 Materials flammability classification based on the UL-94 standard.

Vertical Ratings	Requirements
V-0	this means that the material stops burning within 10 seconds after the removal of the flame after both flame applications and there are no flaming drips from the burning specimen.
V-1	this is similar to V-0 with the only difference that the specimen must extinguish within 30 seconds after both flame applications.
V-2	this is also similar to V-1 with the only difference that the flaming drips are allowed to ignite tissue paper lying underneath.

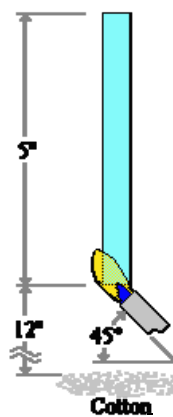


Figure 3.3 Vertical flame test [45].

3.6 Investigation of tensile properties

The tensile properties of cured epoxy resins were measured according to ASTM D638-10 test method [46]. The testing was performed on a Universal Testing Machine model DSS-10T. The specimens were prepared to form dog-bone shaped specimens as shown in **Figure 3.4**. For each sample, at least 5 specimens were tested with the crosshead speed of 5 mm/min and a full scale force at 10 kN.

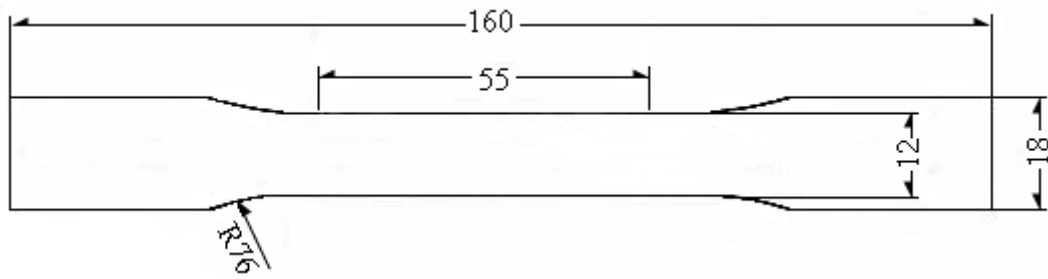


Figure 3.4 Schematic diagram of a tensile test specimen [46].

CHAPTER IV

RESULTS AND DISCUSSION

This chapter has been divided into 3 parts. The first has been focused on the synthesis and characterization of two phosphorus-containing diamine diamides. The second part, epoxy polymers were prepared by using various amines as crosslinking agents. Finally, epoxy polymers were characterized to determine the cure kinetics, thermal properties, flame retarding properties, and tensile properties.

4.1 Synthesis and characterization of phosphorus-containing diamine.

4.1.1 Synthesis and characterization of phenyl phosphonic ethylene diamine diamide (PPEDD).

Phenyl phosphonic ethylene diamine diamide (PPEDD) was synthesized through the condensation reaction of phenylphosphonic dichloride (PPDC) and ethylenediamine (EDA). In the process of the synthesis, the nucleophilic chlorine in PPDC could serve as a reactive site for the electrophilic hydrogen in EDA using sodium methoxide as an acid acceptor. The condensation reaction of PPDC with EDA may be controlled by use of excess EDA. In addition, PPDC gradually added into the reaction vessel. The crude product was further purified by column chromatography using dichloromethane/ methanol, 9:1 v/v and 1 %v/v TEA in mixed solvents, as eluent. The phosphorodiamidate was obtained as a white solid in 24% yield. The formation of phosphorus-containing reactive amine groups is confirmed by ^1H NMR, ^{13}C NMR, ^{31}P NMR, FT-IR and MALDI-TOF-MS.

The ^1H NMR spectrum of PPEDD in D_2O exhibited signals of protons corresponding to the structure shown in **Figure 4.1**. The proton NMR spectrum of PPEDD showed the signal of $-\text{NH}-$ and $-\text{NH}_2$ at 2.84 ppm (a). The signals of methylene and aromatic protons were observed at 3.20-3.18 (b, c) and 7.35-7.56 ppm (d), respectively.

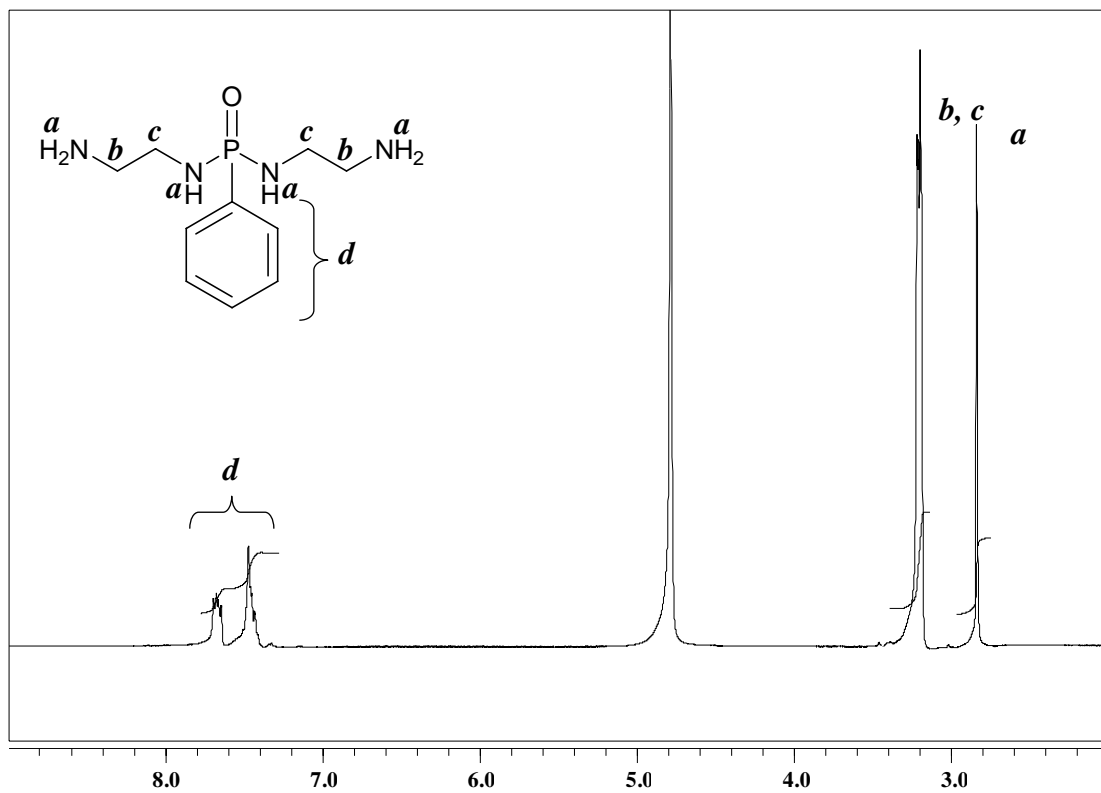


Figure 4.1 ^1H NMR spectrum of PPEDD in D_2O .

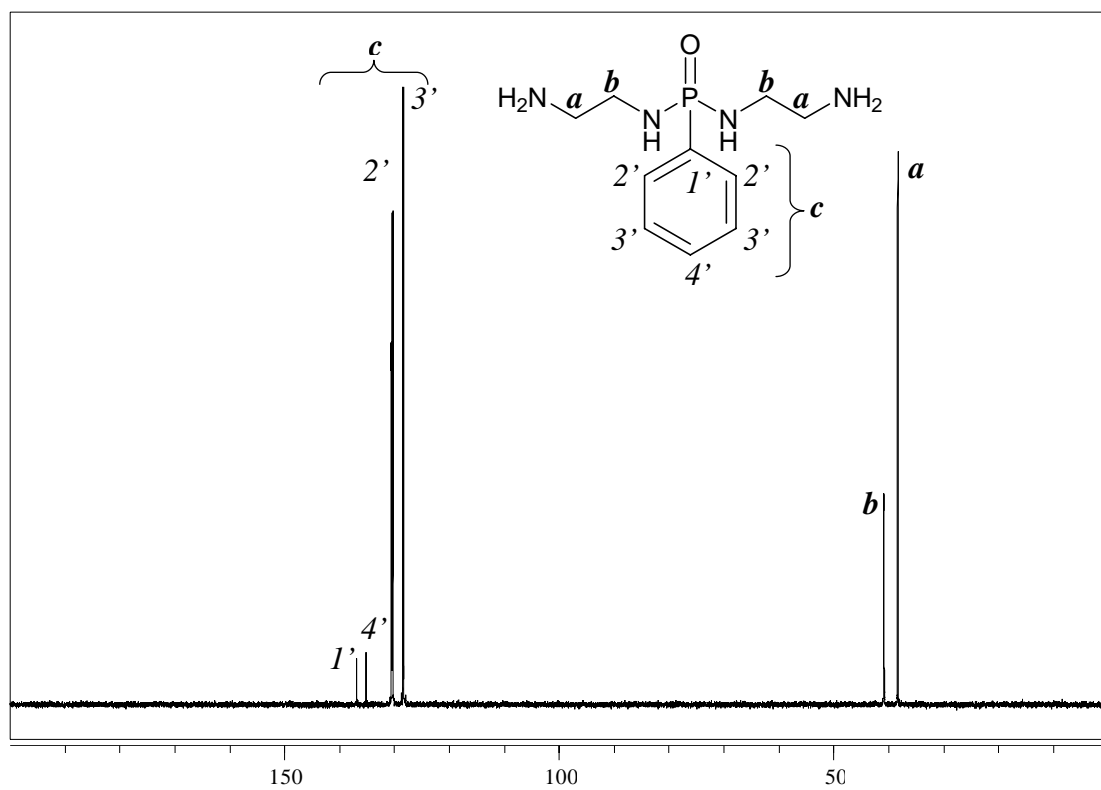


Figure 4.2 ^{13}C NMR spectrum of PPEDD in D_2O .

The ^{13}C NMR spectrum of PPEDD in D_2O , illustrated in **Figure 4.2**, showed the resonance corresponding to all the carbons of the given structure. The signals of methylene carbons appeared at 38.2 ppm ($\text{CH}_2\text{-NH}_2$) (a) and 40.6 ppm ($\text{CH}_2\text{-NH}$) (b). The signals of aromatic carbons appeared in the region of 128.3-137.2 ppm (c).

^{31}P NMR spectroscopy was employed to detect any phosphorus species in the compound. The phosphorus signal in D_2O at 18.73 ppm appeared as a single peak, corresponding to only one compound with a phosphorus atom in the molecule as shown in **Figure 4.3**.

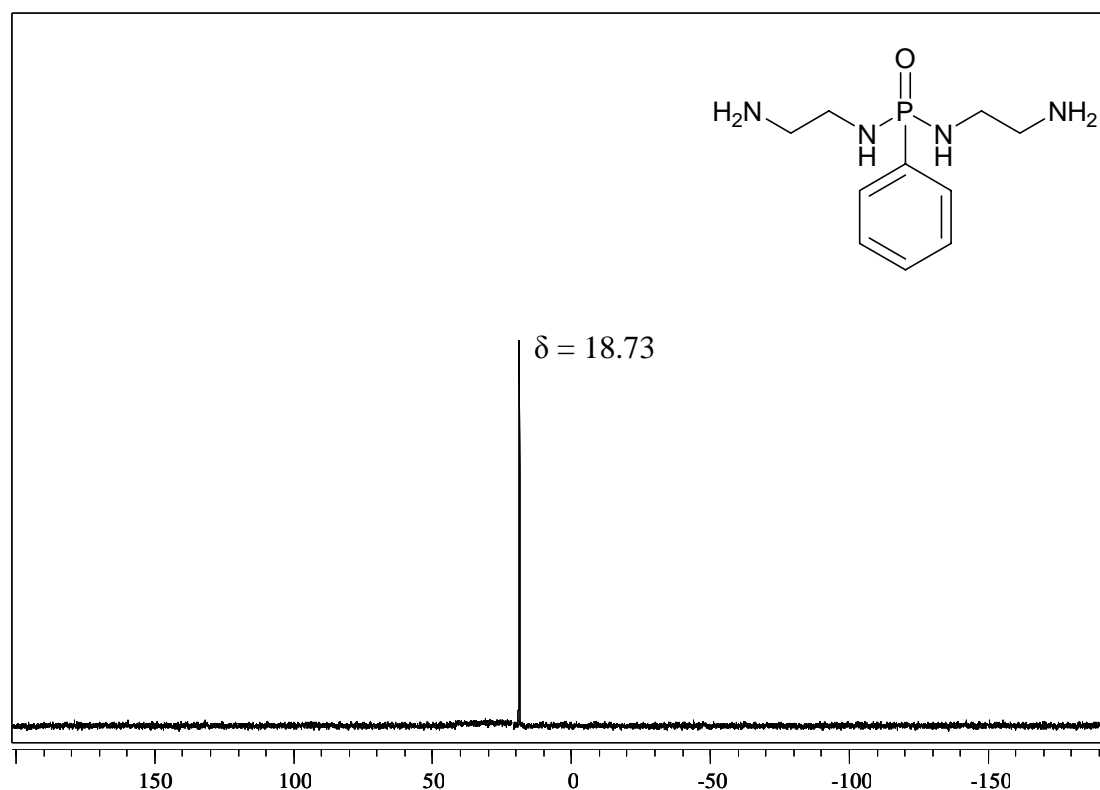


Figure 4.3 ^{31}P NMR spectrum of PPEDD in D_2O .

Functional group presents in the compound were determined by FT-IR spectroscopic analysis. The FT-IR spectrum (**Figure 4.4**) showed absorption peaks of the -NH- and -NH_2 stretching vibration of amine at $3100\text{-}3500\text{ cm}^{-1}$. The absorption band at 1582 cm^{-1} is assigned to be the phosphorus-aromatic carbon stretching vibration in the P-Ph bond of the phenylphosphoramidate. The absorption band at 1209 cm^{-1} indicates stretching vibrations of P=O of phosphoramidate and 945 cm^{-1} indicates

stretching vibrations of P-N of phosphoramidate. In addition, in the MALDI-TOF mass spectrum, only one peak at the mass of 242.69 was observed, as shown in **Figure 4.5**. This corresponds to the mass of PPEDD.

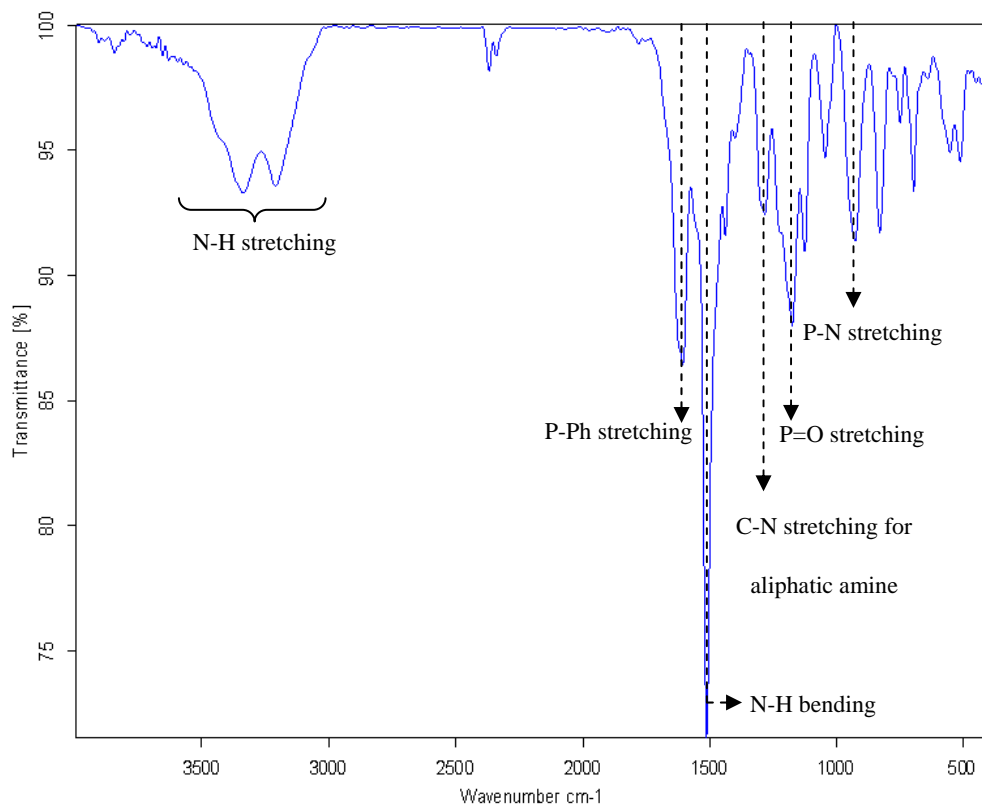


Figure 4.4 FT-IR spectrum of PPEDD.

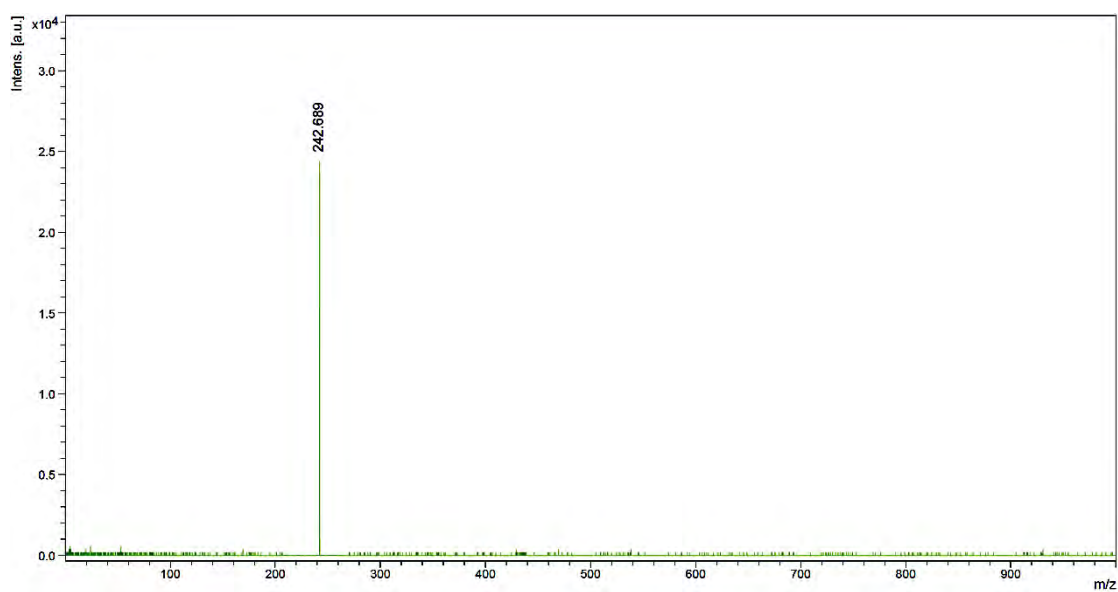


Figure 4.5 MS spectrum of PPEDD.

4.1.2 Synthesis and characterization of phenyl phosphonic *p*-phenylene diamine diamide (PPPDD)

The synthesis of phenyl phosphonic *p*-phenylene diamine diamide (PPPDD) was carried out analogously to the reaction of PPEDD. PPPDD was synthesized *via* a condensation reaction between PPDC and *p*-phenylenediamine in dried THF using triethylamine as an acid acceptor. The crude product was further purified by column chromatography using hexanes/ ethyl acetate, 7:3 v/v and 1 %v/v TEA in mixed solvents, as eluent. The product was obtained as a reddish white solid in 35% yield. The chemical structure of PPPDD was verified by ^1H NMR, ^{13}C NMR, ^{31}P NMR, FT-IR, and MALDI-TOF-MS.

In the ^1H NMR spectrum of PPPDD in DMSO, illustrated in **Figure 4.6**, the signal of -NH- and -NH₂ was observed at 4.16 ppm (a). The signals of ortho- and meta-protons of para-disubstituted aromatic ring appeared at 6.84 ppm (b and c), while those of the phenyl ring were found at 7.38-7.57 ppm (d).

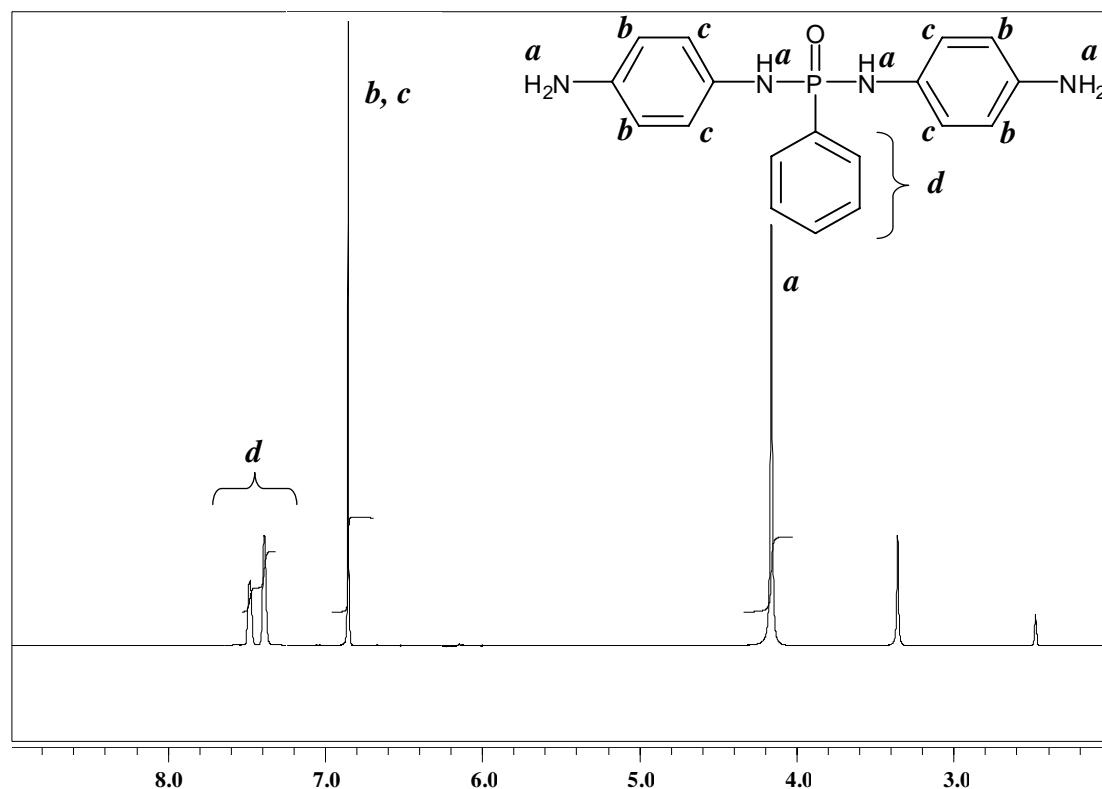


Figure 4.6 ^1H NMR spectrum of PPPDD in DMSO.

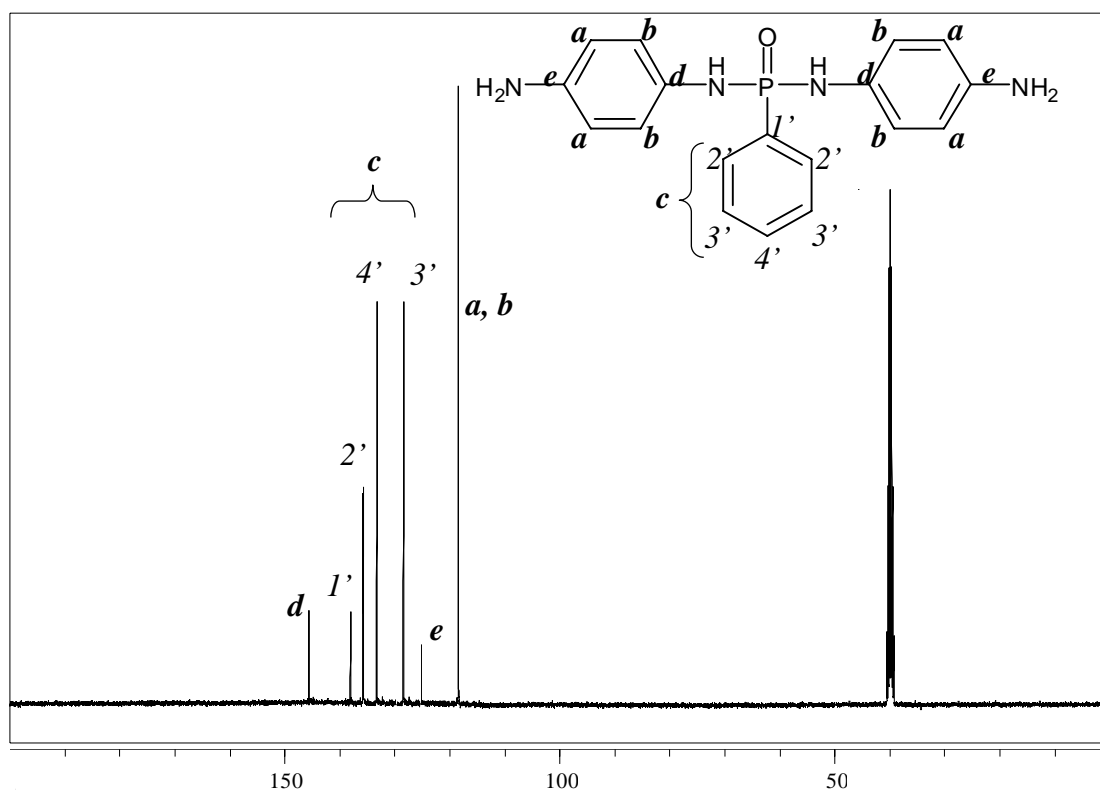


Figure 4.7 ^{13}C NMR spectrum of PPPDD in DMSO.

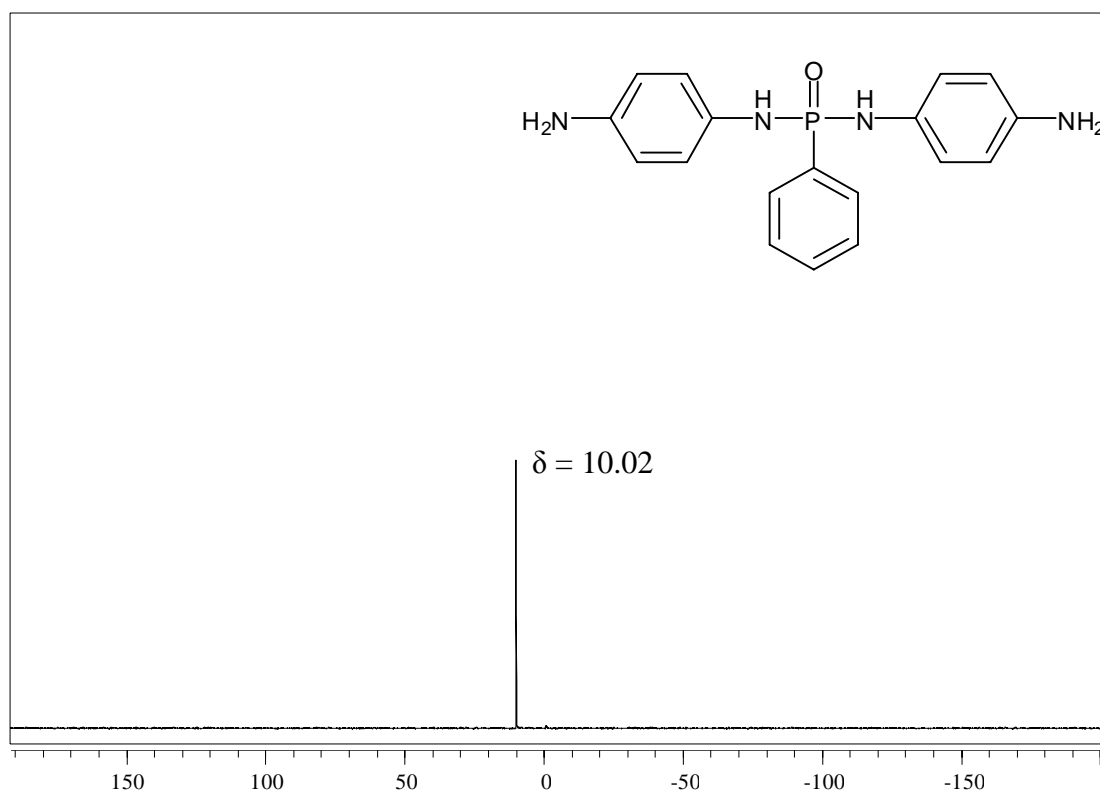


Figure 4.8 ^{31}P NMR spectrum of PPPDD in DMSO.

The ^{13}C NMR spectrum in DMSO (**Figure 4.7**) showed the signals of carbons in para-disubstituted aromatic ring at 118.5 ppm (a and b). C-NH_2 , C-NH signals appeared at 125.4 (d) and 145.2 ppm (e), respectively. The signals of phenyl ring carbons showed up in the region of 128.3 to 138.2 ppm (c).

The ^{31}P NMR spectrum of PPPDD in DMSO is shown in **Figure 4.8**. The phosphorus signal appeared at 10.02 ppm as the only peak. This confirms the presence of only one phosphorus species.

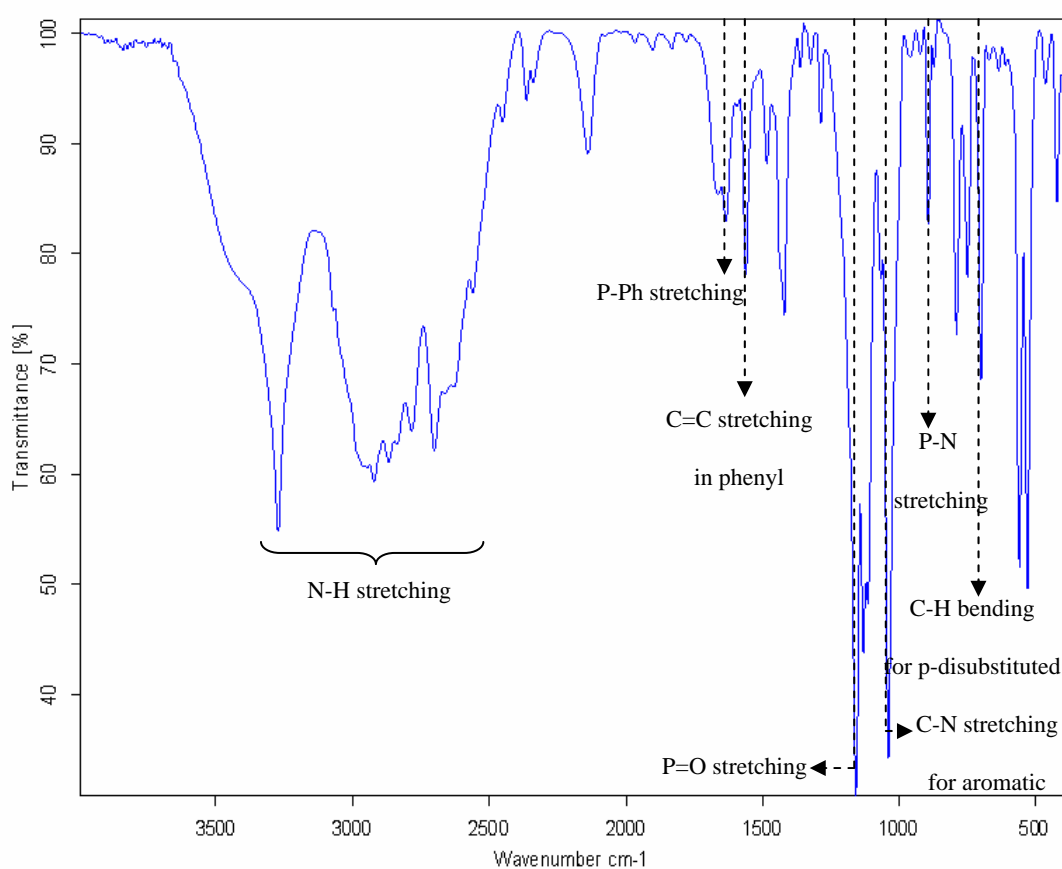


Figure 4.9 FT-IR spectrum of PPPDD.

The FT-IR spectrum showed absorption characteristics of $-\text{NH}-$ and $-\text{NH}_2$ stretching of amine at $2800\text{--}3300\text{ cm}^{-1}$. The absorption band at 1592 cm^{-1} is assigned to be the phosphorus-aromatic carbon stretching vibration in the P-Ph bond of the phenylphosphoramidate. The absorption band at 1209 cm^{-1} indicates stretching vibrations of P=O of phosphoramidate and the 965 cm^{-1} peak indicates stretching

vibrations of P-N of phosphoramidate. A characteristic peak of the C=C stretching in aromatic rings was observed at 1524 cm^{-1} . The absorption band of C-H bending of benzene ring with disubstituents at the para position appeared at 690 cm^{-1} . Only one peak of PPPDD was found at 338.57, as shown in **Figure 4.10**.

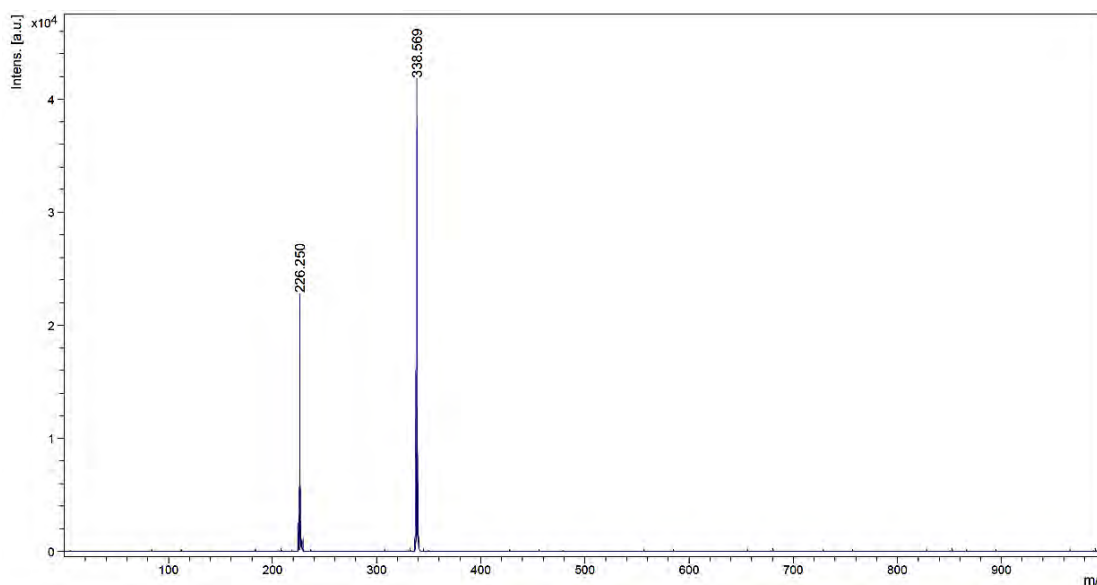


Figure 4.10 MS spectrum of PPPDD.

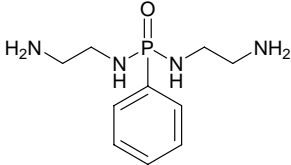
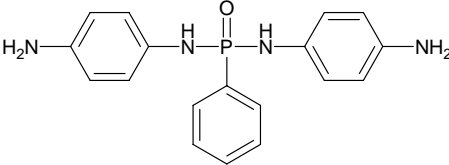
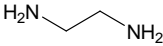
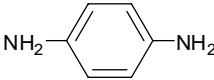
All the data are supportive of the success in the synthesis of the desired compounds.

4.2 Preparation and characterization of epoxy polymers

DSC was employed to investigate whether crosslinking reactions of DGEBA with various diamines could occur. The optimum crosslinking conditions could also be determined by the use of this technique. The results of the calculations of the stoichiometric amount of amine curing agents for curing with the epoxy resin are shown in **Table 4.1**. DSC experiments were performed by heating a mixture of DGEBA and various diamines in an appropriate stoichiometric ratio. A DSC cell was used in a closed aluminum pan. The temperature range used was varying from $23\text{ }^{\circ}\text{C}$ to $250\text{ }^{\circ}\text{C}$ at a heating rate of $5\text{ }^{\circ}\text{C}/\text{min}$.

EDA and PDA have always been popular curing agent for epoxy resins. All properties studied in this work were compared the phosphorus-containing curingagent with EDA and PDA.

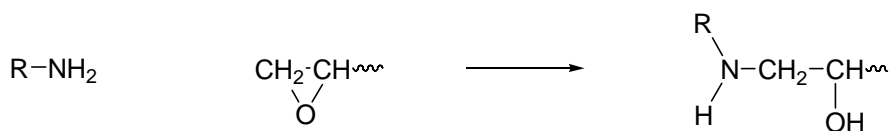
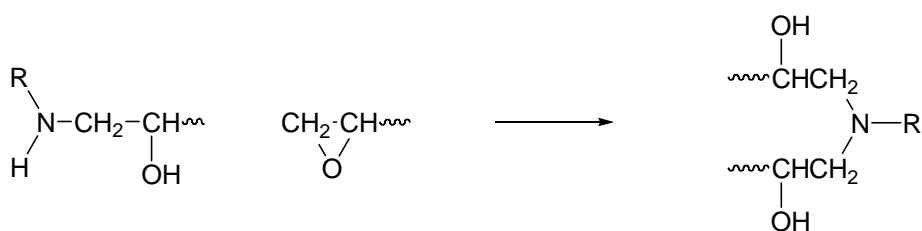
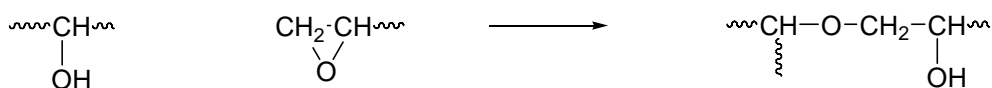
Table 4.1 Equivalent weight ratio of DGEBA and diamine used in the preparation of epoxy polymer.

Curing agent	The chemical structure of curing agent	Amount of curing agent (phr)	P (%) ^a
PPEDD		22	2.3
PPPDD		30	2.1
EDA		8	N/A
PDA		14	N/A

^a P (%) is the percentage of phosphorus after curing.

Figure 4.11 illustrates the thermograms obtained when various diamines (EDA, PDA, PPEDD, and PPPDD) were used. The crosslinking temperatures for preparation of the polymers of each pair of epoxy resin and curing agent were chosen from the peak maximum determined by the DSC thermograms. Therefore, the crosslinking temperature of DGEBA with EDA, PDA, PPEDD, and PPPDD was 88, 188, 217, and, 232 °C respectively. The reactivity of the amine crosslinking agents could be reflected from the crosslinking temperature [47] in such a way that the lower the curing temperature the higher the reactivity of the amine curing agent.

From the DSC thermograms (**Figure 4.11**), therefore, it can be seen that the reactivity of the amine curing agent decreasing in the order is EDA>PDA>PPEDD>PPPDD.

Primary amine-epoxy addition*Secondary amine-epoxy addition**Hydroxyl-epoxy reaction***Scheme 4.1** Epoxy-amine curing reactions [48].

When comparing the non-phosphorus-containing curing agents, EDA and PDA, EDA has higher reactivity than PDA. The rationale to this observation is based on the difference in electron density available on the nitrogen atoms. The electron-pushing ethylene enriches the electron density of amine in EDA, while the electron withdrawing benzyl group reduces the electron density of amine in PDA.

In the case of phosphorus-containing curing agents PPEDD and PPPDD, however, the structures of PPEDD and PPPDD are different. The backbone structure of PPEDD the ethylene groups, would enrich the electron density of the amine group, while PPPDD has the electron withdrawing benzyl group in the backbone structure. This leads to the observation that PPEDD is a little more reactive than PPPDD. Furthermore, the phr of diamine used is different between PPEDD (22 phr) and PPPDD (30 phr) because of difference in the molecular weights. The increase in the molecular weight of the amine results in the reduction of the epoxy content per gram of resin thus, hindering the diffusion of amine toward epoxy.

When comparing between non-phosphorus- and phosphorus-containing curing agents, non-phosphorus-containing curing agents have higher reactivity than phosphorus-containing curing agents. For PPEDA and PPPDD, the P=O group serves as an electron-withdrawing group, consequently reducing their activity in crosslinking

with epoxides compared to the reactivity of the non-phosphorus containing counterparts [49, 50].

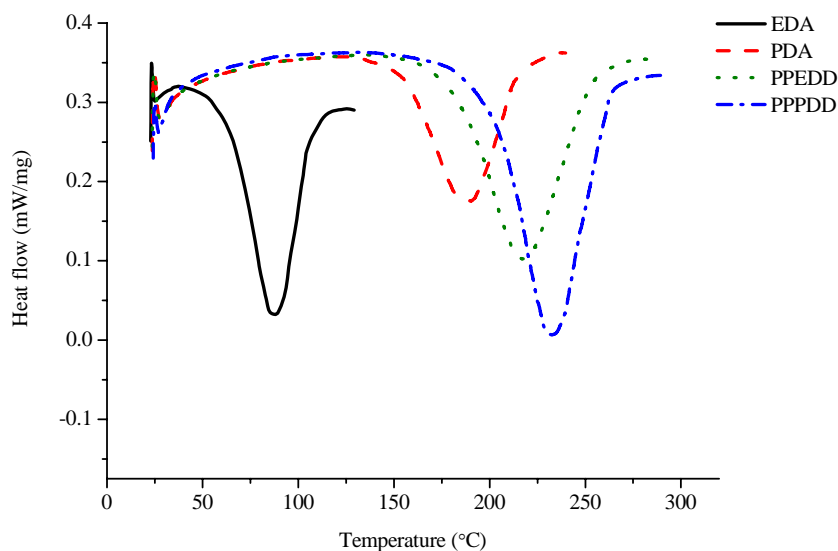


Figure 4.11 DSC thermograms of DGEBA cured with EDA, PDA, PPEDD, and PPPDD.

Table 4.2 Composition and crosslinking condition of epoxy resins with various amine.

Crosslinking agent	Amount of crosslinking agent (phr)	Crosslinking condition	
		Temperature (°C)	Time (min)
EDA	8	88	30
PDA	14	188	30
PPEDD	22	217	40
PPPDD	30	232	40

Infrared spectroscopy was used to study the crosslinking condition by determining the time required for the crosslinking reaction to be complete. The completeness of the crosslinking reaction was confirmed by the disappearance of the characteristic absorption band of the epoxide groups in DGEBA at 917 cm^{-1} . The IR spectra were obtained from heating the mixtures of DGEBA and various diamine at a

stoichiometric balanced ratio and the crosslinking temperature of each diamine. The time required for each reaction to be complete is determined as shown in **Table 4.2**.

When the mixtures were heated at crosslinking temperature for 10 min, the IR absorption band of epoxide group at 917 cm^{-1} was still observed. Therefore, the crosslinking reaction was not complete. However, the time required to complete the reactions were 30, 30, 40, and 40 min for EDA, PDA, PPEDD and PPPDD respectively, illustrated in (**Table 4.2**) as the IR absorption band at 917 cm^{-1} completely disappeared. Moreover, in the first stages of the cure increased the $-\text{OH}$ bands appeared more strongly at around 3500 cm^{-1} , but subsequently decreased. This indicated that the epoxide ring was opened by the primary amine of the crosslinking agents to form a secondary amine and a hydroxyl group. The reaction of the epoxide with the secondary amine, to produce a tertiary amine, leads to an increase in $-\text{OH}$ groups, but decrease in relative intensity of $-\text{OH}$ band in the later stages because of each hydroxyl group can react with an epoxide ring in the presence of tertiary amine catalysts to form an ether linkage [9]. The progresses of the reaction of all compounds are displayed in **Figures 4.12-4.15**.

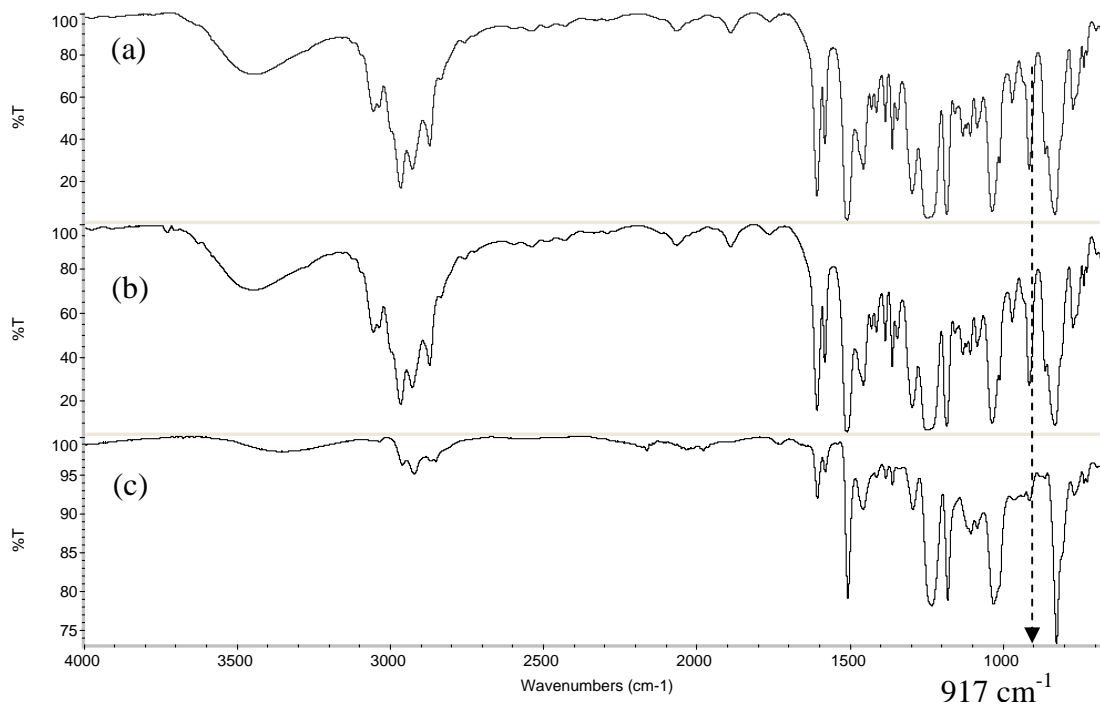


Figure 4.12 IR spectra of DGEBA cured with EDA (a) after heating at $88\text{ }^{\circ}\text{C}$ for 10 min (b) 20 min and (c) 30 min.

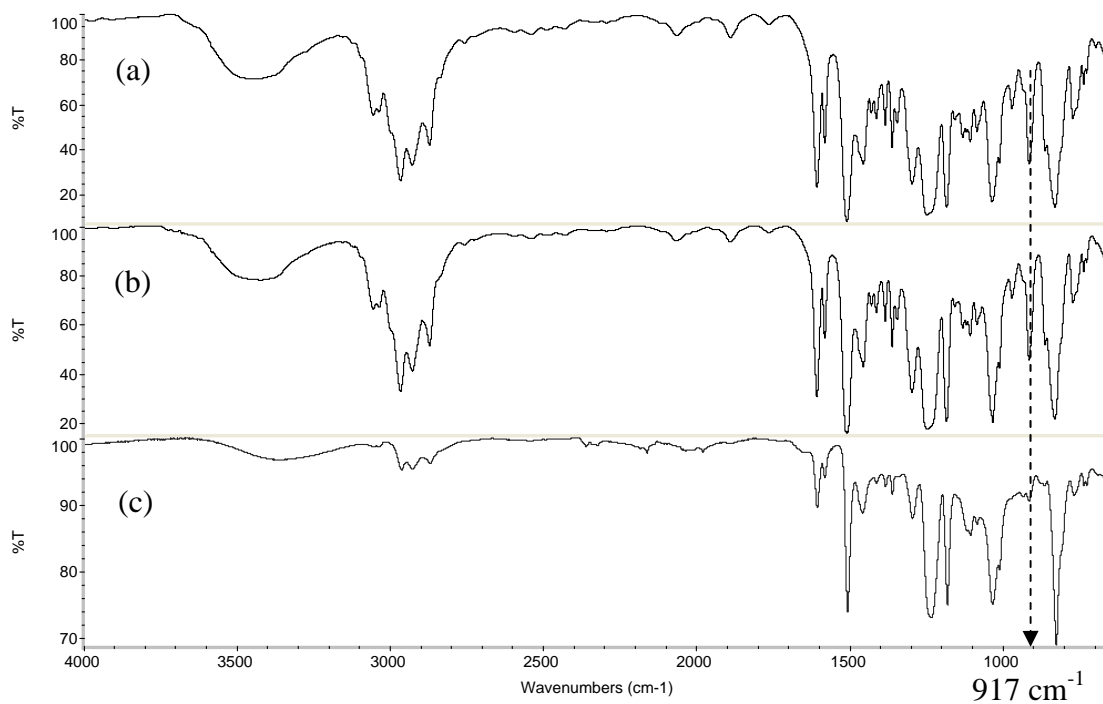


Figure 4.13 IR spectra of DGEBA cured with PDA (a) after heating at 188 °C for 10 min (b) 20 min and (c) 30 min.

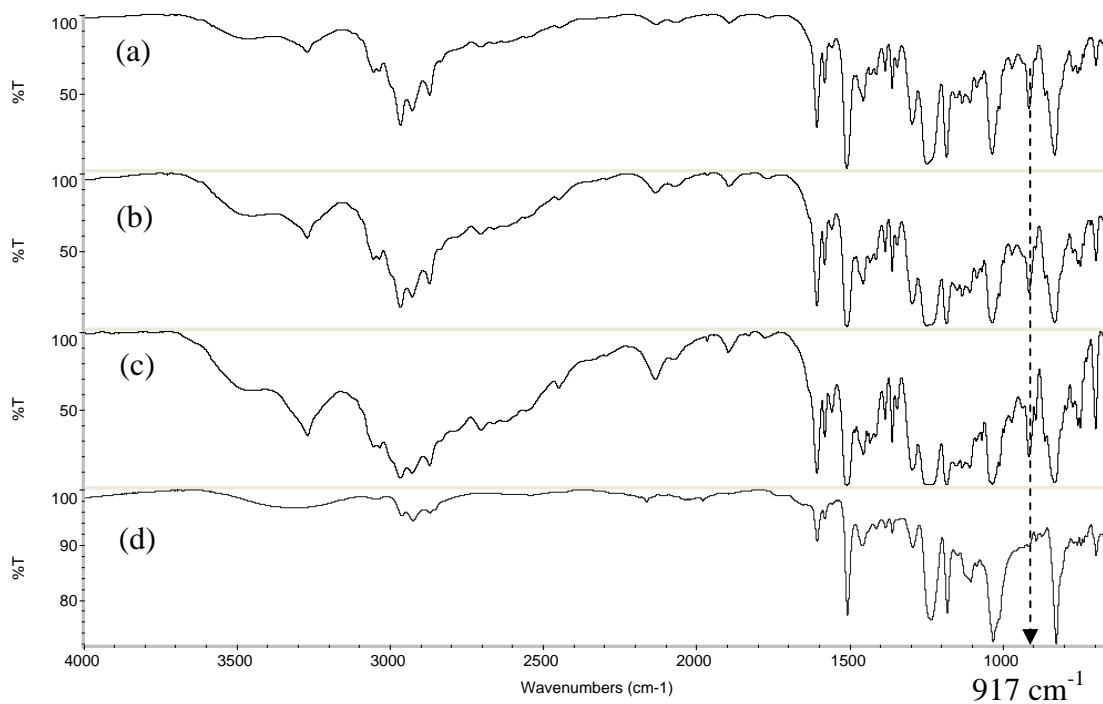


Figure 4.14 IR spectra of DGEBA cured with PPEDD (a) after heating at 217 °C for 10 min (b) 20 min (c) 30 min and (d) 40 min.

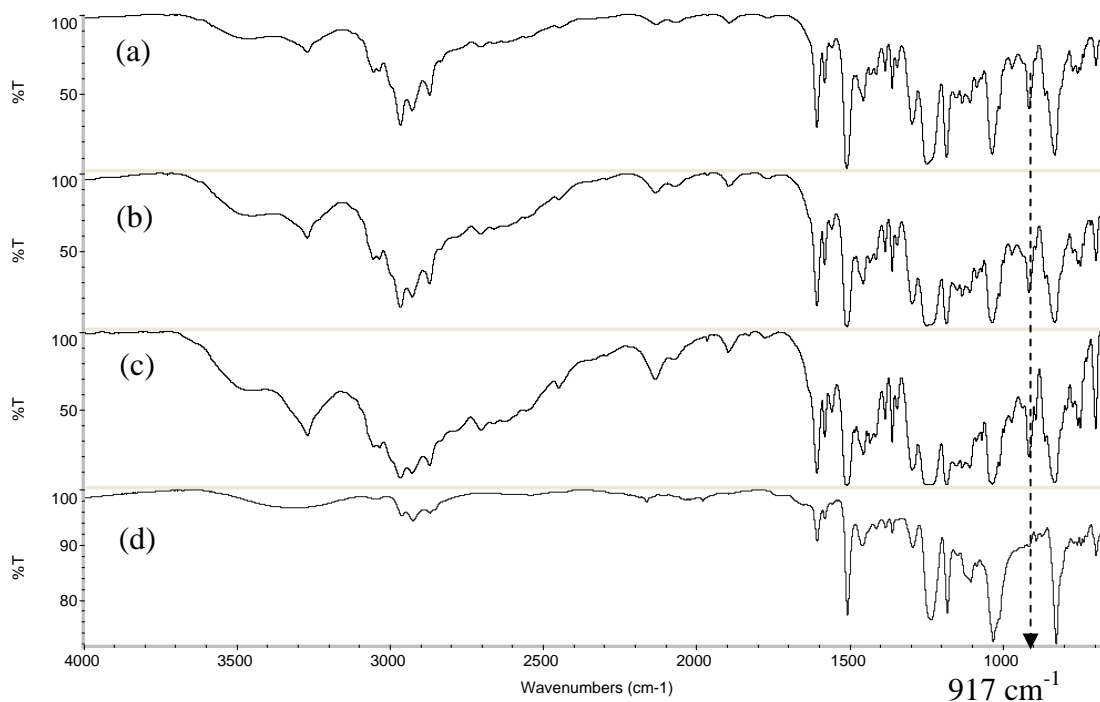


Figure 4.15 IR spectra of DGEBA cured with PPPDD (a) after heating at 232 °C for 10 min (b) 20 min (c) 30 min and (d) 40 min.

4.3 Characterization of epoxy polymer using phosphoramidate as crosslinking agents

The next step was to prepare samples of crosslinked epoxy resins for further characterization. The samples were prepared as described in the experimental section. EDA and PDA were also employed as crosslinking agents for epoxy resin as references in order to compare the properties of the phosphorus-containing crosslinking agents with the known system. Effect of using different diamines of cured epoxy resins was studied in order to determine the crosslinking that yielded polymers with the best properties.

4.3.1 Effect of using different diamines on cure kinetics of cured epoxy resins

The curing reactions of the studied epoxy resins with various diamines were investigated by DSC at four different heating rates. **Figure 4.16** shows the DSC

curves recorded at 5, 10, 15 and 20 °C/min of epoxy resins cured with EDA. This will be discussed first.

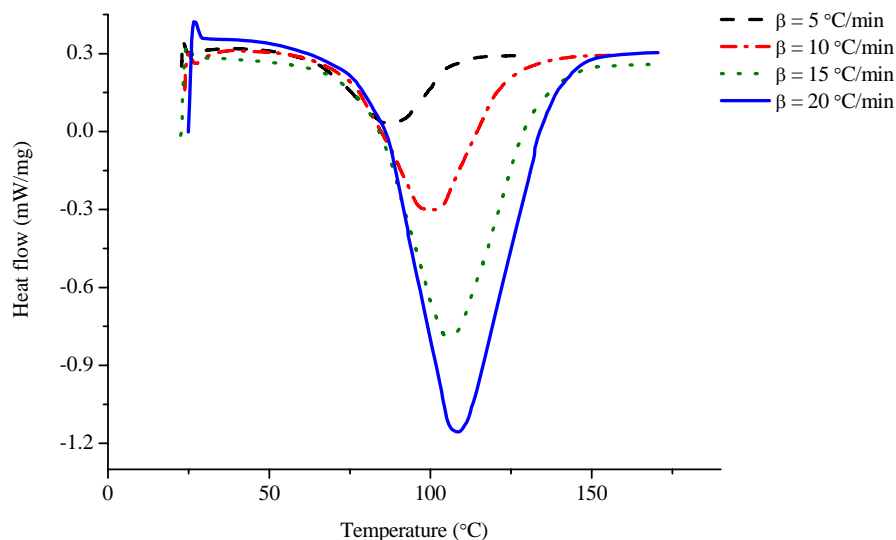


Figure 4.16 DSC curves at different heating rates of epoxy resin cured with EDA.

The DSC test of epoxy resin with EDA (**Figure 4.16**) shows that there is only single exothermic peak on the DSC curve. At the approximation that the rates of reactions of hydrogen atoms in primary and secondary amines of EDA with epoxide occur simultaneously [51]. Moreover, the cure exotherm, the peak temperature (T_p) shifted to higher values with increasing heating rate (β). This is mainly owing to the fact that the polymer responds less promptly to the higher heating rates and initial polarization has to be released in a shorter time [52] (*vide infra*). The DSC tests of epoxy resins with PDA, PPEDD, and PPPDD were carried out in the same way thermograms are shown in **Figures 4.17, 4.18, and 4.19**, respectively. The results obtained for each compound can be analyzed in similar manner as those of EDA.

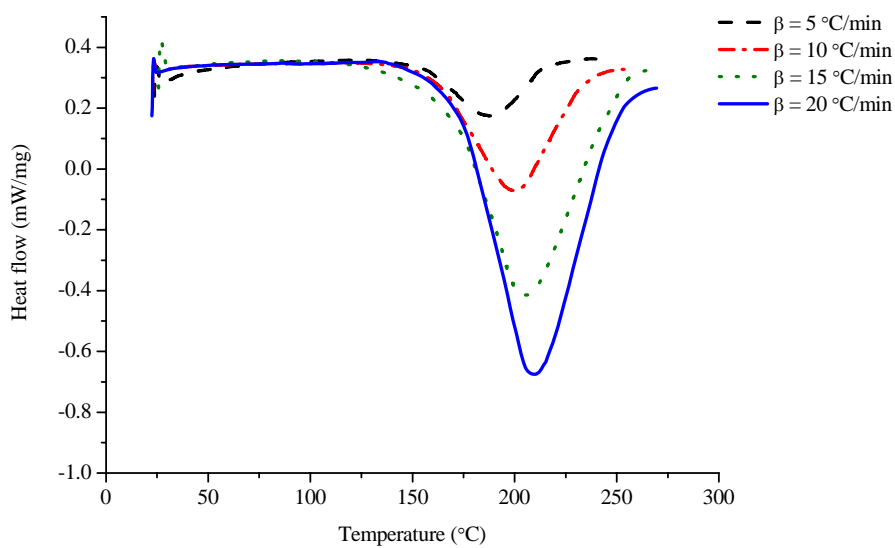


Figure 4.17 DSC curves at different heating rates of epoxy resin cured with PDA.

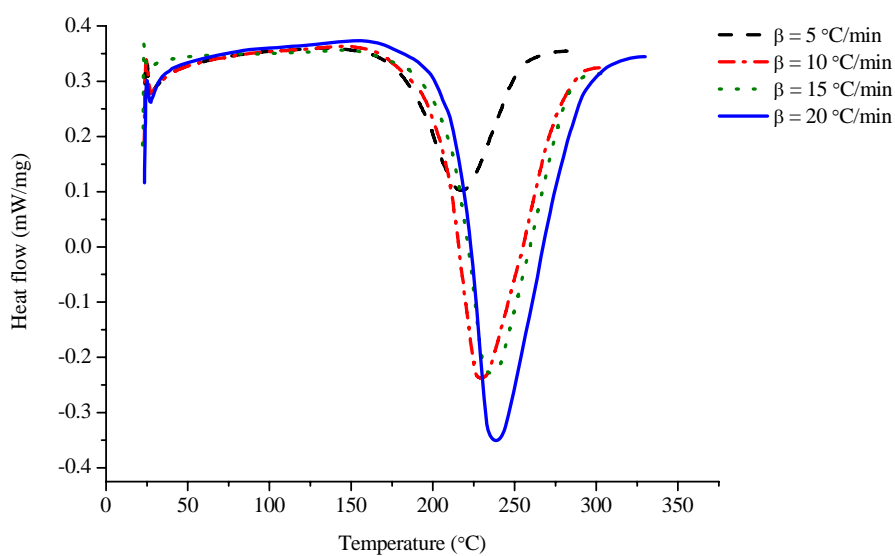


Figure 4.18 DSC curves at different heating rates of epoxy resin cured with PPEDD.

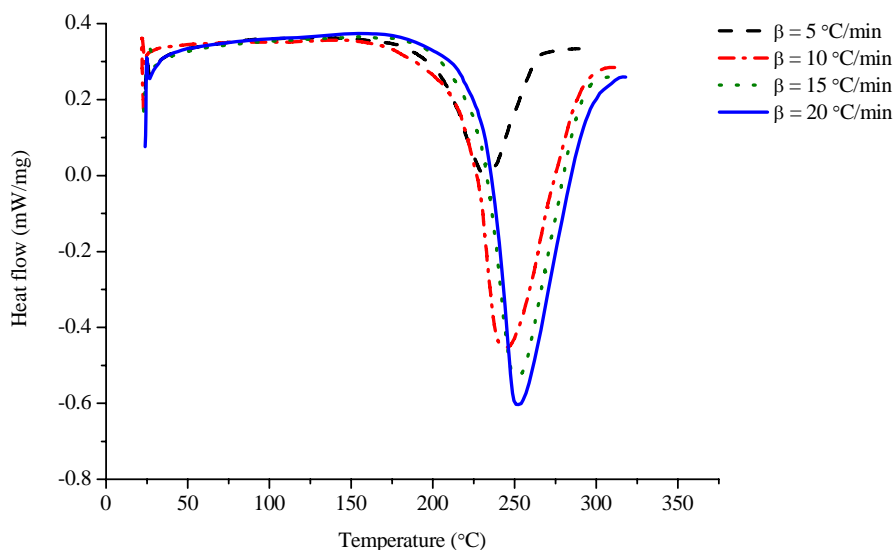


Figure 4.19 DSC curves at different heating rates of epoxy resin cured with PPPDD.

The observed peak-shifting phenomenon caused by an increasing in the scanning rate depends on the activation energy associated with each reaction. Based on this peak-shifting phenomenon, the activation energies of the curing reactions of epoxy resin with various diamine were calculated from calorimetric experiments by the Kissinger equation [53].

$$\frac{d \ln(\beta/T_p^2)}{d (1/T_p)} = -\frac{E_a}{R} \quad (4.1)$$

Where R is the gas constant. The value of activation energy E_a for a curing reaction was evaluated by performing DSC experiments at different heating rates and plotting $\ln(\beta/T_p^2)$ versus reciprocal of the exothermic peak temperature ($1/T_p$). The activation energy was obtained from the slope of the resulting straight line.

Based on equation (4.1), this has been carried out in **Figure 4.20**, showing the experimental data obtained for the epoxy resins cured with EDA, PDA, PPEDD, and PPPDD.

As illustrated, the linear relationships were obtained, thus confirming the validity of the proposed model given in the equation. The activation energy E_a was calculated from the slopes, yielding E_a values shown in **Table 4.3**.

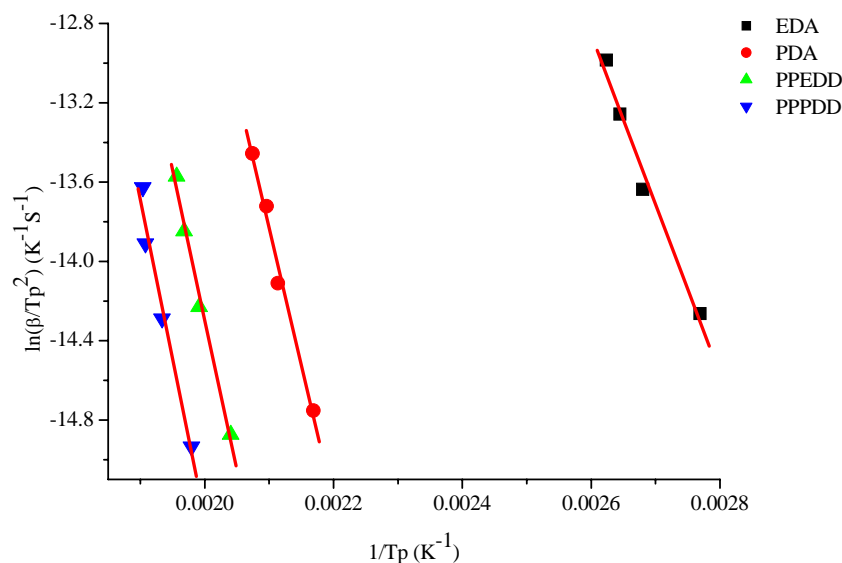


Figure 4.20 Plot of the heating rate against $1/T_p$ of epoxy resins cured with EDA, PDA, PPEDD and PPPDD.

Table 4.3 The kinetics of the epoxy curing reaction.

Crosslinking agent	T_p ($^{\circ}\text{C}$) at various β ($^{\circ}\text{C}/\text{min}$)				E_a (kJ/mol)
	5	10	15	20	
EDA	88	100	105	108	71
PDA	188	200	204	209	114
PPEDD	217	229	235	238	125
PPPDD	232	244	251	252	133

From **Figure 4.20** and **Table 4.3**, it is noteworthy that the activation energy for EDA is quite different from PDA, PPEDD, and PPPDD. This is due to the fact that EDA is in a liquid state, therefore it is easy to mix with the epoxy resin while PDA, PPEDD, and PPPDD are a solid and are more difficult to mix into the resin. When comparing between non-phosphorus- and phosphorus-containing crosslinking agents, the activation energy for reactions of epoxy resin with crosslinking agents with phosphorus are much higher than those for reactions of epoxy resin with crosslinking agents without phosphorus. This result is also consistent with the result related by crosslinking temperature. The reactivity of epoxy-amine crosslinking

reaction depends not only on electron-donating group of the amine compound, but also on the diffusion controlled process [54]. The much more bulky and more complex structure of PPPDD than those of crosslinking agents without phosphorus markedly reduces its diffusion rate and reaction mobility in crosslinking reaction. Accordingly, the reaction barrier, E_a , for PPPDD is higher. As for PPEDD even with the electron-donating methylene groups, the P=O may play a more important role. Moreover, with the present of the Ph-P=O group, the structure is more complex than EDA and PDA. As a result the diffusion rate is higher. When comparing PPEDD and PPPDD, the structures of which are different where there are 2 additional rings in PPPDD, the reactions of PPPDD possess higher E_a than those of PPEDD. In contrast, but unsurprisingly, the lowest E_a for EDA is essentially attributed to its having both the simplest molecular structure and the functional group of the diamine that promotes the reactivity of the ring opening.

The Kissinger equation gives only one E_a from the data of T_p . It is necessary that all the reactions involved be equally activated. This is true for a one-step reaction, but it does not relate the intermediate reaction steps that occur during the case of an epoxy-amine reaction. A more complete determination of E_a at any selected conversion can be calculated by the isoconversional equation which is expressed as [55]:

$$\frac{d(\ln(\beta)_\alpha)}{d(1/T)_\alpha} = -\frac{E_\alpha}{R} \quad (4.2)$$

where E_α is the activation energy value at a given conversion degree and T is the temperature of a selected conversion degree at each heating rate. The value of α can be obtained from the area under the DSC curve:

$$\alpha = \frac{Q_n}{Q_{tot}} \quad (4.3)$$

Where Q_n is given by the fractional area and Q_{tot} by the total peak area obtained as a mean of the values at different heating rates.

To perform isoconversional analysis, the original DSC data (**Figure 4.16, 4.17, 4.18, and 4.19**) were transformed into term form α_i versus T_i for each heating rate. These are expressed **Figure 4.21, 4.22, 4.23, and 4.24**.

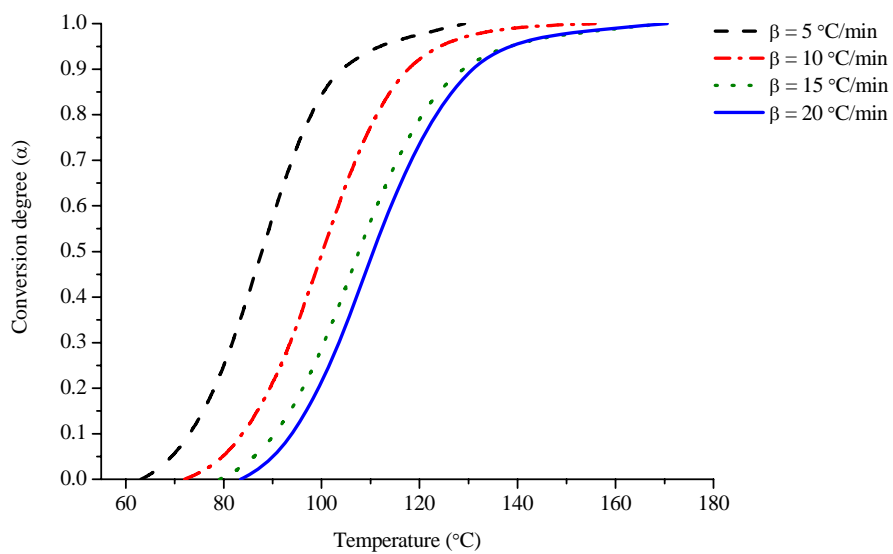


Figure 4.21 Plot of the α_i versus T_i for each heating of epoxy resin cured with EDA.

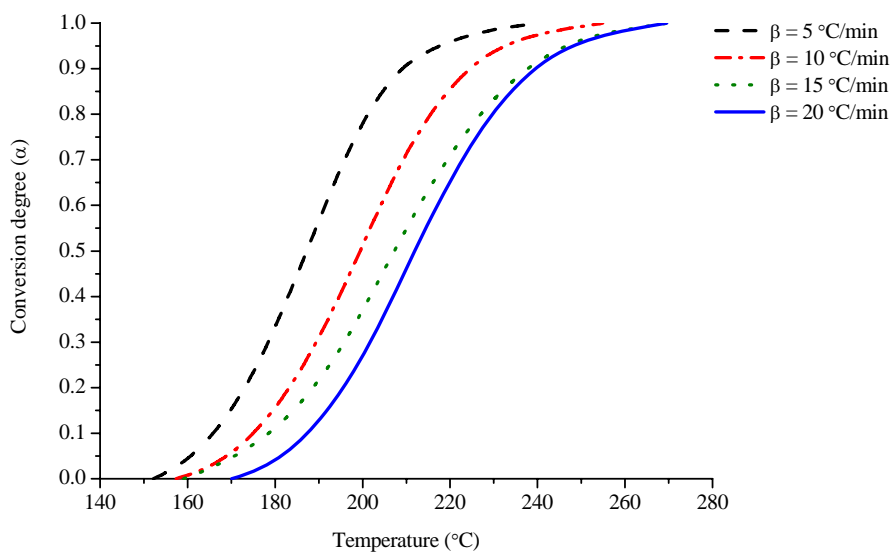


Figure 4.22 Plot of the α_i versus T_i for each heating of epoxy resin cured with PDA.

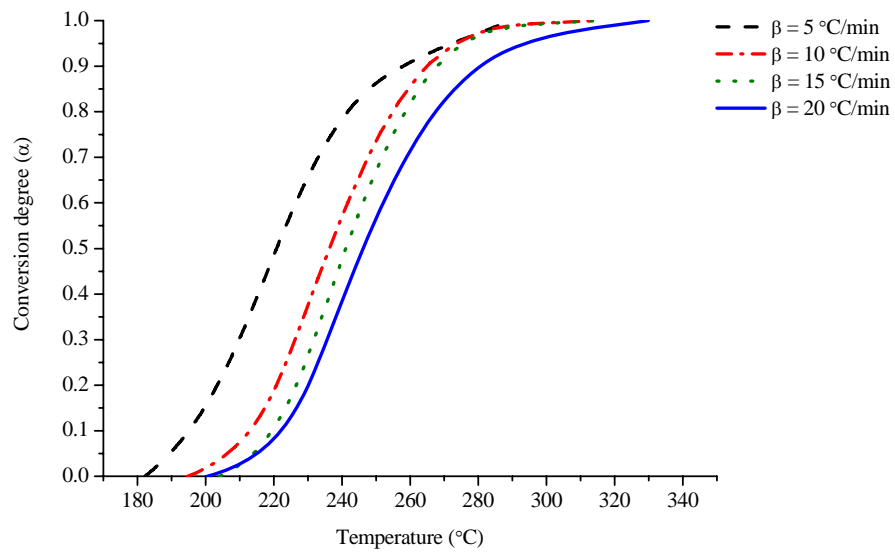


Figure 4.23 Plot of the α_i versus T_i for each heating of epoxy resin cured with PPEDD.

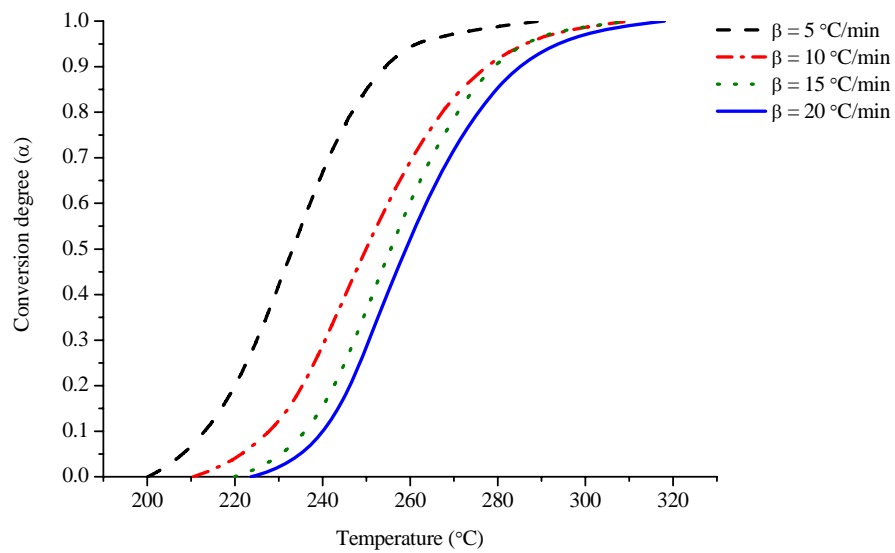


Figure 4.24 Plot of the α_i versus T_i for each heating of epoxy resin cured with PPPDD.

For each degree of conversion, the logarithms of the heating rate of each crosslinking agents were plotted against the inverse of the temperature resulting in plots in **Figure 4.25, 4.26, 4.27, and 4.28**.

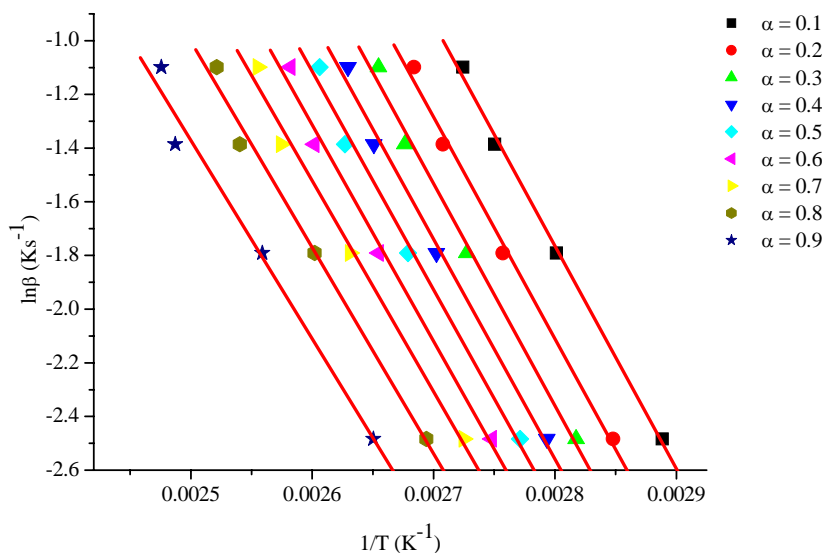


Figure 4.25 Relationship between the conversion degree α and $1/T$ of epoxy resin cured with EDA.

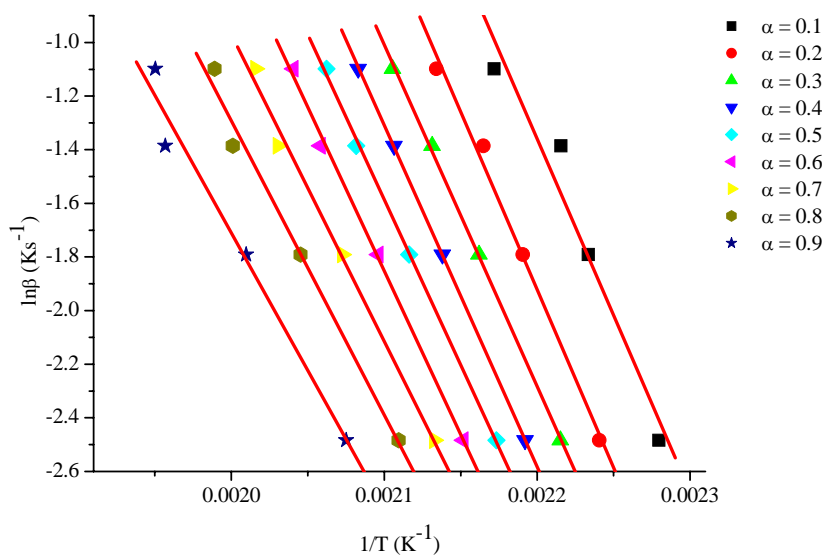


Figure 4.26 Relationship between the conversion degree α and $1/T$ of epoxy resin cured with PDA.

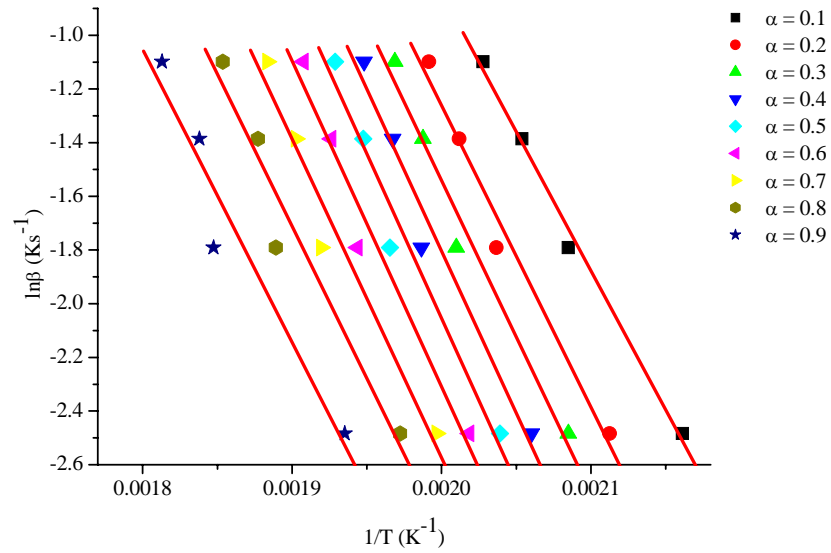


Figure 4.27 Relationship between the conversion degree α and $1/T$ of epoxy resin cured with PPEDD.

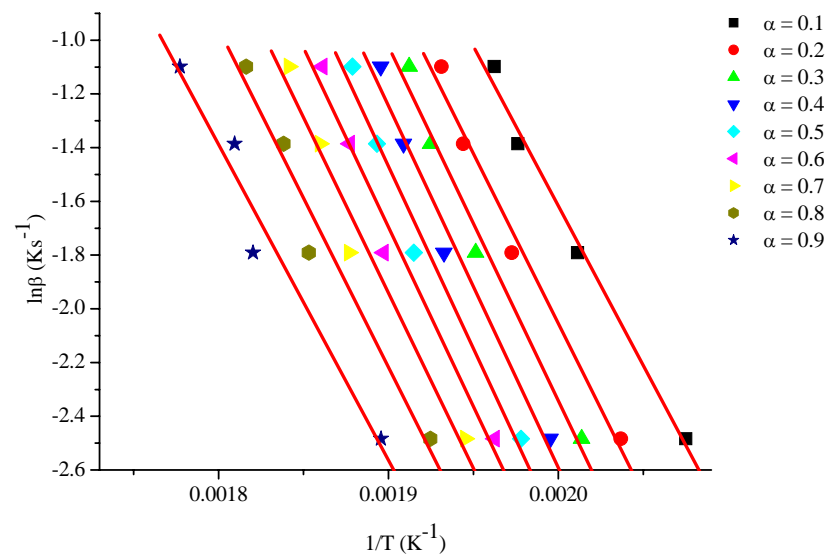


Figure 4.28 Relationship between the conversion degree α and $1/T$ of epoxy resin cured with PPPDD.

For each experimental curve, the slope ($-E_a/R$) of the corresponding plot was calculated. Each point corresponds to $-E_a/R$ at each value of the conversion degree. **Figure 4.29** shows the E_a values obtained by the proposed isoconversional method against the conversion degree (α). This reflects the change in the activation energy as the curing proceeds.

As can be seen in **Figure 4.29**, the activation energy of epoxy resins cured with various amine changes throughout the cure. In the case of epoxy resin cure with crosslinking agents without phosphorus, showing E_a to gradually decrease with the increase in conversion. This can be attributed to the autocatalytic nature of the reaction. The reaction is catalyzed by the hydroxyl groups formed during the epoxy amine addition reaction the higher amount of the hydroxyl group formed, the easier the reaction could proceed. This is good evidence that steric hindrance can not be a crucial factor in the reaction between the epoxy and crosslinking agents without phosphorus [56, 57]. The early stage reaction of epoxy resin cured with PDA, PDA system reduces E_a much than EDA system. It is possible that PDA is a solid and is more difficult to mix with the resin and then the reaction progress the E_a tends to be very decrease.

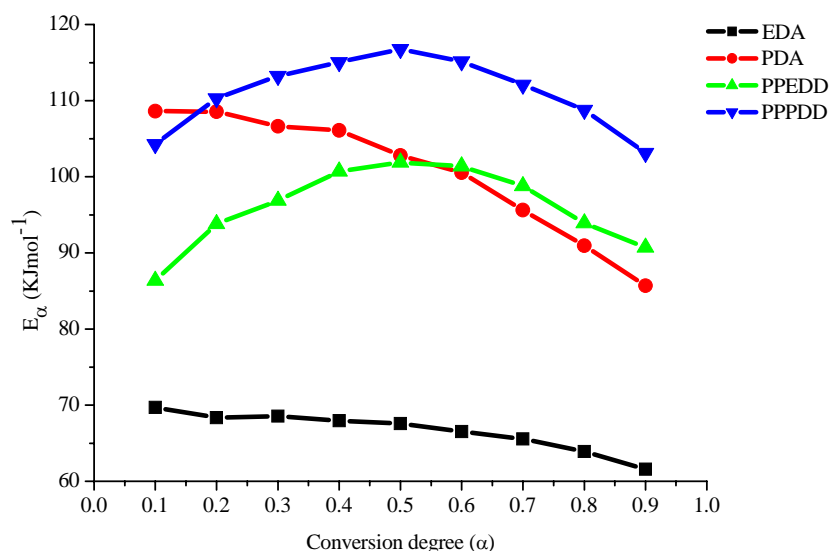


Figure 4.29 Dependence of the activation energy on the conversion degree of the epoxy resins cured with EDA, PDA, PPEDD and PPPDD.

In the case of epoxy resin cured with crosslinking agents with phosphorus (PPEDD and PPPDD), the initial increase of E_a for low conversions follows a plateau at intermediate conversions, whereas at conversions of around 50% and above the activation energy starts to decrease. This may be due to the combined effects of steric hindrance as well as the electron-withdrawing effect of P=O in the structure [50]. However, in all cases E_a values are decreased gradually at higher conversion because of reaction of curing reaction is catalyzed by the hydroxyl groups formed during the epoxy amine addition reaction.

4.3.2 Effect of using different diamines on thermal properties of cured epoxy resins

DSC analysis were performed in order to determine the difference in thermal behavior of epoxy resins cured with different types of diamines. The glass transition temperature (T_g) of the epoxy polymers were measured from a first heating trace with differential scanning calorimetry (DSC) at 10 °C/min heating rate. The thermograms of epoxy polymers are shown in **Figure 4.30**. At T_g there is a change in slope of the curve due to change in the heat capacity of polymer from the glass state to the rubber state. Glass transition at onset temperature is the first value was obtained from the onset temperature in the heat flow curve while Glass transition at midpoint temperature is the latter value was obtained from the peak temperature of the first derivative of the heat flow curve.

The glass transition temperature is the temperature at which there is only enough energy for vibrational to occur. In general the glass transition temperature depends on free volume of the polymer, which is the volume of the polymer mass not actually occupied by the molecules themselves. The higher free volume is the more room the molecules have to move around and the lower T_g . When the introduction of crosslinks into a polymer, the intermolecular linkages will be spaced so closely as reduces the available free volume and thereby increase the T_g and increase stiffness value. This effect increases with increasing crosslink density (**Figure 4.31**) [58].

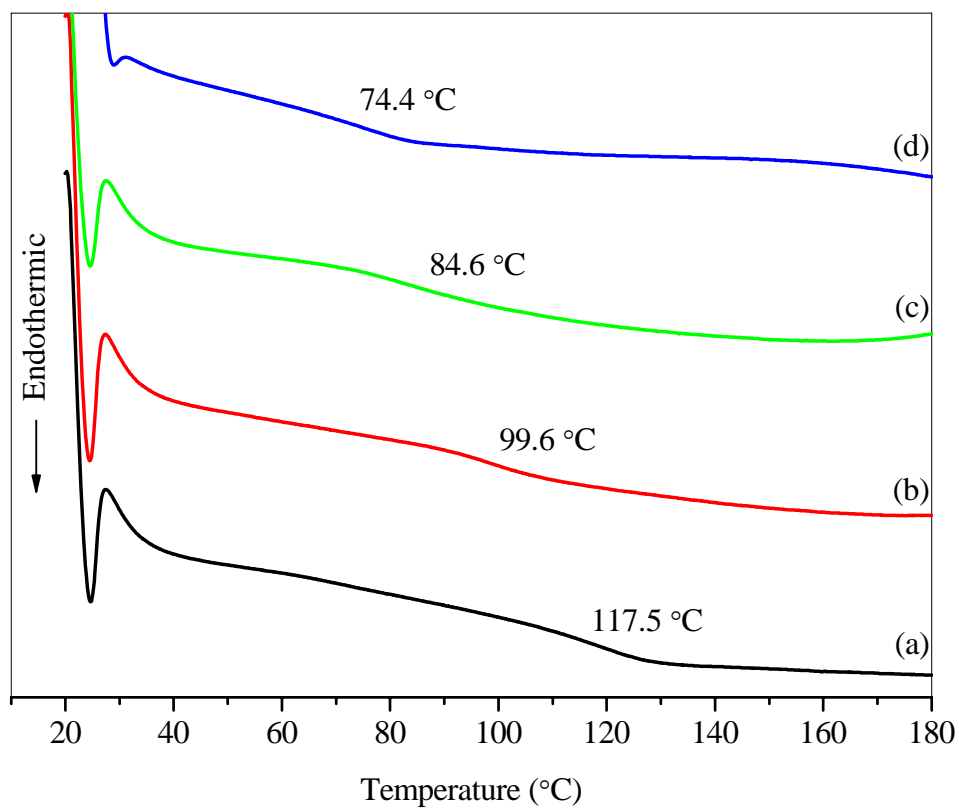


Figure 4.30 DSC thermogram of epoxy resins cured with (a) EDA, (b) PDA, (c) PPEDD, and (d) PPPDD.

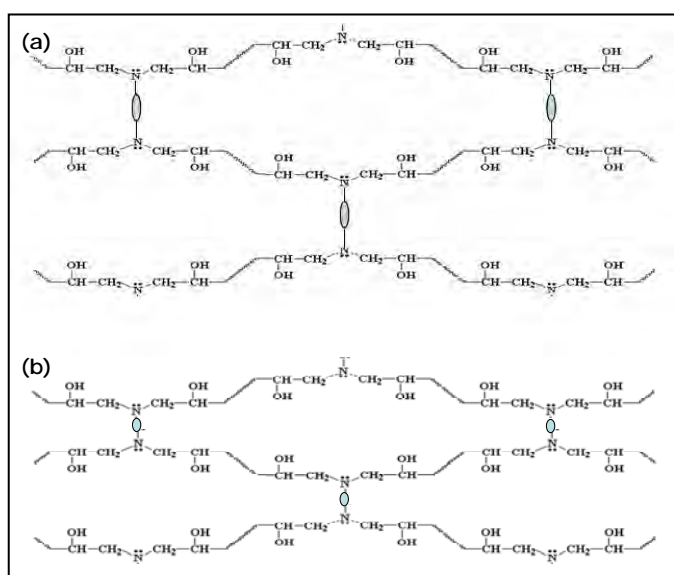


Figure 4.31 Formations of crosslink of epoxy resin cured with (a) large and (b) small structural of crosslinking agent.

Table 4.4 shows T_g of epoxy polymers cured using different crosslinking agents. The T_g values of epoxy resins cured with four crosslinking agents decrease according in the order EDA>PDA>PPEDD>PPPDD. It is possible that the large bulky structural of PPPDD cured with epoxy resin, which may cause more intermolecular distance (free volume) and decreases the entanglement of the polymer chains thus cured epoxy resin has low crosslink density in the epoxy polymer and thereby was the lowest T_g . On the other hand, EDA is essentially attributed to its having both the simplest and small molecular structure, the intermolecular linkages was spaced so closely as reduces the free volume thus the epoxy polymer has the highest T_g .

Table 4.4 Glass transition temperature (T_g) of epoxy resins cure with EDA, PDA, PPEDD and PPPDD.

Crosslinking agent	Glass transition at onset temperature, T_g ($^{\circ}\text{C}$)	Glass transition at midpoint temperature, T_g ($^{\circ}\text{C}$)
EDA	106.8	117.5
PDA	90.6	99.6
PPEDD	73.1	84.6
PPPDD	65.4	74.4

The thermal stability of the aforementioned of cured epoxy resins were assessed by thermogravimetric analysis under nitrogen and air atmosphere and the results are shown in **Figures 4.32** and **Figures 4.33**, respectively. **Table 4.5** is the summary of data obtained from **Figure 4.32** and **Figures 4.33**.

The non-oxidative degradation processes showed a one stage weight loss behavior in temperature range of approximately 240-500 $^{\circ}\text{C}$ (T_1). The decrease in the onset temperature epoxy resins cured with phosphorus-containing crosslinking agents (PPEDD and PPPDD) is mainly attributed to the form action of the compact char to protect the polymer from further degradation. This can also be verified by the data in **Table 4.5** which show significant changes in the mass loss at different temperatures.

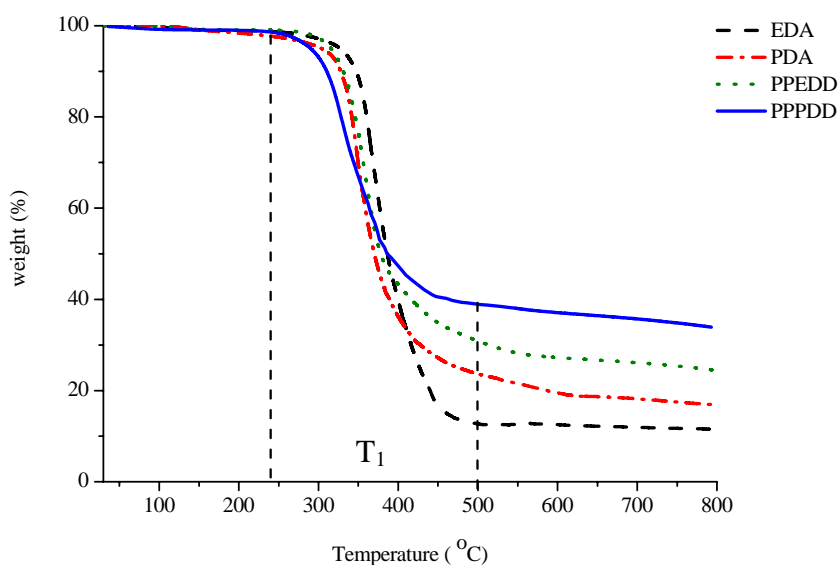


Figure 4.32 TGA thermograms under nitrogen of DGEBA cured with EDA, PDA, PPEDD, and PPPDD.

Epoxy resins cured with non phosphorus-containing crosslinking agents (EDA and PDA) afforded the lowest amount of char residue. Approximate incorporation of 2 wt.% of phosphorus element resulted in increased the char yield because phosphorus-rich char was first formed in the decomposition of the phosphorus containing epoxy resin. This char is relatively thermally stable, thus protecting the resin from heat and resulting in higher char yields compared to non-phosphorus resin. Increasing char formation can prevent further decomposition of the polymers [29, 30]. This phenomenon plays an important role in improving the flame retardant properties of the polymers and will be discussed later. Due to highly aromatic structure of PPPDD, the char yield of PPPDD-cured epoxy resin at 800 °C is higher than that of PPEDD cured epoxy resin. Epoxy resins cured with aromatic-containing crosslinking leads to more intumescent char formed. This can also be observed in the case of EDA compared to PDA.

Table 4.5 Summary results obtained from TGA for epoxy resin systems in both air and nitrogen.

Crosslinking agents	P (%)	T _o (°C)		Char yields at 450 °C		Char yields at 800 °C	
		N ₂	Air	N ₂	Air	N ₂	Air
EDA	-	345	252	16.3	35.4	11.5	0
PDA	-	327	296	27.2	49.7	16.8	0
PPEDD	2.3	330	305	34.9	45.8	24.4	3.9
PPPDD	2.1	301	292	40.5	48.7	33.9	7.4

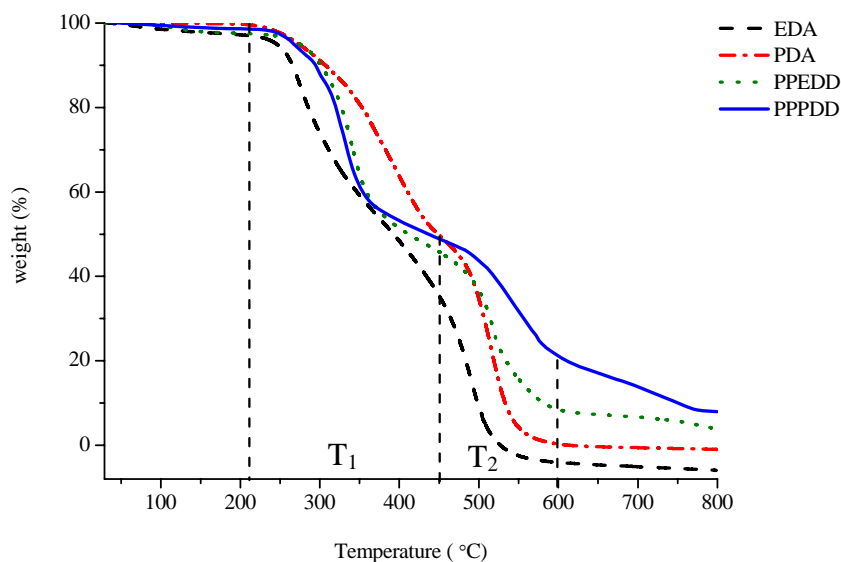


Figure 4.33 TGA thermograms under air of DGEBA cured with EDA, PDA, PPEDD, and PPPDD.

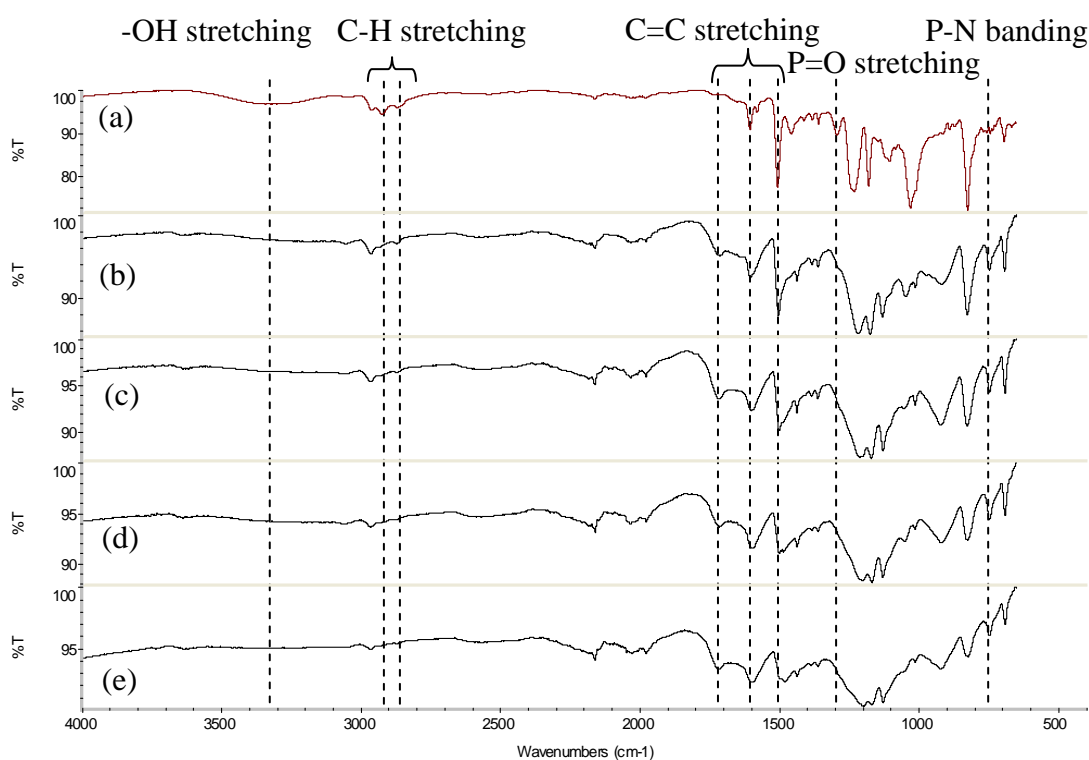
In the case of an oxidative degradation processes, the degradation is more complex and contain approximately two step. In the TGA thermograms obtained from analysis in air, the two-step weight loss process was observed. The first step degradation at approximately 210-450 °C (T₁) and the second step degradation was at a range of approximately 450-600 °C (T₂).

The char yields at 450 °C (at the end of the first step degradation under air) are higher compared to those in the nitrogen atmosphere. However, at 800 °C the result is

reversed where the char yield is much lower than that in non oxidation degradation. This phenomenon is observed for all of the epoxy polymers measured. In this case, an oxidative environment promotes the formation of a char layer earlier (higher yield at 450°C) but they contain unsaturated functional groups rendering them more susceptible to further oxidation, this oxidation reduced the char yields at high temperatures [59]. Also important to note from **Table 4.5** is that epoxy resins cured with non phosphorus-containing crosslinking agents (EDA and PDA), the significance of the difference char yield at 450 °C between in air and in nitrogen but phosphorus-containing crosslinking agents (PPEDD and PPPDD) were not significantly different. It is possible that epoxy resins cured with non phosphorus-containing crosslinking agents (EDA and PDA) are less free volume and higher crosslink density in the structure. These will also tend to decrease diffusion rates of volatiles released react with oxygen, thereby increasing char yields is to produce denser carbons. In addition, epoxy resin cured with aromatic-containing crosslinking agents (PDA, PPEDD and PPPDD) are more char formed at 450 °C. The aromatic ring content of polymer decomposes into aromatic fragments that fuse *via* condensation reactions to produce moderate to high amounts of char. Aromatic rings are the basic building blocks from which char is formed, and therefore the char yield increases with increases aromatic ring groups in the polymer [60].

In the second step degradation (450-600 °C) under air, epoxy resins cured with phosphorus-containing crosslinking agents (PPEDD and PPPDD) provide rate of degradation less than epoxy resins cured with non phosphorus-containing crosslinking agents (EDA and PDA) as seen from the slope in **Figure 4.33**, when rate of degradation decreases with decreasing value of the slope for the curve. The phosphorus-nitrogen (P-N) in PPEDD and PPPDD played a critical role in forming P-N rich char in the degradation of epoxy polymer. The P-N rich char was more thermally stable to show the retarded weight loss [61]. The more oxidative stability of the char of epoxy resins cured with phosphorus-containing crosslinking agents (PPEDD and PPPDD) were noteworthy with the higher char yield at 800 °C. When comparing PPEDD and PPPDD, Epoxy resin cured with highly aromatic structure of PPPDD had been shown to give more stable char than that cured with PPEDD.

To better understand the char formation in various stages of combustion of epoxy polymers cured with PPEDD and PPPDD, the solid residues obtained after degradation at the desired temperature were investigated by FT-IR analysis. The degradation was carried out under air in the TGA apparatus. After reaching at the desired temperature, the residue was taken out and FT-IR measurement was carried out. The FT-IR spectra of the residues of epoxy resin cured with PPEDD and PPPDD are shown in **Figures 4.34** and **4.35**, respectively.

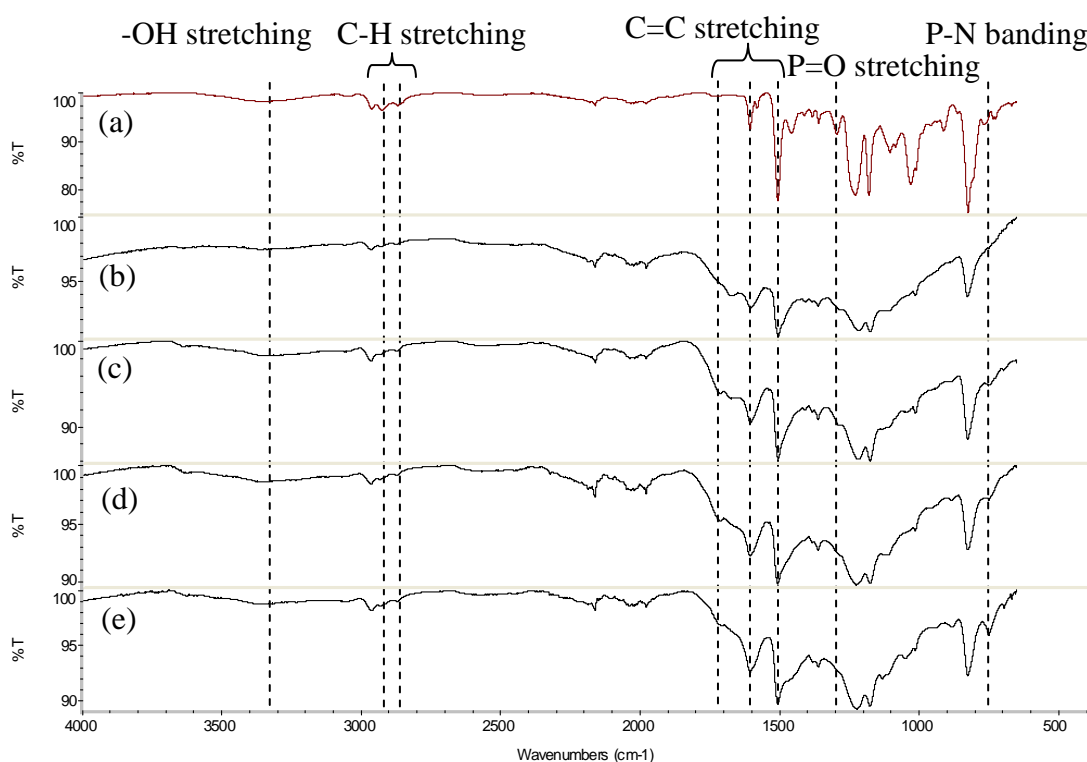


Figures 4.34 FT-IR spectra of initial epoxy resin/PPEDD (a) and of its solid products of thermal decomposition obtained under air in TGA at 300 °C (b), 320 °C (c), 340 °C (d), and 360 °C (e).

For epoxy resin cured with PPEDD, the residue showed an increase in the intensity of the absorption peak at 1713 cm^{-1} due to an increase in C=C bond with increasing temperature indicating dehydration of the epoxy structure during the initial stages of degradation to yield the allylic one. On the other hand, the absorption peak at 2862-2921 cm^{-1} (C-H stretching) decrease more quickly. More importantly, the -OH absorption band at 3100-3500 cm^{-1} and $-\text{C}_6\text{H}_4\text{-O-CH}_2-$ at 1023 cm^{-1}

eventually disappeared. In addition, decrease in the intensity of the band of the aromatic ring ($1502, 1601\text{ cm}^{-1}$) which are attributed to thermal decomposition and volatilisation of the epoxy resin sample begins

It was also observed that the absorption band of P=O at 1292 cm^{-1} diminished while that of the P-N bond at 745 cm^{-1} increased. This was attributed to a possibility that the residue undergoes further decomposition by eliminating more hydrocarbons and forming the P-N in char [61].



Figures 4.35 FT-IR spectra of initial epoxy resin/PPPDD (a) and of its solid products of thermal decomposition obtained under air in TGA at 300 °C (b), 320 °C (c), 340 °C (d), and 360 °C (e).

For epoxy resin cured with PPPDD, the degradation behavior of polymer was analogously similar that of to the epoxy resin cured with PPEDD. However, in the case of PPPDD, the degree of decreasing intensity of aromatic ring is lower than in the case of PPEDD. Char-forming polymer often swells and intumesces during their degradation, the inclusion of aromatic in the flame retardant structure approach is to promote the formation of such intumescent char [16] thus it is highly possible that

epoxy resin cured with PPPDD promote formation of such intumescent char to a higher extent than PPEDD.

4.3.3 Effect of using different diamines on flame retardant properties of cured epoxy resins

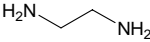
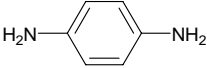
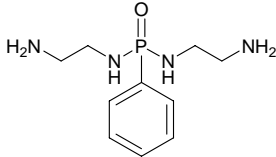
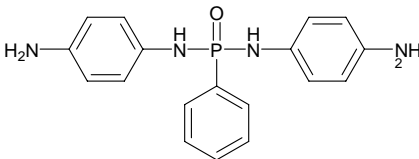
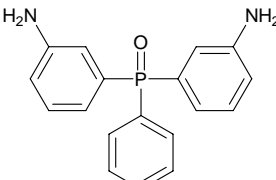
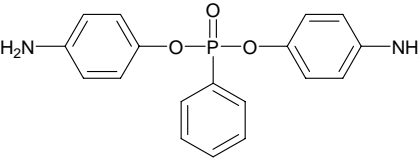
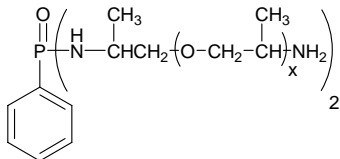
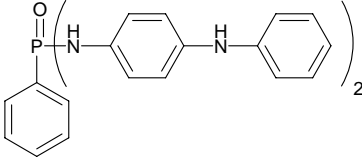
The flame retardant properties of epoxy resins cured with EDA, PDA, PPEDD, and PPPDD were further examined by measuring the limiting oxygen index (LOI) which is defined as the minimum concentration of oxygen in a nitrogen/oxygen mixture needed to support combustion. A material has fire retardant performances of interest if its LOI value is higher than 21% which represents the concentration of oxygen in the air. The higher this value is, the better the flame retardant properties of the material are. The results of LOI and UL-94 test of DGEBA cured with crosslinking agents in this study and other literatures [30, 35] are shown in **Table 4.6**.

From **Table 4.6**, On the other hand, epoxy resin was cured with PPEDD and PPPDD, the resulting epoxy resins exhibited LOI values of 27 and 31, respectively. These are higher than those of epoxy resin cured with EDA (20) and PDA (21). Therefore, the high LOI values imply that these phosphorus-containing crosslinking agents are applicable in flame retardant of epoxy resins. The reasons probably are that decomposition of phosphorus in epoxy polymer dilutes the volatile combustibles on the sample surface, and the formation of protective oxides char reduces the oxygen diffusin in the reactive centre. These chars can retard the heat transfer and result in the improvement of flammability properties. Furthermore, epoxy resin cured with highly aromatic structure of PPPDD present higher LOI values that cured with PPEDD. The more thermal stability of aromatic structures in polymers gives rise to a more effective intumescent char and lower level of flammable gases are available to feed a flame [16], which was consistent with the results by TGA.

Liu *et al.* [30] report improvement of epoxy polymer fire retardancy properties by curing DGEBA with BAPPO and BNPPPO. The LOI values are higher than that of epoxy resin cured with PPEDD and PPPDD. It is possible that the increase of the phosphorus content in the epoxy polymer of BAPPO and BNPPPO systems resulted in increase of the LOI values. However, phosphorus content in the epoxy polymer of

BAPPO and BNPPO systems are much higher, but there were slightly significant difference in LOI values than the PPEDD and PPPDD systems.

Table 4.6 LOI values and UL-94 rating of DGEBA cured with various crosslinking agents.

Curing agent	The chemical structure of curing agent	P (%) ^a	LOI	UL-94
EDA		N/A	20	HB
PDA		N/A	21	HB
PPEDD		2.3	27	V1
PPPDD		2.1	31	V0
BAPPO		5.1	34	-
BNPPO		4.2	35	-
PPDCPOA		2.3	21	-
PPDCPDA		2.5	27	-

^a P (%) is the percentage of phosphorus after curing.

In other study, Jeng *et al.* [35] have used PPDCPOA and PPDCPDA as crosslinking agent of DGEGA. The LOI values of PPDCPOA and PPDCPDA systems presented lower LOI values compared with PPEDD and PPPDD systems. It is possible that the large structural of PPDCPOA and PPDCPDA cured with epoxy resins, which may cause more free volume and higher crosslink density. These will also tend to increase diffusion rates of volatiles released react with oxygen.

From the LOI values experiments, it is clearly observed that phosphorodiamidates (PPEDD and PPPDD) have high flame retardant efficiency in epoxy resins.

4.3.4 Effect of using different diamines on UL-94 of cured epoxy resins

From **Table 4.6** results, epoxy resin cured with PPPDD showed V0 ratings according to the UL-94 standard or standards required by e.g. components and enclosures for electrical and electronic application. The epoxy resin cured with PPEDD showed lower efficiency V1 ratings, which suggests that the flame retardancy of epoxy polymer increased with phosphorus containing crosslinking agents. Besides epoxy cured with PPPDD much more flame retardant than cured with PPEDD, it also generated fewer fumes and drips than cured with PPEDD. Epoxy resin cured with highly aromatic structure of PPPDD had been shown to give more stable char than epoxy resin cured with PPEDD. This result is also consistent with the result of TGA and LOI.

4.3.5 Effect of using different diamines on tensile properties of cured epoxy resins

The effect of different crosslinking agents on the mechanical properties of epoxy polymer was investigated. In this study, tensile tests were performed and reported in terms of tensile strength and elongations at break (**Table 4.7**)

From **Table 4.7** shows that the tensile strength of epoxy polymer increased while the elongation at break decreased. Overall, the incremental extent of the tensile strength and the decrease extent of the elongation were comparable. Epoxy resin cured with PPPDD with the lowest crosslink density showed the lowest tensile strength and the highest elongation at break, whereas epoxy resin cured with EDA

with the highest crosslink density demonstrated the highest tensile strength and the lowest elongation at break. The tensile strength of polymer is closely related to the crosslink density. The tensile strength increase as the crosslink density increases due to at higher crosslink density, the segments of macromolecules become immobile, the system becomes stiffer and the elasticity decreases [57].

Table 4.7 Mechanical properties of epoxy resins cured with EDA, PDA, PPEDD and PPPDD.

Crosslinking agent	Tensile strength (Mpa)	Elongation at break (%)
EDA	19.61 ±0.25	4.78 ±0.44
PDA	18.24 ±0.20	4.72 ±0.48
PPEDD	14.69 ±0.31	12.30 ±1.24
PPPDD	12.12 ±0.63	14.80 ±1.10

CHAPTER V

CONCLUSION AND SUGGESTIONS

5.1 Conclusion

Phosphorodiamidates including phenyl phosphonic ethylene diamine diamide and phenyl phosphonic *p*-phenylene diamine diamide were synthesized through the condensation reaction of phenylphosphonic dichloride and diamines. It was found these phosphorodiamidates underwent crosslinking reaction with DGEBA to give phosphorus containing epoxy polymers. The order of reactivity of the diamines towards DGEBA was EDA > PDA > PPEDD > PPPDD.

The TGA results of phosphorus containing epoxy polymers showed the decrease in the onset decomposition temperature and the increase in percent remaining of carbonaceous char residue at 800 °C. The best thermal stability was also obtained from epoxy resin cured with phenyl phosphonic *p*-phenylene diamine diamide.

The LOI value and the UL-94 rating of the resulting epoxy resin cured with phosphorodiamidates are higher than that of epoxy resin cured with diamines without phosphorus. The flame-retarding effect of the phosphorus-containing crosslinking agents is demonstrated. Epoxy resin cured with phenyl phosphonic *p*-phenylene diamine diamide shown the highest LOI value and the UL-94 rating reached to V-0. This result is also consistent with the result of TGA.

Phosphorus containing epoxy polymers had lower T_g than epoxy polymers without phosphorus. When epoxy resin cured with phenyl phosphonic *p*-phenylene diamine diamide, the phosphorus containing epoxy polymer showed the lowest T_g value and tensile strength.

5.2 Suggestion for future work

The efficiency of flame retardation of phosphorus basically depends on the amount of char formation. However, the phosphorus rich char is not stable to oxidation at higher temperature (In view of the results from the TGA experiments

under air). Clay-containing polymer are described that can degrade forming thermally stable char [31]. In order to, enhancement flame retardant of epoxy resins will be achieved by incorporation of phosphorus and clay into epoxy resins While under flame exposure, phosphorus provides a tendency for char formation, clay provides an enhancement of the thermal stability of the char and introducing both element of the thermal stability of the char and introducing both elements may successfully combine these two factors in a strong flame retardation mechanism.

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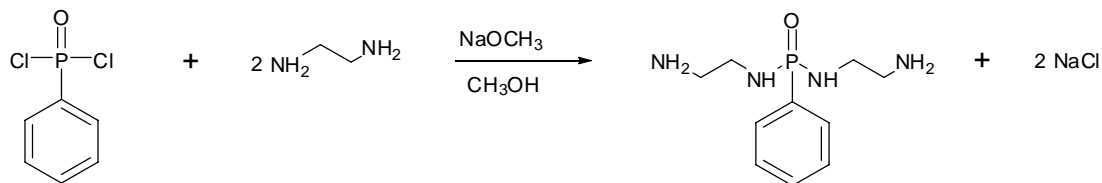
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APPENDIX

- Calculate the percent yield for PPEDD product.



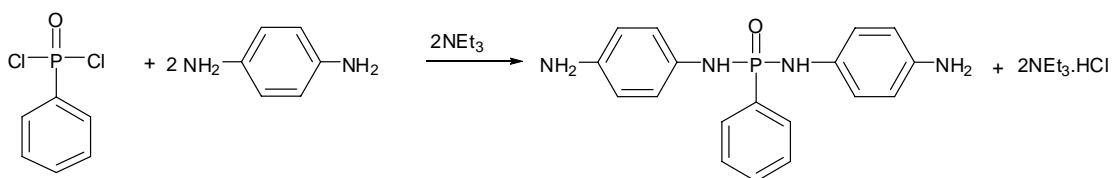
Theoretical yield of PPEDD is calculated:

$$\begin{aligned} \text{g PPEDD} &= 0.05 \text{ mol PPDC} \times \frac{1 \text{ mol PPEDD}}{1 \text{ mol PPDC}} \times \frac{242.26 \text{ g}}{1 \text{ mol PPEDD}} \\ &= 12.11 \text{ g} \end{aligned}$$

Actual yield of PPEDD was given = 2.90 g

$$\text{Percent yield} = \frac{\text{actual yield}}{\text{Theoretical yield}} \times 100 = \frac{2.90 \text{ g}}{12.11 \text{ g}} \times 100 = 24 \%$$

- Calculate the percent yield for PPPDD product.



Theoretical yield of PPEDD is calculated:

$$\begin{aligned} \text{g PPEDD} &= 0.06 \text{ mol PPDC} \times \frac{1 \text{ mol PPEDD}}{1 \text{ mol PPDC}} \times \frac{338.13 \text{ g}}{1 \text{ mol PPEDD}} \\ &= 20.29 \text{ g} \end{aligned}$$

Actual yield of PPEDD was given = 7.10 g

$$\text{Percent yield} = \frac{\text{actual yield}}{\text{Theoretical yield}} \times 100 = \frac{7.10 \text{ g}}{20.29 \text{ g}} \times 100 = 35 \%$$

VITAE

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Presentation in Conference:

- | | |
|--------------|---|
| July 2010 | The 1 st Graduate Conference the 25 th anniversary
Program of Petrochemistry and Polymer Science,
Faculty of Science. Chulalongkorn University, Bangkok,
Thailand. |
| October 2010 | The 1 st Polymer Conference of Thailand, Chulabhorn
Research institute, Bangkok, Thailand. <u>Best Poster
Presentation Award</u> |