

# **A STUDY OF THE CURING KINETICS OF POLYESTER RESIN FROM PALM OIL**

**LOH WEE KEAT**

Thesis submitted in partial fulfillment of the requirements  
for the award of the degree of  
Bachelor of Chemical Engineering

**Faculty of Chemical & Natural Resources Engineering  
UNIVERSITI MALAYSIA PAHANG**

MAY 2014

©LOH WEE KEAT (2014)

## ABSTRACT

In the present work, curing kinetics of polyester resin from palm oil was studied. The main objective of this research was to cure the unsaturated polyester resin (UPR) with different composition of methyl ethyl ketone peroxide (MEKP) in the presence of cobalt naphthenate or lead naphthenate as dryer, and analyse their curing kinetics. Besides, a comparison was drawn between cobalt naphthenate and lead naphthenate in terms of drying time for the best composition of UPR and MEKP ratio. The findings suggest that the best composition of UPR/MEKP was 45 phr (parts per hundred gram of sample) UPR: 20 phr MEKP, with the shortest drying time (7 h), while cobalt naphthenate was found to be more suitable dryer that helped to accelerate the curing reaction. After that, the curing of 45 phr UPR: 30 phr styrene: 20 phr MEKP: 5 phr cobalt naphthenate was studied by differential scanning calorimetry (DSC) at different heating rates such as 10, 15 and 20°C/min. Two exothermic peaks were found as confirmed by the DSC thermogram. A set of kinetic parameters such as activation energy, reaction rate, rate constant and reaction order for the first peak were calculated by using different equations and established methods. Result analyses revealed the activation energies as 44.21, 25.71 and 18.60kJ/mol for heating rate of 10, 15 and 20°C/min, respectively. Additionally, the order of reaction for each heating rate was obtained from the plotting of graph and stated as 2.0508 for 10°C/min, 1.0933 for 15°C/min and 0.5197 for 20°C/min. Moreover, glass transition temperature of the UPR also analysed and found to be -5°C, which was quite low.

## ABSTRAK

Dalam kajian ini, menyembuhkan kinetik resin poliester daripada minyak sawit telah dikaji. Objektif utama kajian ini adalah untuk menyembuhkan resin poliester tak tepu (UPR) dengan komposisi yang berbeza daripada metil etil keton peroksida (MEKP) di hadapan naphthenate kobalt atau naphthenate plumbum pengering, dan menganalisis kinetik pematangan mereka. Selain itu, perbandingan yang telah dibuat antara naphthenate kobalt dan naphthenate utama dalam masa pengeringan untuk komposisi terbaik nisbah UPR dan MEKP. Hasil kajian menunjukkan bahawa komposisi terbaik UPR / MEKP adalah 45 bsg (bahagian per seratus gram sampel) UPR: 20 bsg MEKP, dengan pengeringan masa singkat (7 h), manakala kobalt naphthenate didapati pengering yang lebih sesuai dalam membantu untuk mempercepatkan tindak balas pematangan. Selepas itu, pengawetan 45 bsg UPR: 30 bsg stirena: 20 bsg MEKP: 5 bsg kobalt naphthenate telah dikaji dengan kalorimeter pengimbasan perbezaan (DSC) pada kadar pemanasan yang berbeza seperti 10, 15 dan 20 ° C / min. Dua puncak eksotermik didapati seperti yang disahkan oleh termogram DSC. Satu set parameter kinetik seperti tenaga pengaktifan, kadar tindak balas, kadar tetap dan perintah reaksi untuk puncak pertama telah dikira dengan menggunakan persamaan yang berbeza dan kaedah ditubuhkan. Keputusan analisis menunjukkan tenaga pengaktifan sebagai 44,21, 25,71 dan 18.60kJ / mol untuk kadar pemanasan 10, 15 dan 20 ° C / min, masing-masing. Selain itu, perintah tindak balas bagi setiap kadar pemanasan telah diperolehi daripada rancangan jahat graf dan dinyatakan sebagai 2,0508 untuk 10 ° C / min, 1,0933 untuk 15 ° C / min dan 0,5197 untuk 20 ° C / min. Selain itu, suhu peralihan kaca daripada UPR juga dianalisis dan didapati -5 ° C, yang agak rendah.

## TABLE OF CONTENTS

SUPERVISOR'S DECLARATION .....	IV
STUDENT'S DECLARATION.....	V
ACKNOWLEDGEMENT .....	VI
ABSTRACT.....	VII
ABSTRAK.....	VIII
TABLE OF CONTENTS.....	IX
LIST OF FIGURES .....	X
LIST OF TABLES.....	XI
LIST OF ABBREVIATIONS.....	XII
1 INTRODUCTION .....	1
1.1 Background of study .....	1
1.2 Motivation of Study .....	2
1.3 Objectives of Study.....	5
1.4 Scope of Study .....	6
1.5 Main contribution of this work .....	6
1.6 Organisation of this thesis.....	7
2 LITERATURE REVIEW.....	8
2.1 Introduction.....	8
2.2 Thermosetting polymer .....	8
2.3 Unsaturated Polyester Resin (UPR).....	10
2.3.1 Types of unsaturated polyesters .....	11
2.4 Preparation of Unsaturated polyester resin from palm oil .....	12
2.5 Styrene .....	13
2.6 Methyl Ethyl Ketone Peroxide (MEKP).....	14
2.7 Curing of Unsaturated Polyester Resin .....	15
2.8 Driers.....	17
2.9 Cobalt naphthenate.....	19
2.10 Lead naphthenate .....	20
2.11 Autoxidation reaction.....	21
2.12 Cured UPR and its applications .....	22
3 MATERIALS AND METHODS .....	23
3.1 Introduction.....	23
3.2 Materials.....	23
3.3 Method for preparation of UPR from palm oil .....	26
3.4 Method of curing process.....	26
3.5 Differential Scanning Calorimetry (DSC).....	28
4 RESULTS AND DISCUSSION .....	30
4.1 Curing time of the UPR.....	30
4.2 Effect of cobalt naphthenate in the curing process of UPR .....	32
4.3 Differential Scanning Calorimetry (DSC).....	33
4.4 Kinetic Parameters .....	41
4.5 Glass Transition Temperature .....	45
5 CONCLUSION AND RECOMMENDATIONS.....	46
5.1 Conclusion .....	46
5.2 Recommendations.....	47
References.....	48
Appendix.....	54

## LIST OF FIGURES

Figure 1-1: Graph for the world consumption of unsaturated polyester resins 2011 (Chemical, 2011). .....	4
Figure 2-1: Schematic 2-D representation of thermoset formation: a) A-stage, partially polyfunctional monomer; b) B-stage, linear and branched materials below gel point; c) Incipient state of gel, gelled but incompletely crosslinked network with significant sol fraction; d) Fully cured C-stage thermoset (Billymer, 1984). .....	9
Figure 2-2: Route of UPR preparation: (a) polycondensation reaction between diacids and diols and (b) ring-opening polymerization (Yang et al., 2011). .....	11
Figure 2-3: (a) Alcoholysis and (b) esterification reaction of oil with acid anhydride (Islam, Beg, & Jamari, 2014). .....	12
Figure 2-4: A possible reaction mechanism of peroxidation of MEK (Milas & Golubovic, 1959). .....	15
Figure 2-5: Drier formation process (Tracton, 2005). .....	18
Figure 2-6: Chemical structure of cobalt naphthenate (Behr, 2008). .....	19
Figure 2-7: Chemical structure of lead naphthenate (Lewis, 1993). .....	20
Figure 2-8: Autoxidative crosslinking (Sailer & Soucek, 2000). .....	21
Figure 3-1: Chemical structure of UPR .....	23
Figure 3-2: Chemical structure of styrene. ....	24
Figure 3-3: Chemical structure of MEKP. ....	24
Figure 3-4: Chemical structure of cobalt naphthenate. ....	25
Figure 3-5: Chemical structure of lead naphthenate. ....	25
Figure 3-6: Differential scanning calorimeter schematic diagram (Chang R. , 2005)....	28
Figure 3-7: Typical DSC thermogram (Wunderlich, 1990) .....	29
Figure 4-1: DSC heat flow $dHdt$ versus cure temperature at 10 °C/min. ....	33
Figure 4-2: DSC heat flow $dHdt$ versus cure temperature for nonisothermal scans at different heating rates. ....	34
Figure 4-3: Reaction rate $d\alpha dt$ as a function of cure temperature at different heating rates .....	37
Figure 4-4: Reaction rate $d\alpha dt$ as a function of cure time at different heating rates ....	38
Figure 4-5: Degree of conversion $\alpha$ as a function of cure temperature at different heating rates. ....	39
Figure 4-6: Degree of conversion $\alpha$ as a function of cure time at different heating rates. ....	40
Figure 4-7: The whole DSC test operation .....	45

## LIST OF TABLES

Table 3-1: Compositions of UPR, styrene, MEKP and cobalt naphthenate respectively. ....	27
Table 3-2: Compositions of UPR, styrene, MEKP and lead naphthenate respectively..	27
Table 4-1: Curing time of UPR and styrene with MEKP and cobalt naphthenate at different compositions. ....	30
Table 4-2: Curing time of UPR and styrene with MEKP and lead naphthenate at different compositions. ....	31
Table 4-3: Heat of reaction $\Delta HR$ , peak temperature $Tp1$ and $Tp2$ at different heating rates $\beta$ .....	36
Table 4-4: Kinetic parameters for each heating rate .....	44

## LIST OF ABBREVIATIONS

DCPD	Dicyclopentadiene
DSC	Differential scanning calorimetry
MEKP	Methyl ethyl ketone peroxide
PMMA	Poly(methylmethacrylate)
T <sub>g</sub>	Glass transition temperature
UPR	Unsaturated Polyester Resin

# 1 INTRODUCTION

## *1.1 Background of study*

Polymers are substances that containing a large number of structural units by some linkage to form long chains. Polymers form a very important class of materials and if without them, our life seems very difficult. Recently the field of polymer science has attracted greater attraction of the research community due to the enormous advantages offered by the polymer based materials (Thakur & Thakur, 2014). Because of the extraordinary range of properties of polymeric materials, they are playing an essential and ubiquitous role in the contemporary world by contributed a number of applications starting from daily needs to biomedical and defense fields (Yang et al., 2012). Nowadays, there are many methods to synthesis polymers including polymerization, polymer blends, composites, hybrids and so forth (Wang et al., 2014).

Generally, polymers can be classified into three groups which are natural polymers, semi synthetic polymer and synthetic polymer (Chanda M., 2006). The polymers which occur in nature are called natural polymer and also known as biopolymers. Examples for such polymers are proteins, starches, cellulose, and latex. These materials and their derivatives offer a wide range of properties and applications. Natural polymers tend to be readily biodegradable, although the rate of degradation is generally inversely proportional to the extent of chemical modification. Natural polymers are widely used in pharmaceutical industry as adjuvant, emulsifying agent and adhesive in packing and also well suited for cosmetic product and pharmaceutical development (S.Shanmugam et al., 2005).

Semi synthetic polymers are the chemically modified natural polymers such as cellulosic, natural rubber, cellulose nitrate, hydrogenated, methyl cellulose, etc. While the polymers that synthesized from low molecular weight compounds are called synthetic polymers. These are also known as manmade polymers. Typical examples are: PVC, polyethylene,



terylene and nylon (V R Gowariker et al., 1999). Synthetic polymers have been used for numerous pharmacologic and biomedical purposes. These include drug carriers, prosthetic implants and suture material (Guerin, 2006).

Curing in polymer chemistry is a chemical process that converting a pre-polymer or a polymer into a polymer of higher molar mass and connectivity and finally into a network (Jones et al., 2009). Curing of polymers which means toughening or hardening of polymer material through cross-linking of polymer chains normally takes place under the action of curing agents or through the reaction of reactive oligomer groups upon exposure to ultraviolet light, high-energy radiation or heat (The Great Soviet Encyclopedia, 3rd Edition, 1979). The curing reaction enhanced the properties of polymers such as the cured epoxy resin will exists as rigid and glassy or soft and flexible, with glass transition temperature ranging from below room temperature until 260 °C (Boyle et al., 2001), radiation-cured polymeric nanocomposites have proven exceedingly efficient in modifying the viscoelastic properties of UV and EB (Gläsel et al., 2003) and poly(methylmethacrylate) (PMMA)/clay nanocomposites is used as photo-curable coatings to improve the anti-scratch and adhesion properties of organic glasses (Mohamadpour et al., 2011).

## ***1.2 Motivation of Study***

Unsaturated polyester resins (UPR) were first commercially developed in the 1940s and have grown to be one of the most important high performance thermosetting polymeric materials which are used widely as polymer matrices for fiber reinforced composites (Burs, 1982). Although being widely used for several decades, their excellent properties still attract lots of scientific and technical interests. UPR generally possess excellent characteristics: dimension stability, high strength, good corrosion properties, low weight and low price (G. Lubin et al., 1969). UPR need to react with a large number of chemical species called curatives or hardeners to achieve outstanding properties (Boenig, 1964)

Although UPR provided excellent characteristics but when the UPR is cured, the cured resins generally facing shrinkage with the cross-linking monomer. For the typical UPR, approximately 7-10% shrinkage of total volume occurs during cure (Bartkus & Kroekel, 1970). Besides, the curing time for the polyester resin will also be one of the major problems. In order to solve this problem, different sets composition of UPR and styrene with MEKP as catalyst will be prepared and used to determine the shortest curing time. Besides that, dryer also played an important role in solving this disadvantage.

Moreover, the demand for UPR is growing rapidly to enable the production of stronger, lighter, fiberglass composites for automotive, bridges, construction, pipes, wind turbine blades and a highly varied range of consumer products. The unsaturated polyester resin industry is mature and highly dependent on general economic conditions. The figure below showed that the consumption growth will be highest in China, with an average annual growth rate of just over 5% for 2011–2016. While for Asia, the growth will increase at an average annual rate of almost 5% on the same period. Besides that, the Middle East and Africa will also have an average annual growth rate of almost 5%. Meanwhile, Central and Eastern Europe will have an average annual growth rate of about 4.5%, as will Central and South America. Consumption will grow in North America at an average annual rate of 3.5%. However in Japan, unsaturated polyester resin consumption will grow at an average rate of 0.7% per year during the period (Chemical, 2011). Hence, it is worth to explore the best composition for the curing of natural polyester resin and MEKP to reduce the drying time since the product can attribute many functions to industrial sector and polymer material science.

## World Consumption of Unsaturated Polyester Resins—2011

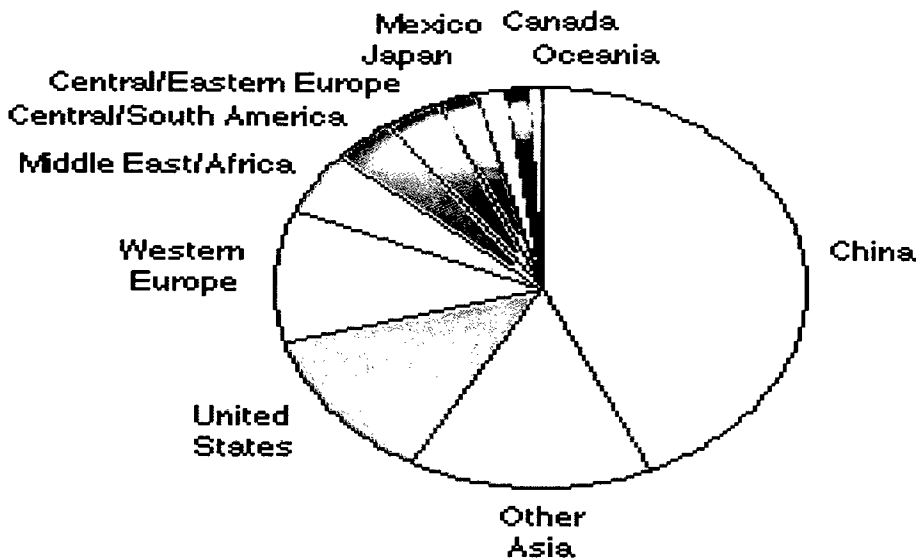


Figure 1-1: Graph for the world consumption of unsaturated polyester resins 2011 (Chemical, 2011).

The use of plant based materials in the synthesis of polymer is receiving world-wide attention due to increased worldwide awareness of environmental concerns and depletion of world oil pool. Naturally renewable resources possess many advantages such as biodegradability, renewability and low cost (Singha et al., 2004). Among biobased resources, triglyceride-based vegetable oils are important for polymer synthesis. Vegetable and modified oils such as palm oil have been used as main raw materials for resin preparation.

Malaysia is currently the world's largest exporter of palm oil accounting for 11% of the world's oils & fats production and 27% of export trade of oils & fats although it is second largest producer of oil after neighboring country, Indonesia (Journal of oil palm environment & health, 2012). Malaysia currently accounts for 39 % of world palm oil production and 44% of world exports. Today, total 4.49 million hectares of land in Malaysia is under oil palm cultivation to produce 17.73 million tonnes of palm oil and 2.13 tonnes of palm kernel oil. The industry provides employment to more than half a

million people. China is the largest consumer of oils and fats, followed by the India, United States, and the EU based on the figure 1.3 below (MVO, 2010). The world's largest plantation companies are two Malaysia-based companies which are FELDA and Sime Darby (Italian Trade Agency report, 2012).

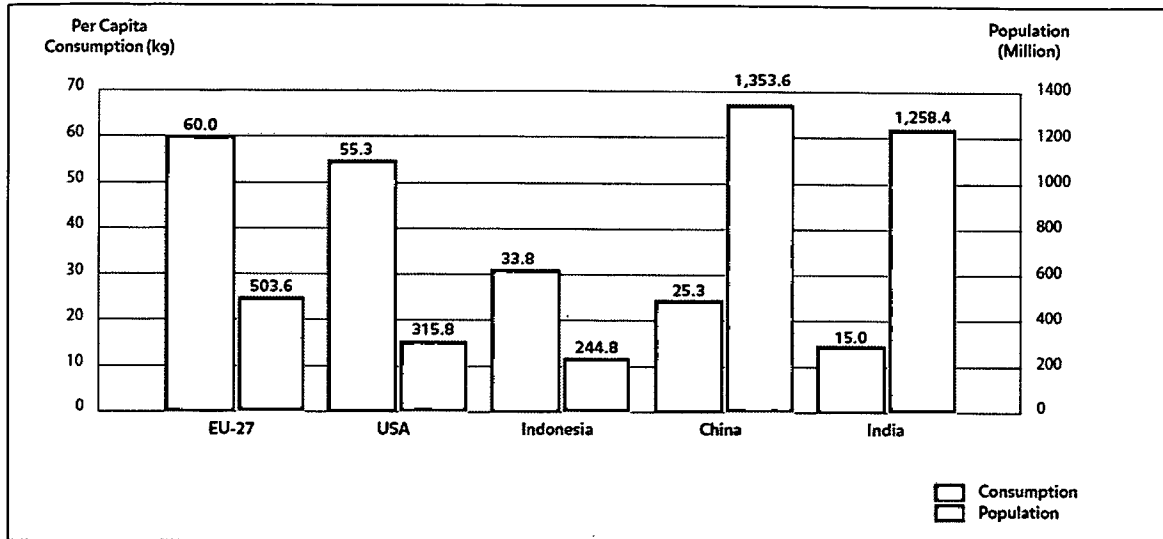


Figure 1-2: Per Capita consumption of Oils and Fats in year 2012 (Organization of the Petroleum Exporting Countries, 2013)

### 1.3 Objectives of Study

The objective of this study is divided into:

- (i) To study the curing kinetics of polyester resin from palm oil.
- (ii) To reduce the drying time for curing of unsaturated polyester resin (UPR) from palm oil using styrene with Methyl Ethyl Ketone Peroxide (MEKP) as catalyst.
- (iii) To determine the best dryer in the process of curing of polyester resin.

## ***1.4 Scope of Study***

The study will be focusing on the curing of unsaturated polyester resin using MEKP. In order to achieve the objective of this work, the following scopes have been identified:

- i) To improve the drying time for the curing for eight sets of different compositions of polyester resin from palm oil and MEKP with fixed composition of cobalt naphthenate or lead naphthenate as dryer at 5.00 phr (part per hundred resin) and fixed composition of styrene with 30.00 phr such as 60.00 phr UPR: 30 phr styrene: 5.00 phr MEKP: 5.00 phr dryer, 55.00 phr UPR: 30 phr styrene: 10.00 phr MEKP: 5.00 phr dryer, 50.00 phr UPR: 30 phr styrene: 15.00 phr MEKP: 5.00 phr dryer and 45.00 phr UPR: 30 phr styrene: 20.00 phr MEKP: 5.00 phr dryer.
- ii) To determine the best dryer by using two different types of dryer either cobalt naphthenate or lead naphthenate during curing of polyester resin.
- iii) To study the curing kinetics of cured polyester resin with a technique like differential scanning calorimetry (DSC).

## ***1.5 Main contribution of this work***

In this study, by curing the UPR using MEKP with the best composition, a cured polyester resin is produced and with desire curing time. The cured product is much more resistant to hydrolysis and lesser curing time. The rapidly cured resin can be used in the construction industry as it can accelerate a construction process or shorten the production cycle of precast members (Rebeiz & Sami, 1992). Moreover, the rapidly cured resin is highly demand in composite industries in order to improve productivity and at the same time to cut down production costs (Vella et al., 1985).

Besides, the suitable dryer that can help to speed up the curing reaction and hence reduce the curing time of UPR can also be known through this study. Thus UPR with desire curing time can be widely used commercially as automotive, bus shelters, cooling tower, dustbin, aerospace, sorting equipment, composites, fibres, plastics and for coatings applications too.

## ***1.6 Organisation of this thesis***

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a description of the properties, chemical reaction and application of materials used in this experiment. A general description on the curing reaction between unsaturated polyester resin (UPR)/ methyl ethyl ketone peroxide (MEKP) and cobalt naphthenate or lead naphthenate are presented. This chapter also provides a discussion of the applications of cured UPR. A summary of this chapter is also presented.

Chapter 3 gives a review on the method used to carry out curing of UPR. Besides, this chapter also gives a discussion on the techniques that used to study the curing kinetics such as differential scanning calorimetry (DSC).

Chapter 4 is devoted to the results of the experiment. A set of data for the curing kinetics is determined.

Chapter 5 draws together a conclusion and some recommendations for the experiment.

## **2 LITERATURE REVIEW**

### ***2.1 Introduction***

Polymers play a very important role in human life. Over the past few decades, the polymers have replaced many of the conventional materials in various applications due to their advantages provided. The most important advantages of using polymers are the cost reduction, productivity, and ease of processing (SAHEB & JOG, 1999). There are both naturally occurring and synthetic polymers. Curing of polymers is the most common method that used to improve the properties of the polymers. The polymers with excellent properties can be used in various fields such as construction, military, industrial, automotive, aerospace and so forth.

### ***2.2 Thermosetting polymer***

All polymers can be divided into different major groups based on their thermal processing behavior. Thermoplastic polymers are those polymers that can be remoulded, reshaped, recast and are less brittle and soluble in some organic solvents. The examples of thermoplastic include polystyrene, polyethylene, polypropylene and polyvinyl chloride. On the other hand, thermosetting polymers do not soften on heating but rather become hard in the case of prolonged heating. They are more brittle and insoluble in organic solvents and more brittle and insoluble in organic solvents. Such properties make thermosets suitable material for adhesive, coating, and composites applications. The examples for the thermosetting polymers include epoxy resins, unsaturated polyesters, and phenol-formaldehyde resin (Fried, 1995)

The reason that thermosets are often used as composite structural materials is due to their ability to strengthen different components because of their high glass transition temperatures, initial low viscosity and good dimensional stability under stress. All these superior properties are due to their network structure. During crosslinking reaction, the reactive monomer grow in molecular weight to form branched structures and eventually interlink to form three-dimensional network thus the crosslink reaction is only achieved when polymer are formed. In these cases, polymerization occurs first followed by crosslink reaction between developing molecules (Billymer, 1984). The reactant molecules must have more than two functional groups per molecule to form branch in the polymerization. The variation of chemical structure during curing is shown below:

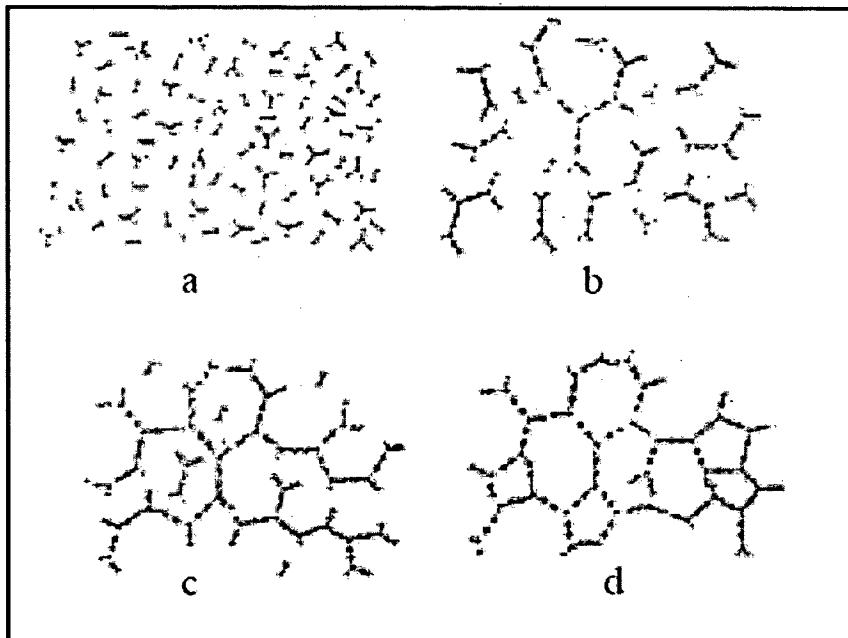


Figure 2-1: Schematic 2-D representation of thermoset formation: a) A-stage, partially polyfunctional monomer; b) B-stage, linear and branched materials below gel point; c) Incipient state of gel, gelled but incompletely crosslinked network with significant sol fraction; d) Fully cured C-stage thermoset (Billymer, 1984).

Besides that, one of the advantages of thermosets resin in composite fields is that they are in liquid form or easy to transform to liquid during process and hence allows for easy mixing of fillers, colorants, processing aids and reinforcements. Moreover, the thermoset



resins can be molded into very complex shapes and capable of wetting the reinforcement fibers due to their low viscosity at the beginning of the process (Pascault et al., 2002).

The useful thermosetting polymers that provided contribution to the industrial application include phenol-formaldehyde networks (resols and novolacs), epoxy networks cured with diamines, acid or anhydrides, unsaturated polyesters, polyurethane, polyurea, amino resins (formaldehyde with urea, melamine or acrylic), silicones, acetylene derivatives, cyanates, polyimides and vulcanization of unsaturated hydrocarbons (Mark et al., 1989).

### ***2.3 Unsaturated Polyester Resin (UPR)***

Unsaturated polyester resins (UPR) are the macromolecules with polyester backbone and belong to the category of thermosetting resin. The consequential motivation for the extensive growth of UPR is due to their outstanding ability in meeting end-use necessities (KG & LS, 2003). UPR is used for a wide variety of industrial and consumer applications all over the world and this has been proven from the fact that they represent approximately 75% of the total resin used. They have been found to have unlimited usefulness in all segments of the composites field because of they can provide excellent chemical and mechanical properties, good weather- and- chemical resistance and cost effective. Furthermore, they can be pigmented, ease of handling, can be easily filled and fiber reinforced in a liquid form (Cao & Lee, 2003).

UPR is extremely versatile in properties and applications and has been a popular thermoset used as the polymer matrix in composites industry since 1930 (Frodet & Arland, 1989). The general methods of preparing UPR are either produced by the condensation polymerization of dicarboxylic acid difunctional alcohol (glycols) or through ring-opening polymerization of lactones as shown in Figure 2.2 below. In 1929, Arvin and Carothers successfully developed UPR by reacting maleic acid and ethylene glycol at temperature 1750-1850 °C (Arvin & Carothers, 1929). After that, Ford Motor

Co. Ltd synthesized UPR from maleic anhydride and phthalic anhydride reacted with propylene glycol at 1000°C and then at 2500°C till the acid number diminished to the value less than 50 (mg of KOH per gm of sample) (Ford Motor Co.Ltd., 1965).

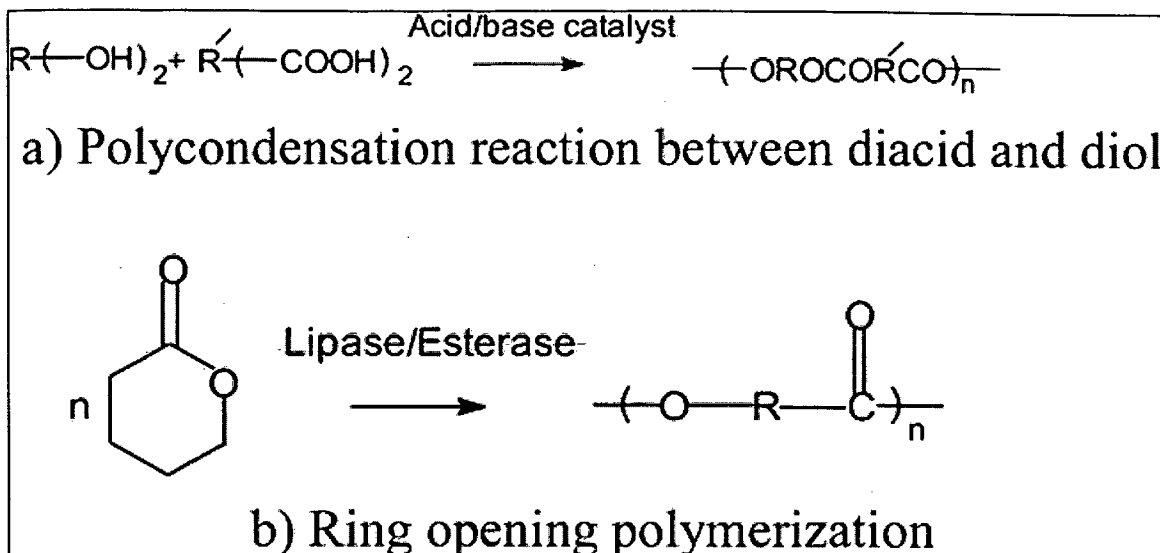


Figure 2-2: Route of UPR preparation: (a) polycondensation reaction between diacids and diols and (b) ring-opening polymerization (Yang et al., 2011).

### 2.3.1 Types of unsaturated polyesters

Unsaturated polyesters can be divided into different classes according to their structures of basic chemical building blocks. Some common examples of unsaturated polyesters are Isophthalic resins, Ortho resins, Dicyclopentadiene (DCPD) and Bisphenol A (BPA) fumarate resins.

Isophthalic resins are synthesized based on isophthalic acid and maleic anhydride. The incorporation of isophthalic acid produced a high molecular weight resin with good thermal/chemical resistance and good mechanical properties. Meanwhile, Bisphenol A (BPA) fumarate resins are prepared by reacting propoxylated BPA with fumaric acid. Relatively nonpolar polyester with a reduced number of ester linkages is produced. Excellent corrosion resistance is caused by the reduced number of ester linkages (Pepper, 2001).

## 2.4 Preparation of Unsaturated polyester resin from palm oil

The common method used to produce UPR from the plant oils is the monoglyceride method, which involves alcoholysis followed by esterification or polycondensation. The process is shown in Figure 2.3 below. In this process, the oil is first under underwent alcoholysis to produce monoglyceride or diglyceride in the presence of an acid or base catalyst such as CaO, NaOH, PdO and so forth. After that, polycondensation or esterification is carried out between monoglycerides and anhydrides (aromatic or aliphatic). Different types of anhydrides can be used in this process such as phthalic, maleic, succinic and glutaric anhydrides. The properties of the UPR depend on the oil length and the types and content of anhydrides. Aromatic polyesters have higher heat and moisture resistances if compared to aliphatic-based polyesters due to the presence of a stable benzene ring (Islam, Beg, & Jamari, 2014).

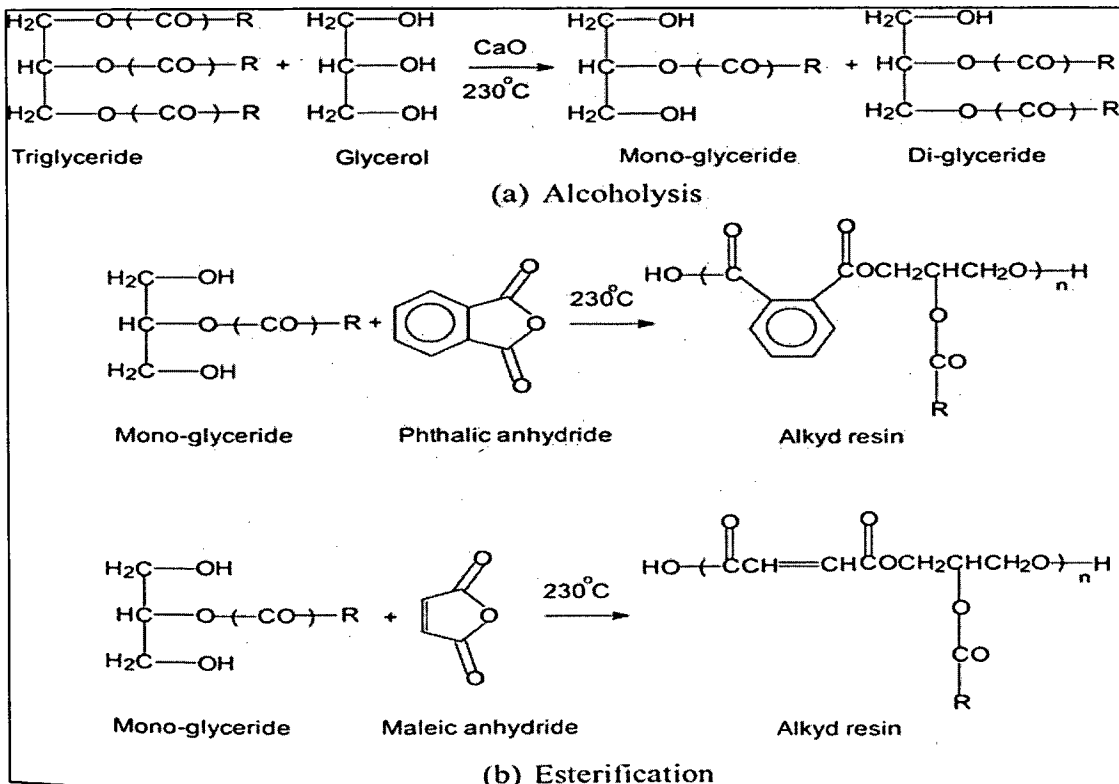


Figure 2-3: (a) Alcoholysis and (b) esterification reaction of oil with acid anhydride (Islam, Beg, & Jamari, 2014).

## 2.5 Styrene

Styrene is an organic compound which exists as a colourless, viscous liquid with a pungent odour and tendency to polymerize. Styrene is slightly soluble in water while very soluble in benzene and petroleum ether. The chemical formula for styrene is  $C_6H_5.CH=CH_2$ . Styrene is the precursor to polystyrene and several copolymers (James & Castor, 2007).

Styrene is one of the most important monomers worldwide. Styrene occurs naturally as a degradation product from plant that contained cinnamic acid such as balsamic trees and as a by-product of fungal and microbial metabolism (SHIMADA et al., 1992). Styrene is also can be produced by the catalytic dehydrogenation of ethylbenzene. Ethylbenzene is mixed in the gas phase with 10 to 15 times of its volume in high temperature steam, and passed over a solid catalyst bed. Iron (III) oxide is most common used catalyst in this process, promoted by several percent potassium carbonate or potassium oxide.

Styrene and its copolymers are widely used in different field of applications such as latex, paints, plastics, coatings and synthetic rubber (MILLER et al., 1994). Besides that, styrene also widely used as curing agent in curing process of UPR. Styrene is so widely used today because of its strength, safety and durability.

## ***2.6 Methyl Ethyl Ketone Peroxide (MEKP)***

Methyl Ethyl Ketone Peroxide (MEKP) is an organic peroxide which present as a colorless and oily liquid. MEKP is still widely used in industry as catalyst for the curing process of unsaturated polyester resins, as cross-polymerisation agent in polymer fabrication processes, or as catalyst for acrylic resins. MEKP as the most commonly used organic peroxide in curing UPR is due to its ease of use and good performance (Quinn, 1999).

MEKP can be produced by reacting methyl ethyl ketone (MEK) with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). A series of reactions will occurred when the MEK is mixed with an acidified hydrogen peroxide solution (Milas & Golubovic, 1959). Commercial MEKP does not exist as a single compound but several isomers with the same name. There are totally seven different types of MEKP might exist. They can be either straight chained or cyclic peroxides (Society of Plastics Engineers, 1999). MEKP is highly explosive and the synthesizing process for MEKP is highly exothermic. Moreover, MEKP is also highly sensitive to shock, friction, flame or other sources of ignition and hence leading to potential risks in its storage and transportation (Yeh et al., 2003). There were still a number of accidents occurred in recent years although many strict measures were issued and followed for safe production, storage and handling of MEKP (Fu et al. 2003).

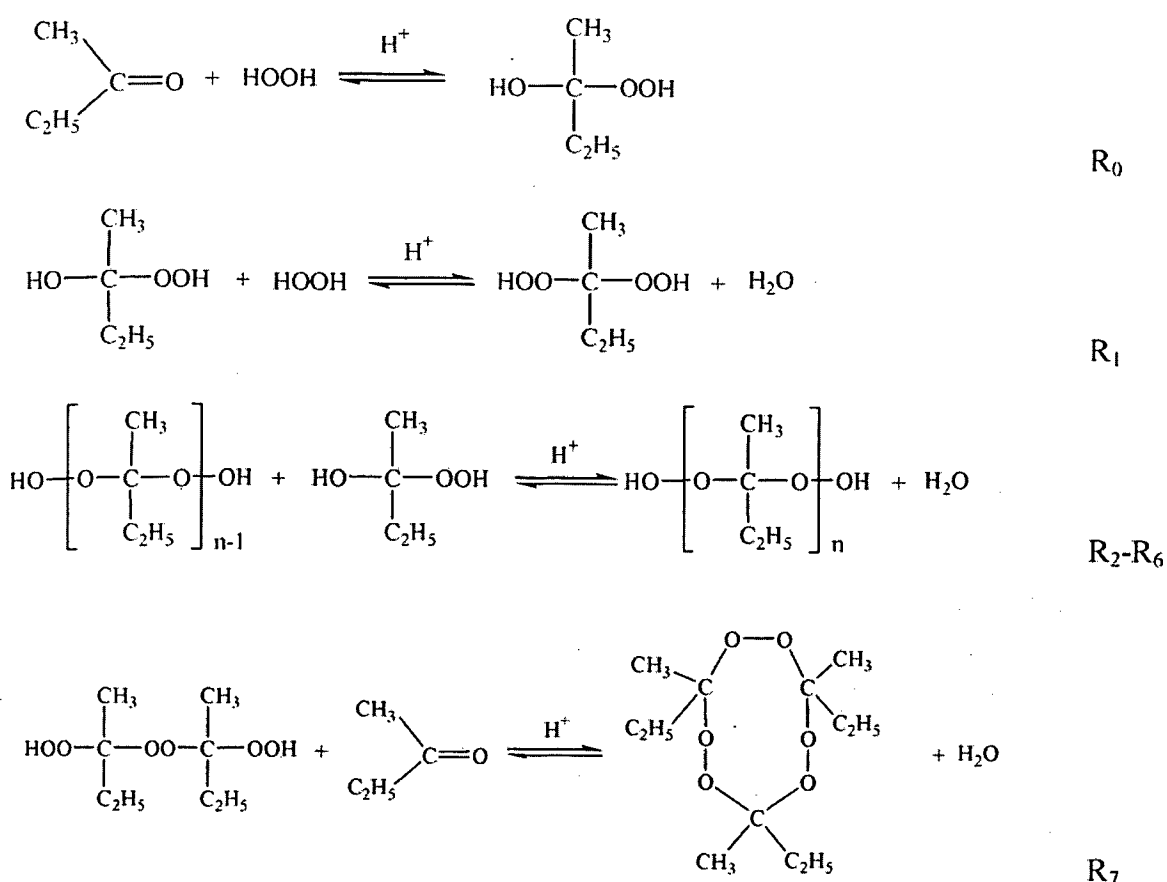


Figure 2-4: A possible reaction mechanism of peroxidation of MEK (Milas & Golubovic, 1959).

## 2.7 Curing of Unsaturated Polyester Resin

Free radical copolymerization between the styrene monomer and the polyester double bonds origination from the unsaturated dicarboxylic acid can be carried out in order to get a rigid and structural material (Skrifvars, 2000). The curing reaction is initiated by peroxides activated through a redox reaction with either cobalt salts or thermally. A dramatic physical revolution is occurred when the resin undergoes gelation through the crosslinking. The viscosity increases rapidly, the resin becomes elastic and hence begins to behave like rubber (Åström, 1997). Then, the chemical reaction continues in the gel

state, and more polyester is linked to the network. The crosslinking reaction is a highly exothermic reaction and the temperature is depending on the resin composition, initiator system, and laminate thickness (Skrifvars, 2000). There will be unreacted styrene monomers and double bonds left in the final solid state. Post curing can be carried out in order to solve this residual reactivity by heating at a temperature higher than the glass transition temperature of the crosslinked UPR.

The curing reaction for UPR is initiated by adding small quantities of a catalyst or curing agent such as aliphatic azo compound or organic peroxide (like MEKP, benzoyl peroxide), to the liquid mix. This reaction involves a free radical chain growth polymerization (Waigaonkar et al., 2011). With the application of heat (in the temperature range of 107-163°C), the curing agent decomposes rapidly into free radical, and react with the styrene molecules and break the [C = C] bonds. After that, styrene radicals are then joined with the polyester molecules at the unsaturation points and eventually formed cross-links between them. The cross-linking reaction allows one polymer chain to link with other polymer chains, and hence produced a three dimensional network which converts the resin from a viscous liquid form into a hard thermoset solid (Cao & Lee, 2003).

The curing time depends on the decomposition rate of the curing agent. The decomposition rate can be increased by increasing the curing temperature. However, optimum temperature which all the free radicals are utilized in curing the resin is existed in this curing system. Wasteful side reaction and deterioration of the curing reaction are occurred due to free radicals are formed so rapidly above the optimum temperature. On the other hand, the curing reaction is very slow if below the optimum temperature. Small amounts of accelerator such as cobalt naphthate can be added to improve the decomposition rate of curing agent (Martin, 2007).

The major drawbacks of unsaturated polyester resins are their high polymerization shrinkage with the cross-linking monomer and low resistance against crack propagation (Ahmadi et al., 2012). The compound tends to pull away from the mold surface and

shrink away from the fibrous reinforcement, which reduces the accuracy of mold surface reproduction and leaves the fiber pattern at the surface because of the volume shrinkage (Melby & Castro, 1989). Moreover, the volume shrinkage also created many other processing problems such as internal cracks and voids in thick sections, warpage and poor dimension accuracy of molded parts, uneven depressions (called sink marks) on the molded surface and so on (Wigotsky, 1990). Internal cracks, warpage, and poor dimension accuracy are occurred due to stresses resulting from the non-uniform shrinkage.

## **2.8 Driers**

Driers are metal soaps of carboxylic acids. Driers are widely used to promote drying and hardening of alkyd resin due to they can effectively accelerate the autoxidation reactions (JC et al., 1997). Excellent properties of alkyd resin can be obtained using driers. Driers act as catalyst in drying process and hence should be soluble in the system to which are added.

Driers can be manufactured in different ways such as direct metal reaction, double decomposition/precipitation process, or fusion process. In direct metal reaction, some driers, such as manganese are formed under reducing condition, while others are manufactured under oxidizing condition, such as cobalt (Tracton, 2005). Next, an inorganic metal salt, such as a nitrate or sulfate, reacts with the sodium salt of a carboxylic acid in the double-decomposition reaction. For the fusion process, metal oxide or hydroxide reacts with a carboxylic acid at temperatures up 450 °F. Water is removed resulting in metal carboxylate complexes that are solubilized in hydrocarbon solvent. This reaction occurs slower at relatively lower temperature compared to the double-decomposition reaction. The drier formation process is shown in the figure below.