

STUDY OF THE CURING KINETICS OF SYNTHETIC AND NATURAL POLYESTER BLENDS

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Thesis submitted in partial fulfilment 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

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ABSTRACT

This work reports on the curing kinetics of the natural and synthetic polyester blends cured with methyl ethyl ketone peroxide (MEKP) as initiator and Cobalt Naphthenate as accelerator. Palm oil based natural polyester was produced from alcoholysis and esterification process, whereas synthetic polyester was derived from petroleum. Generally, blending of two polymers is usually required in order to have better properties than a single polymer. In recent year, much attention was paid to blending of natural and synthetic polymer due to environmental issues, lack of petroleum, poor properties of natural vegetable oil based polymers or resins. The main objectives of this research work are to study curing kinetics and curing time of the best composition of polymer blends of natural and synthetic polyester. The kinetics curing of best composition of natural and synthetic polyester blends was studied by DSC analysis at different heating rates such as 10, 15 and 20°C/min. The analysis was based on the exothermic peak raised due to the double bonds breaking to give crosslinked macromolecules. Additionally, the kinetics parameters for each heating rates such as activation energy, degree of conversion and number of orders were calculated based on the established method and equations. Result analysis revealed that the DSC thermogram shows one exothermic peak. The curing time of the polymer blends decreased as the composition of synthetic polyester increased from 10%wt to 40%wt. Besides, the curing time also decreased as the composition of the curing agent increased from 0.05%wt to 0.2%wt. The best drying time is 180 minutes with the composition of 27phr of natural polyester, 18phr of synthetic polyester, 30phr styrene, 20phr MEKP and 5phr of CoNp. Furthermore, the glass transition temperature of the best composition of natural and synthetic polyester blends is about -2.5°C. Moreover, the activation energy and reaction orders are decrease as the heating rates increase.

ABSTRAK

Kajian ini dibuat untuk menghasilkan polimer campuran antara resin poliester tak tepu (UPR) dan poliester semula jadi, MEKP dan CoNp. Poliester semula jadi dapat dihasilkan daripada minyak kelapa sawit selepas melalui alcoholysis dan polycondensation proses. Kajian ini dibuat kerana produk yang dihasilkan melalui polimer campuran lebih berkualiti berbanding dengan produk yang sebelum ini. Setiap tahun, terdapat 600 jenis polimer campuran baru dihasilkan di dalam pasaran dunia. Objektif utama kajian ini ialah penghasilan produk polimer campuran yang berkualiti antara resin poliester tak tepu (UPR) dan poliester semula jadi. Di samping itu, pengurangan masa pengawetan juga merupakan salah satu objektif kajian ini. Selain itu, pengawetan kinetik juga merupakan salah satu objektif kajian ini. Pengawetan kinetik akan dianalisis dengan menggunakan DSC. Keputusan yang dapat melalui DSC akan digunakan untuk mengira kinetik parameter. Melalui keputusan yang didapati, masa pengawetan semakin berkurang apabila komposisi MEKP meningkat. Masa yang paling singkat yang dapat dicapai ialah 180 minit.

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1 CHAPTER 1

INTRODUCTION

1.1 Background of Study

Over the past few decades, polymers have been used to replace many of the conventional materials in different applications. The use of polymer materials has simplified the modern life. Polymer can be defined as a chemical compound with high molecular weight and made up of a large number of molecules (monomers) that arranged in a simple repeating structure to form a larger molecule. The highly uses of polymer is due to its advantages over the conventional materials. The most important advantages are the ease of processing, productivity and low cost (SAHEB & JOG, 1999). Generally, polymer can be categorized into three groups which is natural polymers, synthetic polymers from natural monomer and semi synthetic polymers. For instance, starch, protein and cellulose is the example of natural polymer, polylactic acid (PLA) is one of the example of synthetic polymers from natural monomers while vulcanized rubber is one of the example of polymer from semi synthetic polymers.

Natural polymers are biodegradable and also known as a biodegradable polymer. Natural polymers are occurs in nature and can be extracted through some technique. Normally, they are

often in water based. Biodegradable polymers are available in large quantity from the renewable sources (Bregg, 2005). Biodegradable polymers can be classify into two groups which natural biodegradable polymers and synthetic biodegradable polymers. Natural biodegradable polymers are the polymers that synthesized by living organisms such as animals, plants, algae and microorganisms (Dodiuk & Goodman, 2013). For example, starch, polysaccharides, proteins, lipids and cellulose. In the other hands, synthetic biodegradeble polymers are the polymers that produced from oil such as polyester, poly vinyl alcohol and poly vinyl acetate.

Synthetic polymers are that derive out from the natural sources such as petroleum. Nowadays, the use of synthetic polymer leads the world of polymer due to the development of the crude oil industry in 20th century. It is estimated that the annual worldwide plastic production will increases to 300 million tons (14-18% are thermosets). The examples of the synthetic polymers are nylon, polystyrene, polypropylene, polyvinyl chloride, teflon and so on. Good mechanical properties and thermal stability are the advantages of synthetic polymers overs the natural polymers (Bregg, 2005). Besides that, synthetic polymers can be classify into two class due to different of preparation methods which are condensation polymers and addition polymers. In condensation polymerisation, the polymers are obtained by reacting two functional molecules and elimination a small molecule such as water. In the other hands, addition polymers are formed from unsaturated monomers in a chain reaction. (Goddard, 1999)

Semi synthetic polymers are the polymers that derived from naturally occurring polymers by chemical modifications. For example, cellulose diacetate polymer, vulcanized rubber, gun cotton and cellulose diacetate. Cellulose diacetate polymer is formed when cellulose on acetylation with acetic anhydride in the presence of sulphuric acid.

Curing of polymers is a process where the liquid polymers which in low molecular weight are irreversibly converted into solid, insoluble and infusible three dimensional polymers. Besides, curing is also a process of deliberately crosslinking a polymer to improve its mechanical properties such as stiffness. In the other hands, the mechanical properties such as solubility and swellability will decrease with increasing of crosslinking due to cure process (Alger, 1997). Curing of polymers can be take place after addition of curing agents or through the interaction of

reactive oligomer groups upon exposure to heat, ultraviolet, or high energy radiation. Ultraviolet light is the most popular alternative to evaporative curing among all of type of process (Reynolds, 2006). Curing agents can be defined as an additive used with a polymer in order to increase the rate of cure (Alger, 1997). The curing mechanism is determined by the nature of reactive groups in the oligomer, the curing agents and the specific conditions of the process. In plastic industry, the curing process will convert the linear or branched thermoplastic into a hard and stiff thermoset material.

Nowadays, mechanical and physical properties polymer can be improved through polymer blend. Polymer blend is one of the most important methods to produce a new polymeric materials. Polymer blend is in which two or more polymer or copolymer are mix together to form a new type of polymer. Acrylonitrile butadiene styrene resin is the one of the significance example of polymer blend which contains blending of three polymers which is polybutadiene, styrene-acrylonitrile copolymer and polybutadiene grafted styrene-acrylonitrile copolymer (Alam et al., 2005). Blending of conventional polymers is a convenient way of developing materials with novel or selectively enhanced properties which are possibly superior to those of the component (Chang, 1997). Besides, blending of polymer is a technological way for providing materials with full set of desired specific properties at the lowest price such as combination of strength, toughness and solvent resistance. Therefore, polymer blends experience a significant growth.

There are three types of polymer blends that can be distinguished: firstly is completely miscible blends, secondly is partially miscible blends and thirdly is fully immiscible blend. Miscible define as the capable of two or more liquid can be mixed. For completely miscible blends, it only exhibits one phase and only one glass transition temperature. On the other hand, partially miscible blends, two phases are observed and each phases exhibit a glass transition temperature. For fully immiscible blends, immiscible blends are characterized by two or more phases that separated by interfaces and have two glass transition temperatures will be observed. Commonly, it is observed that most of the polymer blends are partially immiscible and fully immiscible. This is because the low entropies of mixing associated with mixing chain like molecules to produce homogeneous solution. Besides that, polymer blends can be either in homogeneous or heterogeneous. In homogeneous blends, the final property is the average properties of the blend

components which means the properties are divided equally. In the heterogeneous blend, the properties of all blend components are present (He et al., 2004).

Physical blending and chemical blending are the two possible routes to generate polymer blends. Physical blending such as melt or solvent blending are the most common route to generate polymer blends. In the other hand, chemical blending is used for the blending of reactive components. In chemical blending method, chemical reaction such as graft or copolymerization reaction are take place (Alam et al., 2005).

As conclusion, blending also benefits the manufacturer by: i) Improved process ability, product uniformity, and scrap reduction ii) Quick formulation changes iii) Plant flexibility and high productivity iv) Reduction of the number of grades that need to be manufactured and stored v) Inherent recyclability (Utracki, 2003)

1.2 Motivation and Problem Statement

Nowadays, over 30% of commercial polymers used worldwide are polymer blends or alloys in one form or another but there is less attention of polymer blending of thermosetting resin such as synthetic unsaturated polyester resin with natural unsaturated polyester. According to report published by Transparency Market Research, the worldwide demand for unsaturated polyester resin is 4305.6 kilo tons in 2012 and expected to growth 7.5% per year between 2013 and 2019.

Blending of two polymers will usually give rise to a new class of material having better properties than a single polymer. Furthermore, natural polymers are usually biocompatible while synthetic polymers possess good mechanical properties and are more stable during the lifetime of the polymers (Bregg, 2005). Unsaturated polyester resin is one of the thermosetting resins that play an important role in industry (Bai et al., 2014). This is due to the unsaturated polyester resin have the characteristics of low density, high modulus, strength, durability and chemical resistances. Besides, low cost of unsaturated polyester resin and adaptability to transform into large composite structures make it widely used in industry (Salamone, 1996) (Bonnia et al., 2010). Nevertheless, the brittleness, volume shrinkage and low impact resistance of unsaturated

polyester resin limit its application for some material requirements (Moghbeli et al., 2011). This is due to high cross-linking density after curing or polymerization (Raquez et al., 2010). Besides, the curing time is also one of the motivations to do this research. This is because by reducing the curing time, the costs of production can be optimized (Avella et al., 1985). In order to have a better curing time, different composition of Methyl Ethyl Ketone Peroxide (MEKP) is used as a curing agent to cure the polymers blends of natural and synthetic unsaturated polyester resins.

In the past few decades, society is more concern about the environment issues, climates changes and limited fossil resources such as petroleum. Furthermore, petroleum will be exhausted at a faster rate (Narine & Kong, 2005). These had led to an intensive research to replace the synthetic polymer by natural polymer which is also a bio-based polymer (Dodiuk & Goodman, 2013). Synthetic polymers are often not environmentally friendly because they cannot undergo biodegradation and will release of hundred millions of tons of carbon dioxide to the atmosphere during production of synthetic polymer (Dodiuk & Goodman, 2013) (Narine & Kong, 2005). More usage of natural polymers will reduce the dependency on the synthetic polymers, hence create less environment pollution.

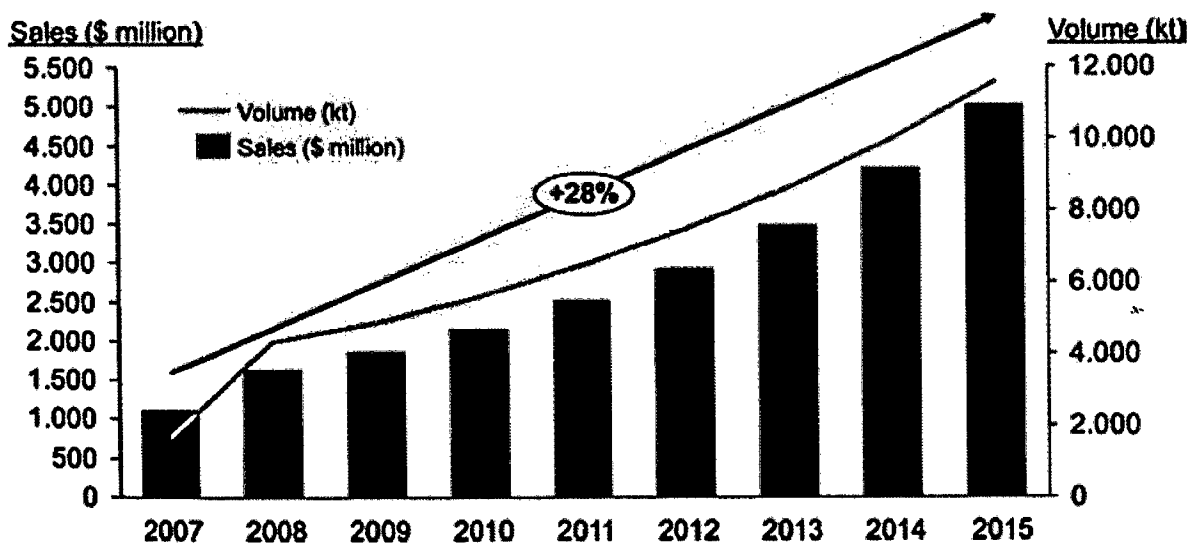


Figure 1.1 : Market analysis of chemicals from renewable raw materials from 2007-2015

Figure 1.1 shows that the market of chemical from renewable raw materials has been increase year by year. Renewable raw material can be defined as agricultural and forestry products that are used by human to generate heat, electricity or to manufacture base chemical. Plant oil is one of the most important renewable raw material which can be use for production of bio-based polymer. This is due to the rich chemistry that the triglyceride structures provide (Dodiuk & Goodman, 2013).

Palm oil is one of the most widely used plants oil in the world, which is grown in a mass plantation in tropical countries such as Malaysia. Malaysia has an abundance supply of palm oil due to the vast quantity of palm oil plantations (M & C.Y, 2009). Nowadays, Malaysia is one of the main exporters of world palm oil market which accounting 11% of the world's oils & fats production and 27% of export trade of oils & fats. Production of crude palm oil in Malaysia is about 18.75million tonnes in year 2012. Thus, palm oil is a readily available raw material for production of natural polyester.

Besides that, the curing process of the polyester was very complex because many reactions occur at the same time during free radical mechanisms (Varga et al., 2012). Therefore, many researcher has use an emperical method will be used to obtain kinectics parameter of the curing of natural polyester. The cure kinetics of natural polyester can be investigated by using DSC analysis. However, there is less research about the curing kinetics of polymer blends between natural polyester and synthetic polyester. Therefore, it is also one of the motivation of this study.

1.3 Objectives of Study

There are 3 main objectives in this research.

- (i) To synthesize and produce the best composition of polymer blends of natural and synthetic polyester based on curing time.
- (ii) To reduce drying time for curing of polymer blends of natural and synthetic polyester by using Methyl Ethyl Ketone Peroxide (MEKP) as a curing agent.
- (iii) To study the curing kinetics of polymer blends of natural and synthetic polyester.

1.4 Scope of Study

There are 3 main scopes in this research.

- (i) To improve the drying time of polymer blends at different composition of natural polyester resin and synthetic polyester resin which the composition are 36phr:24phr, 42phr:18phr, 48phr:12phr, 54phr:6phr, at a fixed compositions of 30phr of styrene, 5phr of methyl ethyl ketone peroxide and 5phr of cobalt naphthenate.
- (ii) To determine the best composition of MEKP on of polymer blends of natural and synthetic polyester based on drying time.
- (iii) To determine the kinetics parameter of polymer blends of natural and synthetic polyester with differential scanning calorimetry (DSC).

1.5 Main contribution of this work

In this study, by curing the polymer blend of natural and synthetic polyester using MEKP with the best composition, the curing time of polymer blends will be decrease. By reducing the curing time, the costs of production can be optimized (Avella et al., 1985). This contribution can be applied to the plastic, automotive, aerospace and construction industry. Besides, the curing kinetics parameter and glass transition of the polyester blends can be obtained through DSC analysis

1.6 Organisation of this thesis

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

Chapter 2 is describes about the main chemical and technique that used in this research. The chemicals that used are thermosets resin which is synthetic synthetic polyester resin, natural polyester resin and methyl ethyl ketone peroxide. Besides, in this chapter, the curing mechanisms of polymer blend of synthetic and natural polyester resin are further describe in details.

Chapter 3 gives a clearly description how the research was carry on. Furthermore, all the operating details of the sample preparation and operation condition of testing machine of DSC are listed out by refer to the past research that have been done.

Chapter 4 is devoted to the preliminary results of the experiment. In this chapter, the curing kinetics based on the result of the experiment that has been done will be discussed.

Chapter 5 draws together a summary of the thesis and outlines the future work which might be derived from the model developed in this work

LITERATURE REVIEW

2.1 Introduction

Polymer blends are capable of providing materials which extend the useful properties beyond the range that can be obtained from single polymer. In the past thirty years, polymer blends are experiences enormous growth in size in terms of scientific base and application (Sionkowska, 2011). Polymer blending is a convenient route for the development of a new polymeric materials. This is because the development of new polymers from polymer blends is far less costly and faster than the development of new polymers from synthesis. The most advantages of polymer blend is the mechanical properties of product can be altered by changing the blend composition (Yu et al., 2006). Besides that, polymer blends offer the possibility of tailor-making products to meet specific end needs. Nowadays, research of polymer blends between natural and synthetic polymer is growing quickly. This is because the biopolymeric materials can improve the quality of life (Bregg, 2005).

2.2 Thermosetting polymer

In recent years, the processing of thermosetting polymer has received increasing attention from industry, especially from automotive and aerospace industries. Thermosetting polymer is a polymer which has a giant macromolecule which consists of covalent bond in repeating unit

during polymerisation process. In other words, thermosetting polymer is cross-linked by strong by strong covalent intermolecular bonds, forming a giant molecule (Pascault et al., 2002).

Normally, thermosetting polymer is produced through homopolymerization. Thermosets resins are widely used in composites structural materials due to its ability to consolidate the different components. This is because of the low viscosity, high transition temperature, high modulus, high creep resistance, and good dimensional stability of thermosets resin at elevated temperature after cured. This cross-linked molecular structure after cure make thermosets polymer different with other polymer. During curing of thermosets resins, the molecular weight of monomers will increase to form branched structures and eventually interlink to form the three-dimensional network (Pascault et al., 2002). At the same time, three dimensional network is form when some of the reactant molecules have at least two or more functional group per molecule in case to initiate branching in polymerization. Figure 2.1 shows the variation of chemical structure during curing process.

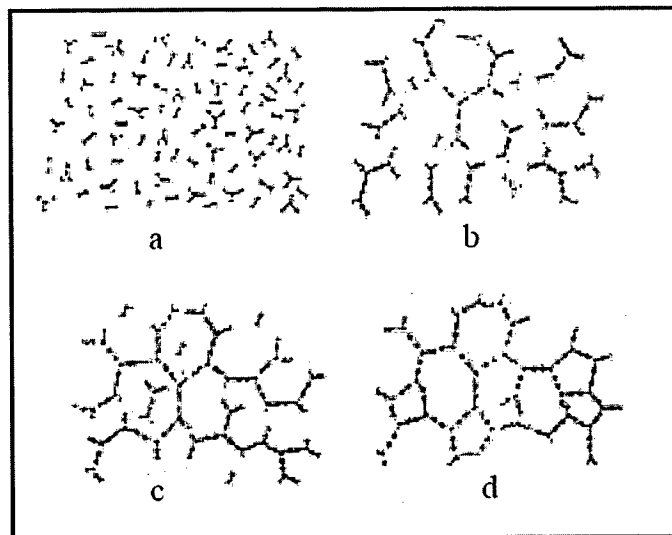


Figure 2.1: Schematic 2-D representation of thermoset formation: a) A-stage, partially polyfunctional monomer; b) B-stage, linear and branched materials below gel point; c) Incipient state of gel, gelled but incompletely cross-linked network with significant sol fraction; d) Fully cured C-stage thermoset (Billymer, 1984).

For instance, unsaturated polyester resins and epoxy resins are the example of the highly cross-linked thermosets resins. Thermosetting polymer is a polymeric material that undergoes irreversible curing. After the thermosetting polymer is cured, it will continue remains in solid phase and cannot be transforms back to liquid phase like thermoplastics. Besides that, thermosets resins are also widely used as adhesives, potting and encapsulating materials, tooling compounds, electronic substrates, packaging and as a matrix materials for reinforced composites. This is because thermosets can be processing at ambient temperature and low pressure compared to thermoplastics.

In the other hand, there are some disadvantages of thermosets resins by owning high degree cross-linked. Brittleness, poor resistance to crack initiation and propagation and poor fracture toughness are the main disadvantages of the thermosets polymers. This lack of toughness severely impacts the performance of highly cross-linked thermosets in almost all applications. Fracture toughness is a critical mechanical properties which characterizes the resistance of a material to crack propagation or to fracture. The toughness of material is directly dependent on the energy dissipation, or on the energy absorbed in fracturing part (Albdiry et al., 2013). Typically, filler particles such as aluminium, silica, glass, dolomite, aluminium hydroxide, zirconia and thermoplastic particle are added to increase the toughness of the thermosetting polymer. However, the researcher observe that there is only moderate increase in the fracture toughness (Deng et al, 2008)

2.3 Bio-based Polymer

In this few decades, the majority of polymer is derived from petroleum thermosetting due to its low cost, ease of handling, and good balance of mechanical, electrical, and chemical properties. In the other hand, the depletion of the crude oil and environmental issues are causing a growing urgency to develop a new and high environmental friendly bio-based polymer. Synthesis of bio-base polymers will help to reduce dependency of the polymers and plastic industry on petroleum, thus creating more sustainable alternatives. Basically, bio-based polymers can be derived from the renewable resources such as plant oil. Polylactic acid (PLA) is one of the examples for bio-based polymer. It is produced by green plants via its enzymatic hydrolysis into glucose and

subsequent fermentation into lactic acid. The advantages of bio-based PLA are that it is renewable biodegradable, recyclable, compostable, biocompatible and good processability if compared to natural polymers (Dodiuk et al., 2013).

2.3.1 Plant oil

Nowadays, plants oil can be considered as the most important raw materials for the production of bio-based polymer. This is because plant oil is a type of lipid, stored in the form of triglycerides with varying composition of fatty acid (Raquez et al., 2010). Majority of plant oils are extracted from oil seeds such as palm, soybean, sunflower, hemp and so on. Besides, plant oil also called as triacylglycerol. One glycerol is attached to three different types of fatty acids by esterification process to form a triglyceride. Triglycerides are highly functional molecule which always used in the synthesis of crosslinked polymer (Espinosa & Meier, 2011). Generally, fatty acids contributed about 94-96% of the total weight of one molecule triglycerides (Dodiuk et al.,2013). Fatty acid is a carboxylic acid that attach to a long unbranched aliphatic carbon chain and majority fatty acid molecule that found in plant oil consists of 14-22 carbon atoms in length. The fatty acids can be saturated or unsaturated. Saturated fatty acids have no double bond. On the other hand, unsaturated fatty acids have one or more than one double bond (Guner et al., 2006). Recently, certain review has been focused on deriaviates of thermosetting polymer from plant oil (Raquez et al., 2010). This is because plant oil consists of triglycerides that contain actives sites acquiescent of chemically functionalisation to be directly polymerised.

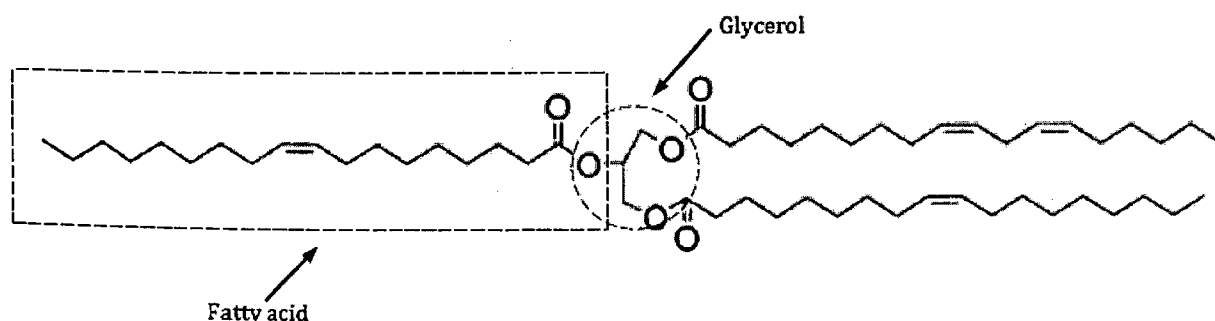


Figure 2.2: Triglyceride molecule (Dodiuk et al., 2013).

	14:0	14:1	16:0	16:1	17:0	17:1	18:0	18:1	18:2	18:3	20:0	20:1
Canola	0.1	0.0	4.1	0.3	0.1	0.0	1.8	60.9	21.0	8.8	0.7	1.0
Corn	0.1	0.0	10.9	0.2	0.1	0.0	2.0	25.4	59.6	1.2	0.4	0.0
Linseed	0.0	0.0	5.5	0.0	0.0	0.0	3.5	19.1	15.3	56.6	0.0	0.0
Olive	0.0	0.0	13.7	1.2	0.0	0.0	2.5	71.1	10.0	0.6	0.9	0.0
Palm	1.0	0.0	44.4	0.2	0.1	0.0	4.1	39.3	10.0	0.4	0.3	0.0
Soybean	0.1	0.0	11.0	0.1	0.0	0.0	4.0	23.4	53.2	7.8	0.3	0.0
Sunflower	0.0	0.0	6.1	0.0	0.0	0.0	3.9	42.6	46.4	1.0	0.0	0.0
High oleic	0.0	0.0	6.4	0.1	0.0	0.0	3.1	82.6	2.3	3.7	0.2	0.4

Figure 2.3: Fatty acid percentage composition of common plant oils (Espinosa & Meier, 2011).

2.3.2 Preparation of natural polyester from palm oil

Recently, monoglyceride method is the most common method used to produce alkyds in order synthesis natural polyester from palm oil. This method includes alcoholysis and esterification or polycondensation process. In this method, palm oil experienced alcoholysis in order to produce monoglyceride or diglyceride in the presence either of acid catalyst or base catalyst (sodium hydroxide, calcium oxide, sulfonic acid). In this step, the temperature are maintained at 230°C with continuous flow of nitrogen gas. Then, alkyds will undergoes esterification process or polycondensation process by react with monoglycerides and anhydrides at 230°C with continuous flow of nitrogen. Different types of anhydrides will influence the properties of the alkyds. The common anhydrides that used are maleic anhydride and phthalic anhydride. After esterification process, the natural polyester is being synthesis (Islam et al., 2014). Figure 2.4 show how the synthesis of alkyds is carried out through alcoholysis and esterification.

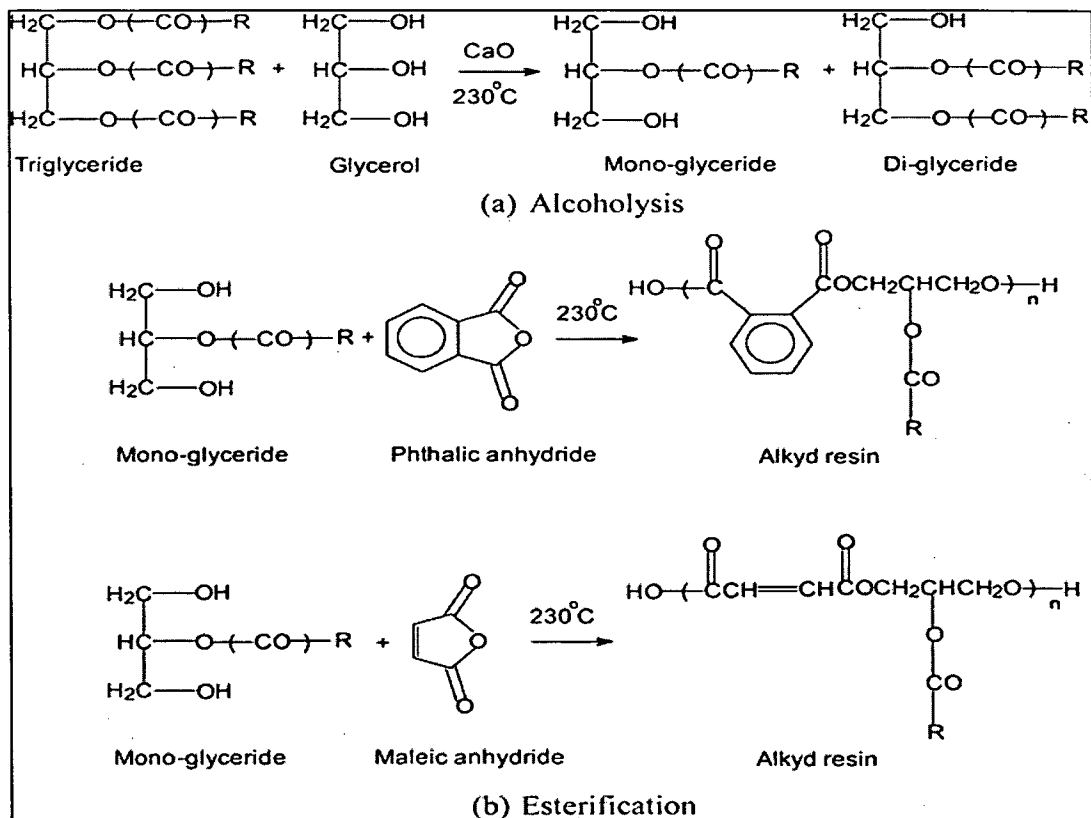


Figure 2.4: Synthesis of alkyd through alcoholysis and esterification process (Islam et al., 2014).

2.4 Unsaturated Polyester Resin (Synthetic polyester)

Unsaturated polyester resin is a macromolecules with a polyester backbone which belongs to the category of thermosetting resins (Waigaonkar et al., 2011). Unsaturated polyester resins are prepared by the condensation of unsaturated acids or anhydrides and diols with/without diacids, and diluted with an unsaturated co-reactant diluents like styrene (Bai et al., 2014). A subsequent cross-linking occur in the unsaturated polyester resin due to present of unsaturation.

Unsaturated polyester resin is start to be develop in 1929 by Arvin and Carathers (Arvin .J.A &Wilmington 1933) After that, it is being modified by Ford Motor Co.Ltd that using maleic anhydride react with phthalic anhydride and propylene glycol. The molar ratio of phthalic anhydride:maleic anhydride ranging is 2:1. Nowadays, unsaturated polyester resin is manufactured by condensation and polymerization of dicarboxylic acid (maleic acid) and dihydric alcohol (glycol) followed by curing with cross-linking agent (styrene). The products

have a good resistance to heat and most chemicals except strong acid and alkalies. Furthermore, it is stabilized unless it is affected by sunlight.

Unsaturated polyester resin is one of the thermoset resins that used widely since 1930. Figure 2.5 shows the demand of the unsaturated polyester resin among the thermosets in North America.

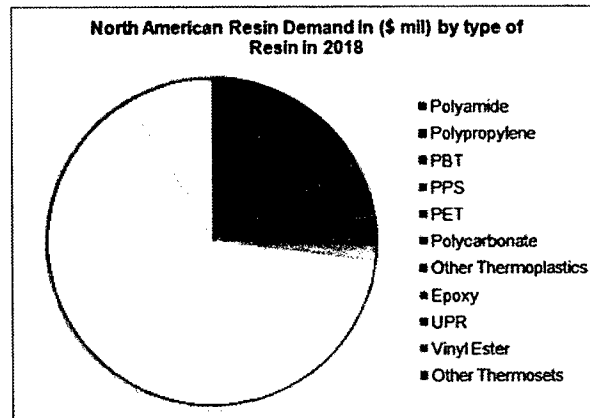


Figure 2.5 : The demand of type of thermoset resin

Thermosets are materials of choice of long term use because they are insoluble and infusible high density networks. Like others thermoset, the unsaturated polyester resins are blended with different fillers and reinforcements to yield thermoset articles having a wide range of chemical and mechanical properties. The resins are used to make trays, boats, swimming pool, water tank and shower stalls. Besides that, unsaturated polyester resin is also playing important role as a matrices for composite applications because it has excellent thermal stability and weather resistance (Waigaonkar et al., 2011). It is useful in insulation coating, fiber reinforced plastic product, sheet molding compound and bulk molding compound in manufacturing automotive parts (Waigaonkar et al., 2011).

Although unsaturated polyester resin have the characteristics of low density, high modulus, strength, durability and chemical resistances but unfortunately it was limited by their brittleness, especially when good impact behaviour is required (Waigaonkar et al., 2011). This is due the high cross-linking degree after curing process by adding curing agent such as styrene (Huajun et