PREPARATION AND CHARACTERISATION OF MgO NANOPARTICLE INCORPORATED BIORESIN USING PALM OIL

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DEDICATION

Highest gratitude to
my supervisor, my family members and my friends
for all your care, support and trust on me.
Special dedication to
Faculty of Chemical Engineering and Natural Resources of
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on providing all the related environment
and appropriate equipment
on finishing my research.

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ABSTRACT

Alkyd resins are the product derivation of polyacid and polyol modified with monobasic fatty acid through polycondensation. Over the recent years, alkyd resins are widely used as the binder for composite and film-forming agent in paints. Vegetable oils were being explored and evaluated to synthesis alkyd resin due to its biodegradability and renewability. Synthesis of alkyd resins involved the alcoholysis of the oil by the polyol (commonly glycerol) and followed by polyesterification with a polyacid (commonly phthalic anhydride). Generally, a homogeneous or heterogeneous base catalyst was used to carry out the reaction. Nanoparticles were said to be a promising catalyst and colloidal form of nanoparticles was discovered in this context. In this work, palm oil based alkyd resin was synthesized over Magnesium Oxide (MgO) nano sol. Colloidal MgO nanoparticles were synthesised in glycerol and subsequently was used in alkyd resin synthesis. The alcoholysis process was conducted in the presence of various concentration of MgO (0.01, 0.02, 0.04 and 0.06wt% w.r.t. palm oil) at 240^{o}C. The monoglycerides yield was found to achieve up to 95% in 40 minutes reaction time for 0.04wt% MgO catalysed system. As for the polyesterification process, fusion method was used since it was seldom discovered by other researchers. The crystallized size of the nanoparticle in sol was analysed by X-ray diffraction technique (XRD). Formation of the alkyd resin was monitored by measuring the acid values at different reaction time. Alkyd resins obtained after polyesterification of the alcoholysis products with phthalic anhydride at 240^{o}C were characterized by employing Fourier Transform Infrared (FTIR) and Nuclear magnetic resonance (NMR) spectroscopy. The antimicrobial activity of MgO incorporated alkyd resin against microorganisms was tested via the Kirby–Bauer method. The MgO incorporated in alkyd resin not only reduced the reaction time but also was also proved to be an effective antibacterial agent which added value to the alkyd resin synthesised. Overall, MgO nanoparticles incorporated alkyd resin showed outstanding performance compared to conventional homogeneous base catalyzed system.

ABSTRAK

Alkyd resin merupakan polyester dihasilkan dari dari tiga monomer iaitu polyol, polybasic acid dan minyak melalui polimerisasi kondensasi. Alkyd resin banyak digunakan dalam dalam industri cat, coating, dan pembentukan film. Penggunaan minyak sayur-sayuran untuk memproduksi alkyd resin bersifat mesra alam dan mempunyai sumber yang mencukupi. Secara dasarnya, penghasilan alkyd resin melibatkan dua reaksi iaitu alkoholisis dengan gliserol dan polikondensasi dengan phthalic anhydride pada suhu 240^{o}C.

Logam alkali oksida atau hidroksida seperti MgO, LiOH, NaOH, KOH dan $Ca(OH)_2$ adalah katalis alkoholisis yang biasa digunakan oleh para penyelidik. Dalam konteks ini, MgO nano sol (0.01wt%, 0.02wt%, 0.04wt% dan 0.06wt %) akan dihasilkan dalam gliserol dan seterusnya bereaksi dengan minyak kelapa sawit. Monogliserida yang disintesis daripada alkoholisis akan diuji dengan menggunakan teknik X-ray diffraction (XRD). Penghasilan alkyd resin selepas polikondensasi akan diperhatikan dengan mendapatkan acid values pada setiap masa tertentu. Seterusnya, analisis FTIR, ^{1}H NMR and ^{13}C NMR akan dijalankan untuk mengesahkan kewujudan alkyd resin. Berdasarkan keputusan yang didapati melalui eksperimen, hasil alkoholisis iaitu Monogliserida dapat mencapai setinggi 95%. Alkyd resin yang dihasilkan akan dianalisis dengan Fourier Transform Infrared (FTIR) dan Nuclear magnetic resonance (NMR) spectroscopy. Activiti alkyd resin terhadap bakteria juga diuji dengan cara Kirby–Bauer. Secara kesimpulannya, penggunaan MgO nano sol bukan sahaja dapat memendekkan masa reaksi namum juga dapat dijadikan agen antibakteria yang efektif.

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D	Average crystalline size
Λ	CuKα radiation
β	Full width at half maximum (FWHM)
θ	Braggs angle
X	Conversion of triglycerides
S	Selectivity of monoglycerides
P	Extent of reaction
C_o	Initial acid value
C_t	Acid value at time t
W_{oil}	Weight of oil
W_{alkyd}	Weight of finished alkyd
W_{H20}	Weight of water evolved during esterification

LIST OF ABBREVIATIONS

AV	Acid value
DG	Diglycerides
DP	Degree of polymerisation
FTIR	Fourier Transform Infrared
HPLC	High performance liquid chromatography
MG	Monoglycerides
NMR	Nuclear magnetic resonance
TG	Triglycerides
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Background

Alkyd resins are polymers resulting from the esterification of a polybasic acid, a polyol and oils or fatty acids. (Kienle & Ferguson,1929a) introduced the word ‘alkyd’ which originated from ‘al’ and ‘kyd’ corresponding to alcohol and ‘cid’ from acid which was later converted to ‘kyd’.

The first alkyd resin was synthesized in the mid-1920s by Kienle, who combined the already known technology of producing polyester resins based on glycerol and phthalic anhydride (the so-called Glyptals). It was found that alkyd resins were produced commercially in full scale starting from the year 1933 at General Electric and it was followed by other companies in 1935 (Hofland,2012).

Ever since, alkyds were already discovered and introduced many years ago. Van Bemmelnz (1856) prepared resins from succinic acid, from citric acid, from a mixture of benzoic and succinic acid, by heating with glycerol. Smith (1901) was the first to synthesis a resin from glycerol and phthalic anhydride and further attempt was taken into account by General Electric to develop more tractable polymer for electrical end uses. The resin was commercially synthesized in 1921 by available raw materials such as glycerol, phthalic anhydride and fatty acid and used as adhesives. The first report on alkyd resin preparation was published by Kienle and Ferguson (1929b).

Nowadays, alkyds have been widely used as synthetic resins in the paint and surface coating industry because of having properties such as good corrosion resistance, rapid dryness, high gloss and easily being applied over poorly treated surface.

Current arising environmental issue leads to the formation of resins by using renewable sources such as vegetable oils. Starting from the year of 1950, alkyd resin producers developed more environmental friendly version of their products based on the concept of producing relatively high acid value alkyds which upon neutralization with amines can be transferred to a form of colloidal solutions in a blend of water and water miscible solvents of glycol ether types. In the 1970s, multi-application water soluble alkyd resins were discovered by Hofland (2012).

1.2 Motivation

Nowadays, the issues of environmental and the depleting of petroleum sources are arising. Imperative actions should be taken to promote sustainable development where the needs and aspirations of present and future generations can be achieved.

Alkyd resins are extensively applied especially in surface coating industry (Bora et al.,2014b). Hence, it will be a promising development to produce resins from renewable sources. Renewable sources such as vegetable oils can be used to replace the depleting petroleum sources in the synthesis of alkyd resins. After much research works, researchers found that vegetable oil based resins are more preferred compared to mineral oils because of its biodegradability (Alam et al.,2014).

Malaysia was the world's second largest producer of palm oil. Palm oil was edible oil which being utilized as cooking oil. Palm oil can be used for polymer preparation. However, its industrial applications in non-food sectors are still hardly found (Islam et al.,2014).

Furthermore, the arising issue of expensive diesel fuel leads to the use of biodiesel to be an alternative fuel. Large amounts of crude glycerol are generated from the biodiesel production. Due to this reason, Pinyaphong et al. (2012) investigated for the production of more valuable products from crude glycerol, such as monoglyceride (MG), instead of dumping in the landfills. Therefore, glycerol becomes one of the main raw materials to synthesis alkyd resins because of its great availability.

Shortening reaction has become a crucial issue in the alkyd resin production. Currently the part of catalyst development was less emphasised in the process of alkyd resin synthesis. The commonly used catalysts in the reaction are homogeneous base catalyst such as NaOH, KOH and $Ca(OH)_2$

which usually needs longer reaction time. As a result, it will cause low production rate and high production cost. Nanostructured heterogeneous catalysts in colloidal form are promising nowadays due to their ultrafine size, high surface area and good dispersion they are explored to overcome the long reaction time problem (Ong et al.,2015). In this context, palm oil based alkyd resin was synthesised over colloidal MgO nanoparticles and its catalytic behaviour was investigated.

1.3 Problem statement

Conventional homogeneous catalyzed reaction using NaOH usually needs longer reaction time. Looking at the economic aspect, the longer the reaction time, the lower the production rate and hence, the higher the production cost. Therefore, catalyst development in alkyd resin synthesis was needed to be improved.

MgO was said to be a potential heterogeneous catalyst in producing monoglyceride due to the participation of strong basic low coordination of O^{2-} in glycerolysis. (Ferretti et al.,2012) However, most of the research was about synthesising MgO nanoparticles in powder form. The homogeneous distribution of MgO powder in glycerol and oil was difficult through direct mixing. Hence, higher amount of catalyst was required to achieve the desired conversion. Although colloidal metal oxide in glycerol or oil could ensure the homogeneous distribution of the catalyst, its activity has never been explored in alkyd resin preparation.

Furthermore, most of the catalysts are used only in the alcoholysis of vegetable oil, but never been utilized in the polyesterification reaction to prepare alkyd resin. Hence, in this work, MgO nano sol will be incorporated into the synthesis of alkyd resin and the catalytic behaviour was being observed.

1.4 Objectives

- To synthesise colloidal MgO nanoparticles in glycerol at room temperature.
- To investigate the catalytic effect of MgO in preparation of alkyd resin.

1.5 Scopes of study

This research will focus on

- Preparation of MgO nano sol in glycerol medium at room temperature and XRD characterisation of the produced MgO nano sol.
- Quantitative analysis of monoglyceride formation from alcoholysis using an Agilent 1200 Series HPLC system.
- Experimental catalytic analysis of MgO nano sol in the synthesis of alkyd resin by monitoring the acid value.
- Investigation of reaction temperature in synthesising a better quality of alkyd resin.

CHAPTER 2

LITERATURE REVIEW

Throughout this century, extensive research works had been carried out on alkyd resins. Alkyd resins came into commercial use over 50 years ago, and even with the wide array of other polymers for coatings that have appeared in more recent years, they rank as the most important synthetic coating resins and still constitute about 35% of all resins used in organic coatings. Previously, researches were mainly focus on the discovery and synthesis of vegetable drying oils to produce air-drying oil-modified alkyd resins. Later on, works were focused on improving the alkyd resin properties to match with specific application. In fact, properties of alkyd resins of various kinds strongly depend on the availability of raw materials, blending technology, choice of methods applied, catalysts and nanoparticles employed into the alkyd system. Hence, a lot of researches related to alkyd resin have been reported in the scientific literatures.

2.1 Introduction to alkyd resin

Alkyds are oil modified polyesters which synthesised from polybasic acids, polyols and oil/fatty acids. The raw material selection can greatly influence the properties of the resin and the types of process synthesis. The commonly used polybasic acids in synthesis of alkyds are phthalic anhydride, isophthalic acid, maleic anhydride, and fumaric acid. In most of the cases, phthalic anhydride was said to be widely used as it does not suffer from major solubility problem and reacts at low temperature as compare to other anhydrides. Next, the principal types of polyol used include pentaerythritol, glycerol, trimethylolpropane, trimethylolethane, ethylene glycol, and neopentyl glycol. Particularly, a fatty monobasic acid from vegetable oil was used in synthesising alkyd resins.

Alkyds are relatively inexpensive in terms of raw materials and manufacturing costs. Except for phthalic anhydride, being of petrochemical origin, the other raw materials used in the synthesis of the alkyds are from biologically renewable sources (Holmberg,1987). Over the recent years, alkyd resins are widely used in the paint and coatings industry (Blaise et al.,2012). Alkyd resins are easy to pigment. They are also compatible with most substance used in surface coating industries and they can be easily modified for special application.

2.2 Classification of alkyd

Generally alkyd resins are classified based on oil length. The oil length of an alkyd resin was defined as the number of grams of oil used to produce 100 grams of resin. The formula for calculating oil length was expressed as (2.1) and (2.2) respectively (Wicks Jr et al.,2007).

$$Oil\ length\ = \frac{W_{oil}}{W_{alkyd} - W_{H20}} \times 100 \tag{2.1}$$

$$Oil\ length\ = \frac{1.04 \times W_{FA}}{W_{alkyd} - W_{H20}} \times 100 \tag{2.2}$$

Where

W_{oil} = weight of oil

W_{alkyd} = weight of finished alkyd

W_{H20} = weight of water evolved during esterification

1.04 was the correction factor for converting weight of fatty acid to weight of triglyceride oil.

Alkyd resins with less than 40% oil length are called short oil alkyds. Those that have 40%-60% oil length are medium oil alkyds, and those with oil length over 60% oil contents are long oil alkyds. A summary of alkyd resins comparing different oil length alkyds was given in Table 2.1.

Table 2.1 : Properties of alkyd resin based on oil length (Koleske,1995)

Property	Long oil alkyd	Medium oil alkyd	Short oil alkyd
Oil length	Highest	Moderate	Lowest
Drying time	Longest	Moderate	Shortest
Brushing application	Best	Moderate	Worst
Film flexibility	Highest	Moderate	Lowest

Chemical resistance	Worst	Moderate	Best
Gloss retention	Worst	Moderate	Best

Variations in the amounts and types of components special for fatty acids produce a variety of alkyd resins with different mechanical and rheological properties. Table 2.2 shows that alkyd resins can be classified based on oil length.

Table 2.2 : Classification of Alkyd Resins Based on Length of Oil (Aghaie et al.,2012)

Parameter of resins	Classification of alkyd resins based on oil length					
	Short oil	Medium short oil	Medium oil	Long medium oil	Long oil	Very long oil
Oil length, %	25-47	43-47	47-56	53-56	56-74	74-85
Fatty acid, %	30-39	40-45	45-50	50-55	55-70	70-80
Phthalic anhydride, %	38-50	36-38	33-36	30-33	20-30	10-20
Suitable solvent	Aromatic	Aromatic	Aliphatic	Aliphatic	Aliphatic	Aliphatic
Solid of resin, %	45-50	50	50-55	60	60-70	70-100
Preparation of film	Thermoset high temperature	Thermoset high-low temperature	Thermoset low temperature	Thermoplast	Thermoplast	Thermoplast

From Figure 2.1, it can be seen that short oil length alkyds which have resin like property exhibits higher viscosity, tackiness and impart the hardness of coating. Long oil length alkyds which have oil like property are softer, shows higher flow ability and less tackiness. As for the medium oil length alkyd, they corresponds to an even mixture properties of resin and oil.

For drying alkyd (oil iodine value >150) always possess of fast drying properties, while non-drying alkyd (oil iodine value <100) possess of slow drying properties (Patton,1962).

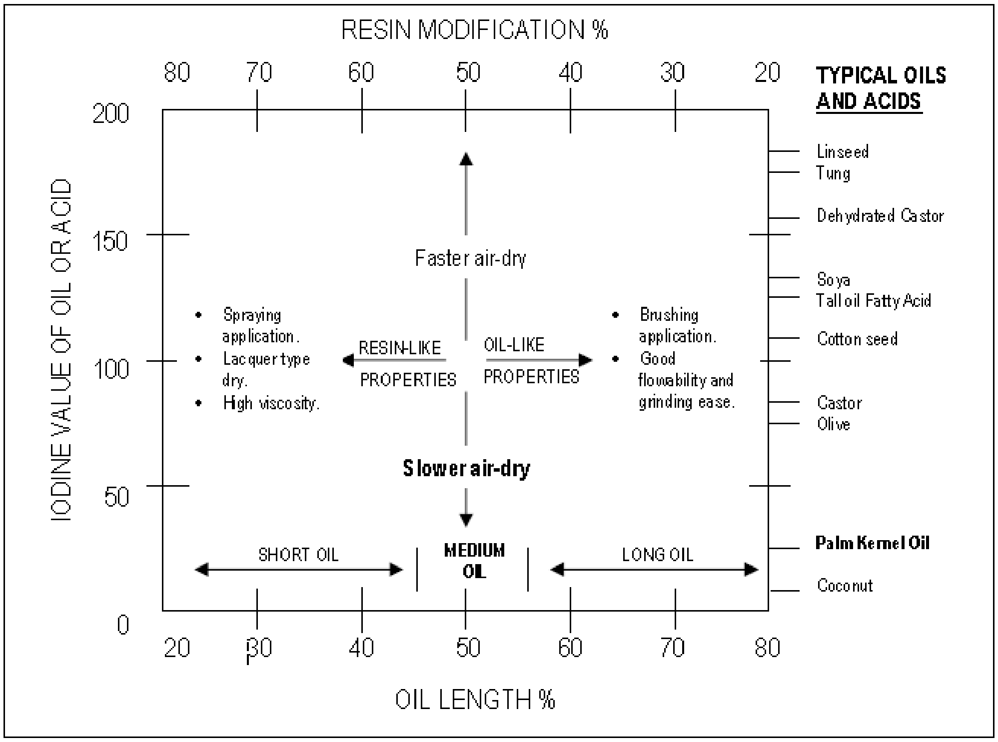


Figure 2.1 : Properties to be expected from the alkyd of different oil length and iodine value (Patton,1962)

Alkyd resins can also be classified into oxidizing and non-oxidizing type. Oxidizing alkyds cross-link by the same mechanism as drying oils. Non-oxidizing alkyds are used as polymeric plasticizers or as hydroxyfunctional resins, which are cross-linked by melamine–formaldehyde (MF), by urea– formaldehyde (UF) resins, or by isocyanate cross-linkers (O.FOsagie 2015).

2.3 Raw materials

The major components in synthesising alkyd resins are oils or fatty acids, polybasic acid and polyols. Theoretically, any oils or polyol or polybasic acid can be used to produce alkyd resins. However when considering cost, only a few raw materials are found to be commercially accepted. The raw material selection can greatly influence the properties of the resin and the overall performance of the resulting film.

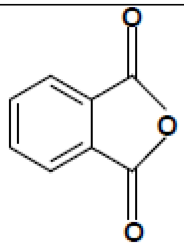
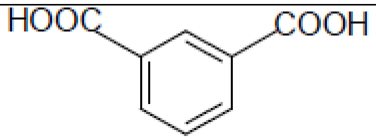
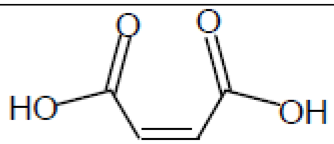
2.3.1 Oils

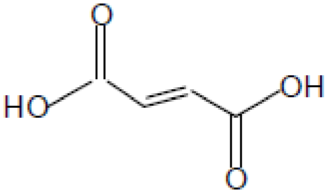
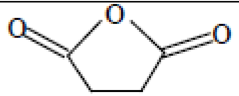
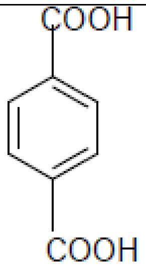
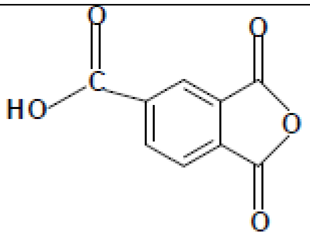
As the use of petroleum-based materials was expected to decline in the near future, vegetable oils, which are readily available, can serve as alternative raw materials for alkyd resin preparation (Blaise et al.,2012). Vegetable oils constitute the single, largest, easily available, low cost, non-toxic, non-depletable, biodegradable family yielding materials that are capable of competing with fossil fuel derived petro-based products (Alam et al.,2014). So far, there are a lot of researchers who try to explore the use of different types of oils to synthesis alkyd resin. The most recent attempt was to use sunflower acid oil to synthesis alkyd resin which was reported by Chiplunkar and Pratap (2016). Furthermore, there are more researches which use different types of oils to synthesis alkyd resin such as Karanja (*Millettia pinnata (L.) Panigrahi*) seed oil (Bora et al.,2014a), Jatropha Curcas oil (Boruah et al.,2012), Hura crepitans L. seed oil (Ezeh et al.,2012), Nahar seed oil (Dutta et al.,2004a), and castor oil (Ogunniyi & Njikang,1998). Aigbodion et al. (2003) also studied the utilization of maleinized rubber seed oil and its alkyd resin as binders in water-borne coatings. Since the oils mentioned above are not for edible purposes, undeniably, they stand out to be a suitable substitute to synthesis alkyd resin. However, there are some edible oils which are being investigated to synthesis alkyd depends on the availability of sources in certain area. In Africa, Aigbodion and Okieimen (2001) investigated the use of African locustbean seed oil to synthesis alkyd resin. Since Malaysia was one of the biggest palm oil producers in the world therefore, the use of palm oil in the area of research in synthesis alkyd resin can be quite promising. Alkyd resin based on palm oil was synthesized and characterized successfully and was found to exhibit excellent adhesion (Cheun,2009).

2.3.2 Polybasic acids

Phthalic anhydride was the most common polybasic acid used in alkyd industry. It has the ability to improve film hardness and chemical resistance of resins. Besides, PA was widely used as it does not suffer from major solubility problem and reacts at low temperature as compare to other anhydrides. The isomer of Phthalic anhydride, Terephthalic acids are also employed in manufacturing alkyd resin. It was in white powder form which was insoluble in water and hence the resins with Terephthalic acids has good water and whether resistance. But it was rarely used in alkyd industry due to certain difficulties faced in synthesis process (Udayakumara S.V.,2015). Furthermore, Trimellitic anhydride was also used in water soluble or water dispersible alkyds. Usually unsaturated dibasic acids such as maleic and fumaric acid are avoided since their use can lead to gelation of the alkyd resin preparation mixture (Kuzma,1980).

Table 2.3 Polybasic acids commonly used to synthesis alkyd resin

Polybasic acids	Formula	Structure
Phthalic anhydride (PA)	$C_8H_4O_3$	
Isophthalic acid (IPA)	$C_8H_6O_4$	
Maleic anhydride (MA)	$C_4H_2O_3$	

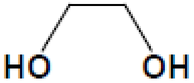
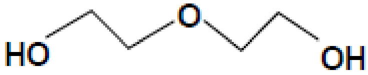
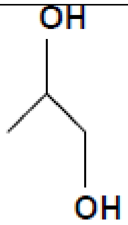
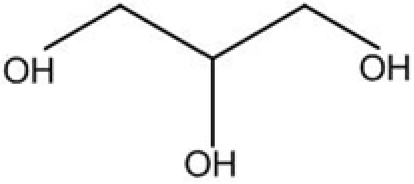
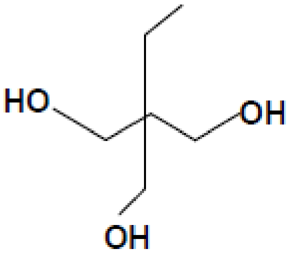
Fumaric acid (FA)	$C_4H_4O_4$	
Succinic anhydride	$C_4H_4O_3$	
Terephthalic acid (TPA)	$C_8H_6O_4$	
Trimellitic anhydride (Lueken et al.)	$C_9H_4O_5$	

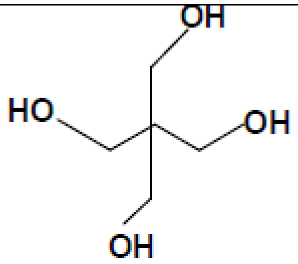
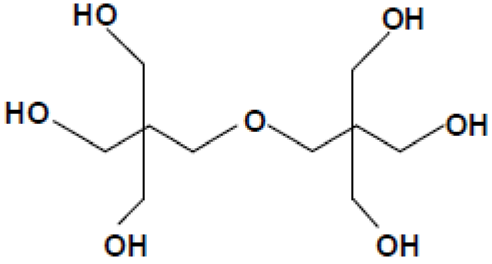
2.3.3 Polyols

The polyol acts as the solvent, a surfactant, as well as the reducing agent Hachani et al. (2016). In general, polyols with functionalities of 2 to 4 are widely used in alkyd formulation. Ethylene glycol, diethylene glycol and propylene glycol are diols; glycerol and trimethylolpropane are triols and pentaerythritol was the best tetraol choice for branching. The flexibility of alkyds will be determined by the distance between two hydroxyl groups (Wang,2013). The most widely used polyols are glycerol and Pentaerythritol. Glycerol contains two primary and one secondary hydroxyl group which enables it to be used in alkyds of all fatty acids. Taking into account also the properties of glycerol such as low toxicity, good biodegradability and low vapor pressure (high boiling point), glycerol has recently been shown to be widely used in alkyd resin synthesis (Thanh et al.,2012).

Pentaerythritol which has four primary hydroxyl groups can form complex resin with better performance properties like rapid drying, greater hardness and better gloss.

Table 2.4 : Polyols commonly used to synthesis alkyd resin

	Formula	Structure
1. Diols		
Ethylene glycol	$HO(CH_2)_2OH$	
Diethylene glycol	$HO(CH_2)_2O(CH_2)_2OH$	
Propylene glycol	$CH_3CH(OH)CH_2OH$	
2. Triols		
Glycerol	$HOCH_2CH(OH)CH_2OH$	
Trimethylolpropane	$CH_3CH_2C(CH_2OH)_3$	

3. Tetraol		
Pentaerythritol	$C(CH_2OH)_4$	
4. Polyol		
Dipentaerythritol	$[(CH_2OH)_3CCH_2]_2O$	

2.4 Manufacture of alkyd resins

In general, there are two alkyd resin synthesis routes (Core & Gündüz,2011):

a) Monoglyceride process
b) Fatty acid process

Where each of the process applied was based on the type of raw materials used.

2.4.1 Monoglyceride process

In this synthesis route, it involved 2 stages which are alcoholysis of oil with glycerol followed by polyesterification. Alcoholysis converts the insoluble polyol and glyceride phases into a single homogeneous monoglyceride phase. Then, the monoglyceride in turn provides a solvent for the phthalic anhydride to be added for the next step, esterification of the monoglyceride with diacid to complete the alkyd reaction (Panda,2010).

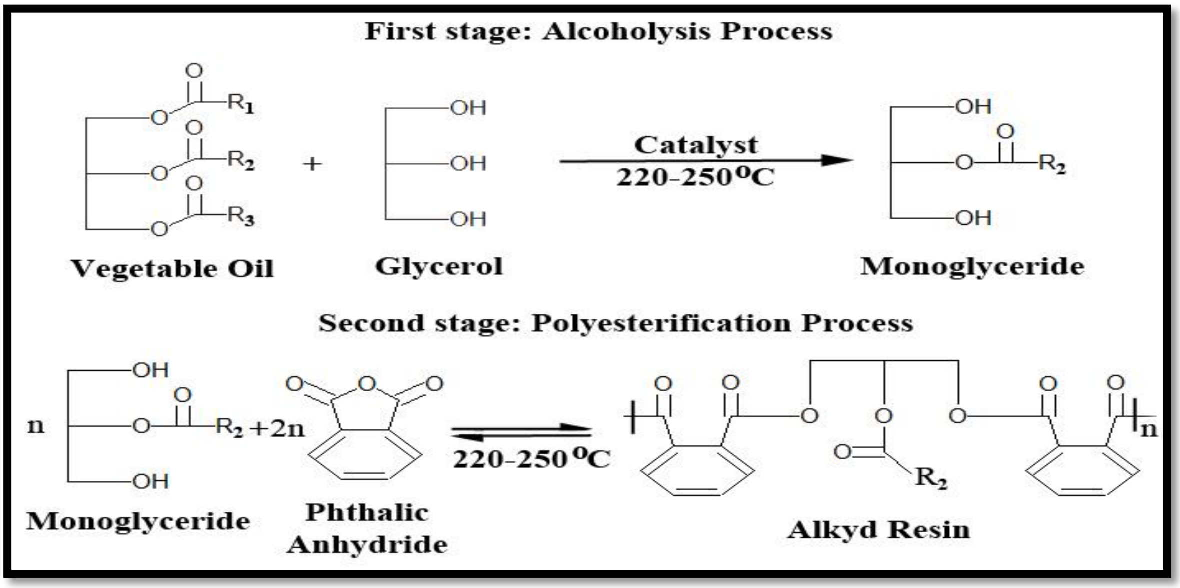


Figure 2.2 : Reaction pathway of two step method (alcoholysis followed by polyesterification) (Ong et al.,2015)

For the alcoholysis reaction, oil was heated with polyol at a temperature of 220-250 ℃ in the presence of base catalyst such as NaOH, KOH and LiOH. This process was conducted under N_2 inert atmosphere to reduce discoloration and dimerization of drying oils. The completion of alcoholysis reaction was monitored by having methanol solubility test (Boaventura,2012).

Practically, the products of this reaction are an equilibrium mixture containing triglycerides, diglycerides, monoglycerides and glycerol. However, α-monoglyceride was the major component in the alcoholysis products where its amount determines the alkyd resin production in polyesterification later.

In the polyesterification process, the alcoholysis products react with polybasic acids to form alkyd resin. The favourable reaction temperature was between 220 ℃ and 250 ℃. The reaction completion was monitored by checking the acid value of the reaction mixture. Reaction was stopped when acid value becomes constant.

2.4.2 Fatty acid process

The fatty acid process involves utilization of free fatty acids in synthesising alkyd resin. This process allows more control of the fatty acid content in the final alkyd. The fatty acid process was also simpler than the monoglyceride process in that it consists of only one `step' (Sailer et al.,1998). In this process, all the raw materials are charged into the reactor and heated to temperature between 190 ℃ and 240 ℃ under inert gas atmosphere. In this case, all the acid components will directly compete to react with the polyols. Since the carboxyl groups of PA react faster with the primary hydroxyl groups from glycerol than those of fatty acids, the polybasic acid and glycerol form the polyester backbone structure of the alkyd (Lanson,1985).

2.4.3 Alcoholysis

2.4.3.1 Reaction parameters affecting alcoholysis

Several reaction parameters are investigated by researchers to achieve high yield of MG. Ferretti et al. (2010) investigated the effect of stirring rate in the synthesis of MGs using MgO. A series of tests with varying stirring rate from 400-700rpm were tested where the other parameters remained the same. The change in stirring rate did not affect much on the conversion of fatty acid methyl ester (FAME) since it was not a mass gradient of liquid-liquid interface. The same test on effect of stirring rate to the alcoholysis reaction was also run by Negi et al. (2007) and found out that no increase of reaction rate with stirring speed can be observed.

Another significant reaction parameter was temperature. (Noureddini et al.,2004) reported that the formation of MG in the process increased when the reaction temperature was increased. It was observed that when the temperature was increased from 200 to 220 ℃, the concentration of MG in the reaction product increased from about 58 to 62 wt% and then levelled off as the reaction temperature was increased further to 240 ℃.

Furthermore, effect of the molar ratio of glycerol/TG was studied. Experiments were conducted with molar ratios of glycerol/TG of 2:1,2.5:1, and 3:1 at a mixing speed of 3600 rpm, temperature of 220 ℃ and reactant volumetric flow rates of 50 mL/min. The results indicated no significant change in the formation of MG over the range investigated for the reactant ratios. MG levels of production were at about 62 wt% in all cases (Noureddini et al.,2004). In the context of large increase of glycerol, it will decrease the amounts of available substrate at the interface between oil and glycerol and hence decreased the MG yield (Pinyaphong et al.,2012).

2.4.4 Polyesterification

There are two types of techniques that can be used in synthesising alkyd resin which are fusion process and solvent process regardless of the monoglyceride process or fatty acid process. In this reaction, it was observed that the longer the reaction, the more viscous the mixture was. Therefore, adequate agitation was necessary for complete mixing of monoglyceride mixture and phthalic anhydride in this stage (Uzoh et al.,2013). Nitrogen atmosphere was required in these two processes.

2.4.4.1 Fusion process

In fusion process, the products formed from alcoholysis are charged into the round bottom flask at a temperature around 220^{o}C and 250^{o}C. Nitrogen purging was required in order to facilitate water removal from the polyesterification reaction. Figure 2.3 shows the experiment set up by using fusion method. The benefit of this process was that only simple equipment set-up was required which then leads to low production cost and less of fire hazard (Sandler,2012). On the other hand, problems associated with loss by volatilization and darkening of resins may happen in this process (Holmberg,1987). Hence, fusion process was not the method of choice for preparing alkyd resin with narrow specification. However, several studies are carried out on alkyd resin preparation using vegetable oil/fatty acid by fusion method.

Reaction parameters such as type of raw materials, catalysts and reaction temperature are varied in preparing alkyd resin which is summarised in Table 2.5.

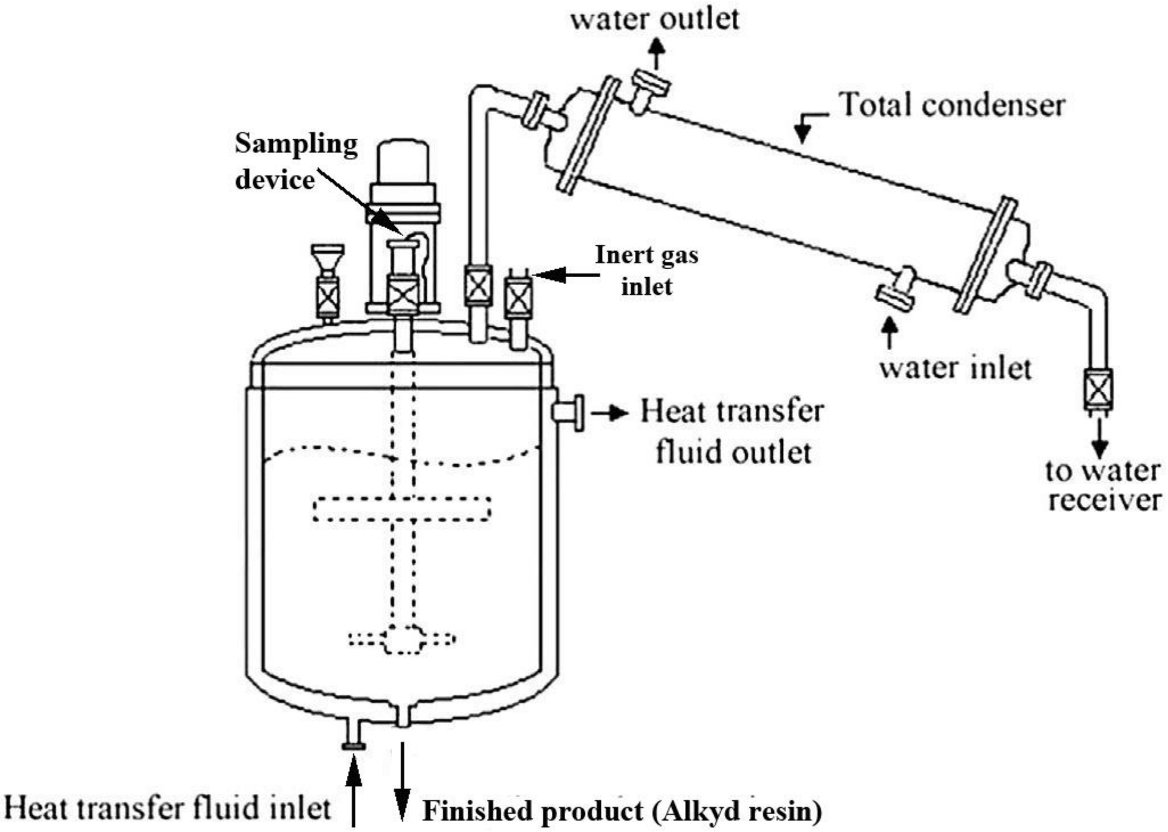


Figure 2.3 : Process diagram of alkyd resin preparation by fusion method (Nanvaee, Yahya & Gan, 2013)

Table 2.5 : Optimization of reaction parameters of alkyd preparation by alcoholysis-polyesterification process through fusion method

Oil/fatty acid	**Polybasic acid**	**Polyol**	**Catalyst**	**Temperature (°C)**	**Reaction time (min)**	**Reference**
Rubber seed oil	Phthalic anhydride	Glycerol	CuO	240	120	(Ong et al.,2016)
Palm oil	Phthalic anhydride	Glycerol	NaOH-CuO	240	120	(Ong et al.,2015)
Sunflower acid oil /Refined sunflower acid oil	Phthalic anhydride ; Maleic anhydride	Glycerol	PbO	225–240	210	(Chiplunkar & Pratap,2016)
yellow oleander (Thevetia peruviana) seed oil	Phthalic anhydride ; Maleic anhydride	Glycerol	PbO	230	60	(Bora et al.,2014b)
Ximenia americana seed oil	Phthalic anhydride	Glycerol	CaO	230-250	120	(Oladipo et al.,2013)
Hura crepitans L. seed oil	Phthalic anhydride	Glycerol	$CaCO_3$	220-240	60	(Ezeh et al.,2012)
Jatropha curcas linnaeus oil	Phthalic anhydride	Glycerol	$CaCO_3$	220-240	40	(Odetoye et al.,2012)

Karawila seed oil; Soya bean oil (50:50)	Phthalic anhydride	Pentaerythritol	CH_3NaO	240	-	(De Silva et al.,2012)
Rubber seed oil	Phthalic anhydride	Glycerol	CaO	240	-	(Aigbodion and Pillai (2001); Ikhuoria and Aigbodion (2006); (Ikhuoria et al.,2011)
Soybean seed oil; Castor oil	Phthalic anhydride	Glycerol	NaOH; KOH; CaO; $Ni(OH)_2$	200-240	210	(Liu et al.,2011)
Jatropha seed oil	Phthalic anhydride	Glycerol	$CaCO_3$	240	210	(Kumar et al.,2010)
Tobacco seed oil	Phthalic anhydride	Glycerol	$CaCO_3$	240	300	(Ogunniyi & Odetoye,2008)
Crude castor oil	Phthalic anhydride	Glycerol	NaOH	230-240	120	(Hlaing & Oo,2008b)
Corn, rice bran, sunflower, soya bean and	Phthalic anhydride	Glycerol	LiOH	210-230	300	(Atimuttigul et al.,2006)

dehydrated castor oil						
Sunflower oil	Glutaric, maleic, phthalic and succinic anhydride	Glycerol	$CaCO_3$	210-230	-	(Aydin et al.,2004)
Nahar seed oil	Phthalic anhydride; Malic anhydride	Glycerol	PbO	240	240	(Dutta et al.,2004b)

2.4.4.2 Solvent process

Solvent process was widely used in synthesising alkyd resins. In this process, reactants are heated together at temperature between 200°C-240°C with a solvent (most commonly used solvent was Xylene) which helps in many ways during the process. Xylene was chosen for this process since it has suitable boiling point and low water solubility (Uzoh et al.,2013). The solvent and water produced from reaction form an azeotropic mixture. It was then distillated off from the reactor, condensed and passed into a separator where water was removed and solvent was recycled to reactor. Here, process time will be reduced without encountering higher temperature. Solvent was being recycled to the reactor which means that the volatile reactants lost from the reactor are mostly returned with solvent to reactor. This method shows better control over process control parameters. Solvent process forms alkyds with higher polymer uniformity, higher molecular weight and higher yield because of less loss of phthalic anhydride or polyol (Engineers,2007). Polyesterification process was monitored by measuring the acid value at regular interval of time until the acid value constant. When this point was reached, the alkyd was cooled down to 180°C to prevent further reaction and diluted with solvent to the required solids or nonvolatile content. Figure 2.4 shows the experimental set up for alkyd resin preparation by solvent method.

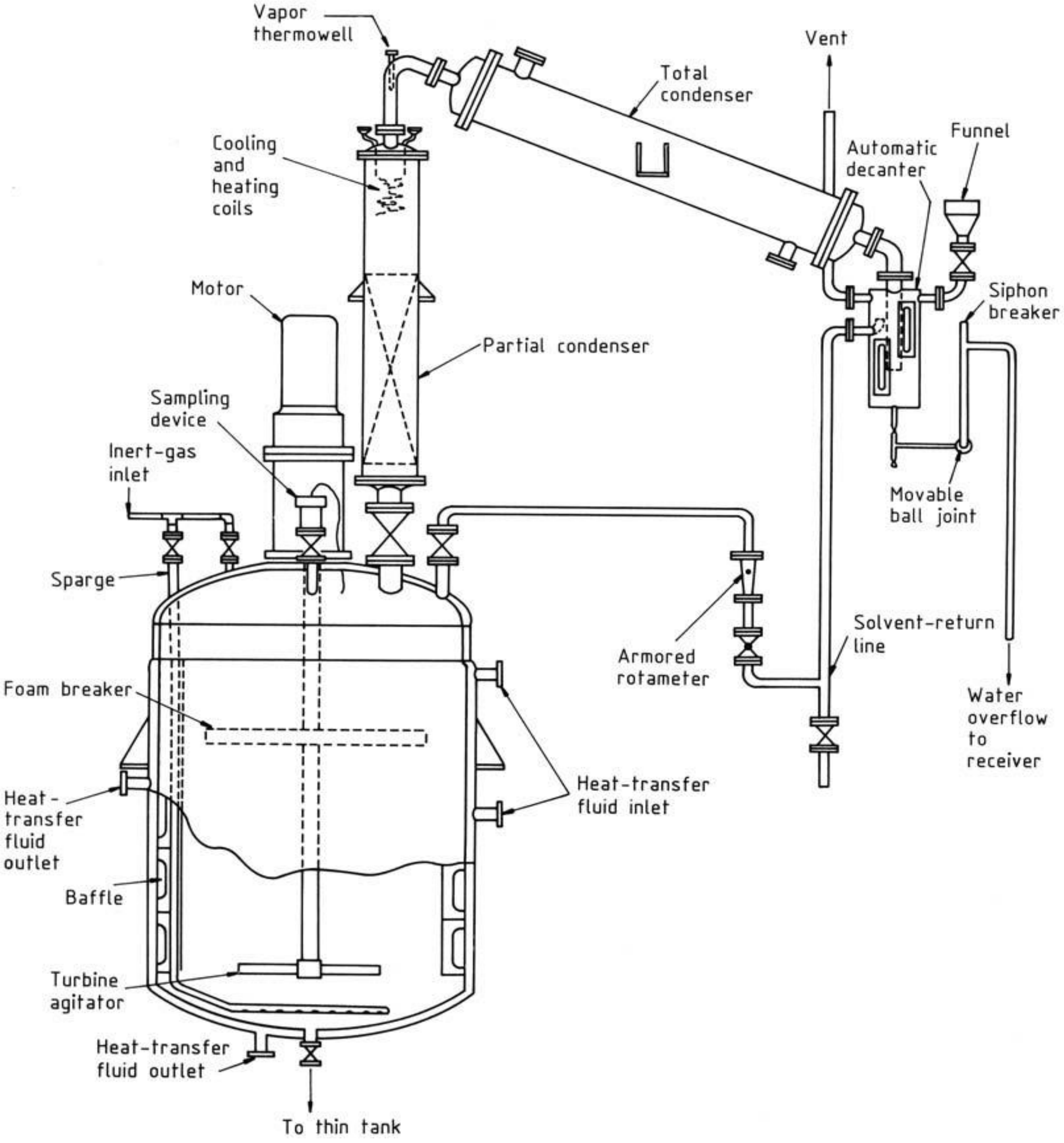


Figure 2.4 : Process diagram of alkyd resin preparation by solvent method (Sonntag, 1979)

2.4.5 Catalysts used in alkyd resin synthesis

Literature about catalyst development in alkyd resin synthesis was seldom reported. Evaluation of the type of catalyst in the alkyd resin synthesis can achieve scientific and economic benefit. This alcoholysis reaction can be catalysed by both acids and bases. It was said that base solid catalysts are more effective than the acidic ones because they do not require high temperature and pressure, thus react more rapidly, have fewer side reactions, have no oxidation, and are more available and cost-effective (Tahvildari et al.,2015). Normally, bases such as metal hydroxides, metal oxides and metal salts of weak acids are used. In the industry, carbonates, oxides, alkoxide of lead, lithium, calcium, tin and zinc are used as alcoholysis catalysts (Karak,2012).

The common catalysts used in the reaction can be classified to homogeneous catalyst such as LiOH, NaOH, KOH and $Ca(OH)_2$ or heterogeneous catalyst such as $CaCO_3$, ZnO/alumina and CaO (Ong et al.,2015).

Uzoh and Nwabanne (2016) prepared castor seed oil based alkyd resin with glycerol and phthalic anhydride using 0.1wt% (with respect to oil) of LiOH, CaO, $CaCO_3$, PbO and NaOH as catalyst. The result of their experiment showed that the rate of decrease in acid value, extent of reaction, degree of polymerization was higher in LiOH and PbO followed by $CaCO_3$, NaOH and CaO. As for the physiochemical properties of the alkyd resin, 0.3 wt% of LiOH and PbO catalysed system produced better quality alkyd resin followed by 0.03wt% of $CaCO_3$, NaOH and CaO catalysed system.

Bora et al. (2014b) and Boruah et al. (2012) reported the alkyd resin synthesis with the presence of PbO catalyst of 0.05 wt% (with respect to the oil). According to Hlaing and Oo (2008a), PbO catalyst used for alcoholysis reaction required a very less amount ranging from 0.01wt% to 0.1wt% with respect to oil. They also mentioned that large amount of catalyst lead to darkening of alkyd resin. In Menkiti and Onukwuli (2011) work, they compared the catalytic performance of three different catalysts : lead (II) oxide (PbO), lithium hydroxide (LiOH) and calcium carbonate ($CaCO_3$) and found out that PbO catalysed system was of the highest rate among them.

In the alcoholysis process where monoglycerides were formed, heterogeneous MgO was said to be an active basic solid catalyst. Its catalytic behaviour on the preparation of the monoglyceride was investigated by Corma et al. (2005) and Ferretti et al. (2009). In Corma's study, he investigated Lewis base catalysts such as single or mixed oxides or Brønsted base catalysts to enhance the selectivity of methyl oleate alcoholysis for monoglyceride production. He found that conversion of methyl oleate can achieve up to 96% in 6 hours with 70% monoglyceride yield by using 4wt% MgO as catalyst (Corma et al.,2005). In Ferretti's study, he showed that the use of MgO (catalyst/reactant ratios = 30 g/mol) in alcoholysis of methyl oleate yield up to 77% monoglycerides in 2 hours which was a much higher yield compared to those conventional liquid base-catalyzed homogeneous process (40–60%) (Ferretti et al.,2010).

Recently, enzymatic-catalysed production of monoglycerides was also being investigated. Lipases are used as biocatalysts because it can function well in mild reaction condition and high catalytic efficiency (Bornscheuer,1995). According to Karak (2012), synthesis of vegetable oil based alkyd resin with Lipozyme IM 60 (lipase from fungus Mucor miehei immobilised on micro-porous anion exchange resin) as catalyst showed lighter colour, good chemical resistance and good reverse impact strength compared to conventional resins.

However, enzymatic processes are not favoured since the setup was difficult, expensive and not very efficient because of enzyme reusability issues (Ferretti et al.,2010). As for the nanostructured heterogeneous catalysts, they are promising in the use of many reactions nowadays due to their ultrafine size and high surface area. According to (Ong et al.,2015), the inclusion of a nanostructured heterogeneous catalyst in a homogeneous catalysis system can provide a new catalytic environment for alkyd resin synthesis. In his recent work, polyol reduction method was used to synthesis CuO in glycerol at room temperature and it was later incorporated in the synthesis of alkyd resin.

2.4.6 Incorporation of Nanoparticles

Vegetable oil based alkyd resin is favourable due to its biodegradability. However, this kind of alkyd resins can be degraded naturally by the action of microorganism such as fungi, bacteria and algae (Karak,2012). Researchers work out hard to find out the way to overcome this drawback. Metal or metal oxide nanoparticle such as Ag (Zinjarde,2012), silver oxide (Ag_2O) (Allahverdiyev et al.,2011), titanium dioxide (TiO_2) (Haghighi et al.,2013), copper oxide (CuO) (Ong et al.,2015), calcium oxide (Jeong et al.,2007) and magnesium oxide (MgO) (Jin & He,2011) are known to be great antimicrobial agents.

Ecco et al. (2014) reported the use of polyaniline and cerium oxide (CeO_2) nanoparticle in improving the anticorrosive properties of an alkyd coating. The presence of CeO_2 nanoparticles into the alkyd coating promoted anticorrosive protection of steel. The addition of polyaniline together with CeO_2 inside the alkyd coating was proven to reduce the rate of corrosion.

Besides, a series of published work regarding to the addition of CuO nanoparticles into the alkyd resin was reported. As reported by Ong et al. (2015), the addition of CuO nanoparticles to conventional NaOH catalytic system not only enhanced the catalytic behaviour of alcoholysis–polyesterification process by shortening the reaction time but at the same time, the CuO incorporated resin also showed antimicrobial properties.

2.5 Summary

Extensive works on alkyd preparation were done by many researchers over the years. Palm oil based alkyd resin was chosen because of the great availability of palm oil in Malaysia. Generally, alkyd resin will be synthesised using glycerol and phthalic anhydride as raw materials together with palm oils at $240^{o}C$ via alcoholysis-polyesterification reaction after reviewing the past works by other researchers. Generally, a homogeneous or heterogeneous basic catalyst was used to carry out the reaction. Homogeneous catalyst such as NaOH, KOH, LiOH, $CaCO_3$ or heterogeneous catalyst such as PbO and CaO were widely used. From the literature survey, most works preferred homogeneous catalysts for alkyd preparation, while less work reported on the use of heterogeneous catalysts. So far, the use of the metal or metal oxide nanoparticles as catalyst was only found to be in the alcoholysis reaction but did not proceed with polyesterification to synthesise alkyd resin. In this context, palm oil based alkyd resin was synthesised over colloidal MgO nanoparticles and its catalytic behaviour was investigated.

CHAPTER 3

METHODOLOGY

3.1 Materials

Magnesium acetate tetrahydrate salt ($Mg(CH_3COO)_2.4H_2O$), Methanol, Ethyl alcohol, Anhydrous glycerol, Potassium hydroxide are bought from R&M Chemicals, Acros Organic brand of hydrazine monohydrate(64%) was used, Diethyl ether from Qrec, Phthalic anhydride, Phenolphthalein from Fisher and refined palm oil was provided by the Malaysian Palm Oil Board(MPOB), Malaysia.

3.2 Research algorithms

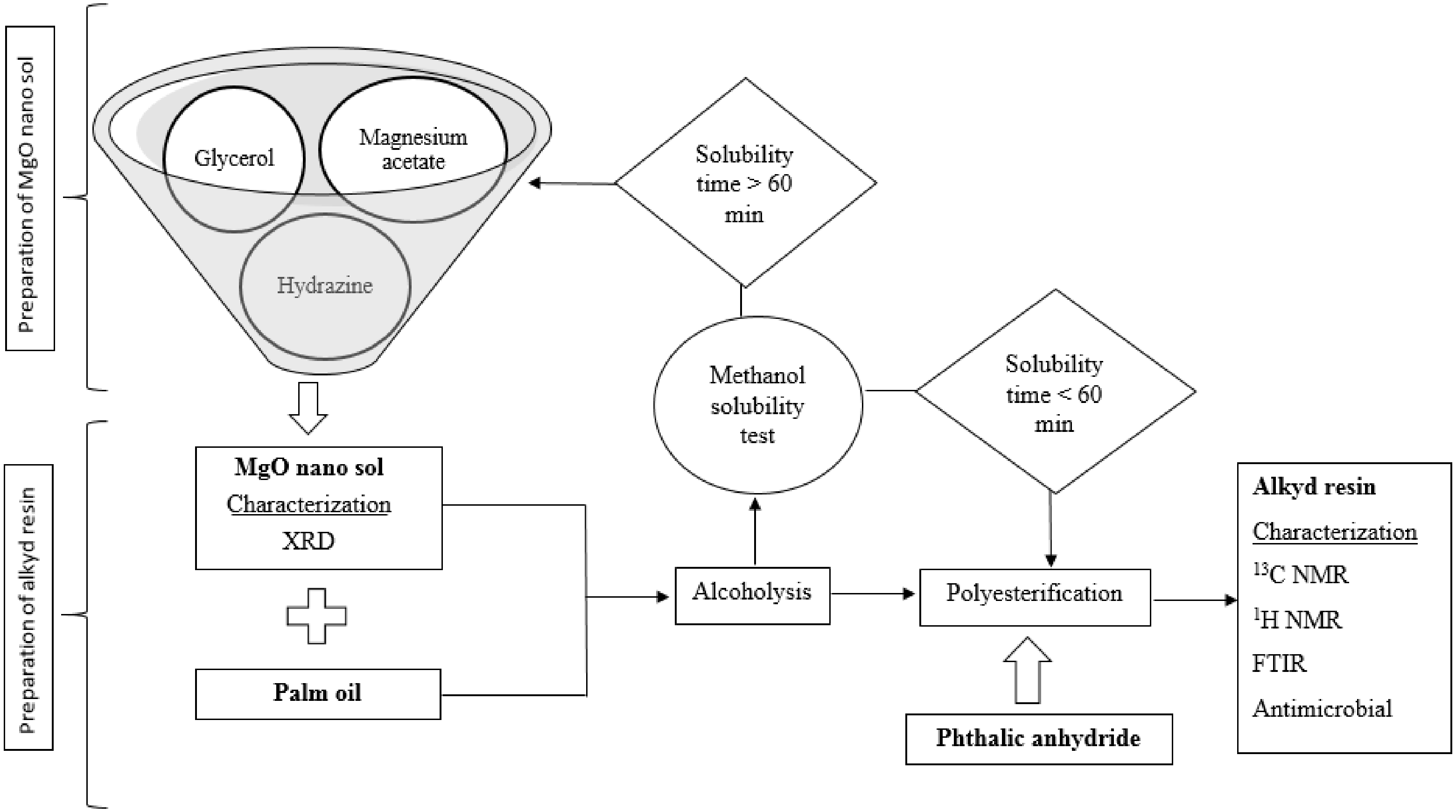


Figure 3.1 : Flowchart of alkyd resin preparation

3.3 Preparation of MgO nano sols

Synthesis of MgO nano sol was performed in a beaker with magnetic stirrer at room temperature. Certain amount of $Mg(CH_3COO)_2.4H_2O$ was dissolved in 100g glycerol. 20ml of the solution was transferred to another beaker and followed by the addition of hydrazine. The solution was stirred continuously for 12 hours at room temperature.

3.4 Preparation of alkyd resins

Synthesis of alkyd resin involved the alcoholysis of palm oil with glycerol followed by the polyesterification with phthalic anhydride. During alcoholysis, palm oil was heated to 240^oC and MgO sol in glycerol (produced previously) with a ratio of 1:2 was incorporated into the system under constant stirring. The reaction was conducted under nitrogen purging. The monoglyceride formation was then determined by methanol solubility test where 1 ml of reaction mixture was withdrawn and cooled to room temperature before adding 4ml of methanol. When the end point of alcoholysis was confirmed, reaction mixture was cooled to 140^oC. 38.7g of phthalic anhydride was then added into the reaction mixture to start the polyesterification process. Reaction temperature was maintained at 240^oC under nitrogen atmosphere. 1ml of sample was withdrawn at each time to determine the acid value as well as to supervise the reaction progress. The acid value of in-process samples taken at intervals were determined by titrating with a 0.1M KOH solution to the phenolphthalein end point after dissolution in a mixture of ethanol and diethyl ether. The experiment set up is as shown in Figure 3.2.

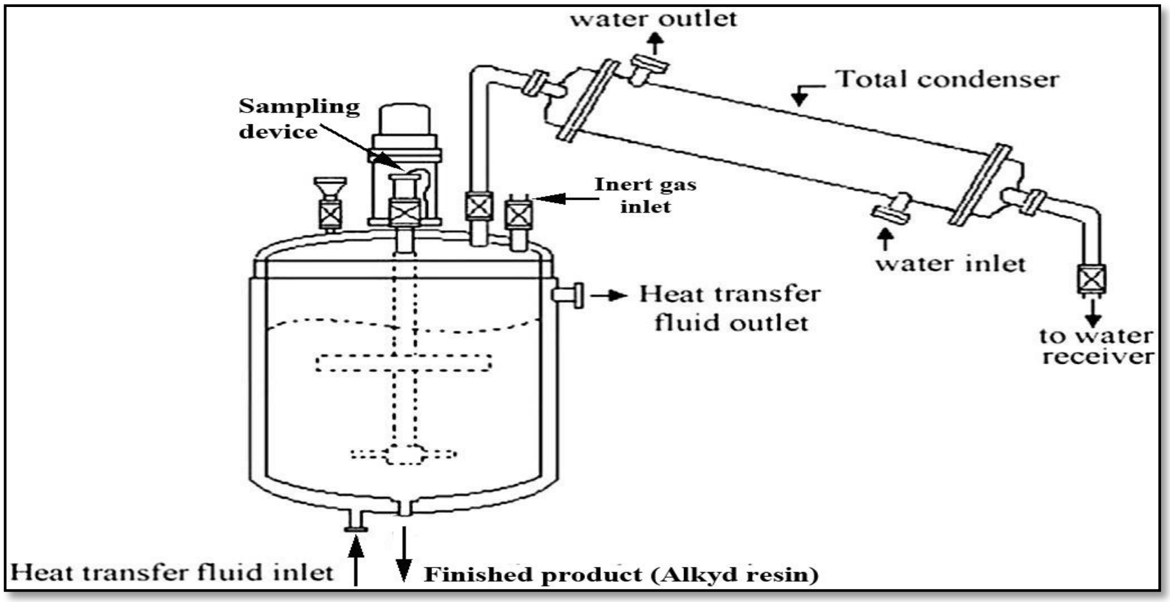


Figure 3.2 : Process diagram of alkyd resin preparation by fusion method (Nanvaee et al.,2013)

3.5 Instrumentation and Characterisation of MgO nano sols

3.5.1 X-ray powder diffraction (XRD)

Phase identification, qualitative and quantitative analysis of MgO was carried out by Rigaku Miniflex X-Ray Diffractometer where the diffractometer was capable of measuring powder diffraction patterns from 3 to 145 degrees in two-theta scanning range. The diffractometer was used with Cu Kα radiation at 15 mA and 30 kV and the detector was performed between 0 ° and 80 ° with a step of 0.02 °2θ. Phase identification was accomplished using a search-match software indexing the peaks against Power Diffraction Files (PDF) and the data were provided by International Centre for Diffraction Data (ICDD). The particle size of MgO can be determined using Debye-Scherrer's equation,

$$d = \frac{0.94\,\lambda}{\beta\cos\theta} \tag{3.1}$$

Where d is the average crystalline size, 0.94 is the particle shape factor which was depend on the shape and size of the particle, λ is the CuKα radiation (1.54A°), β is the full width at half maximum (FWHM) of the selected diffraction peaks (β=1.138), θ is the Braggs angle obtained from 2θ values which was corresponding to the maximum intensity peak in XRD pattern (Agrawal et al.,2015).

3.6 Instrumentation and Characterisation of Monoglyceride formation

3.6.1 High performance liquid chromatography (HPLC)

Quantitative analyses of the alcoholysis products were done using an Agilent 1200 Series HPLC system equipped with a refractive index detector (RID). The temperature of the column was maintained at 35 ℃. Data collection and analysis were performed with Hewlett-Packard (Wilmington, DE) Chemstation software. The mobile phase for the system was 50:50 volumetric ratio of acetone and acetonitrile and was degassed before use in the system. The mobile phase flow rate was set to 1.0 mL/min. The components measured by HPLC include MG, DG, and TG. Standards for MG, DG, and TG were used to establish the calibration charts, which in turn were used to quantise samples that were analysed (Valério et al.,2010). Conversion of TG, selectivity of MG and yield of MG can be calculated based on Equation (3.2) to (3.4).

$$Conversion\ of\ TG, X = \frac{[TG]_0 - [TG]_t}{[TG]_0} \times 100\% \tag{3.2}$$

$$Selectivity\ of\ MG, S = \frac{[MG]_t - [MG]_0}{([MG]_t - [MG]_0) + ([DG]_t - [DG]_0)} \tag{3.3}$$

$$\text{MG yield} = \text{X} \times S \tag{3.4}$$

3.7 Characterisation of alkyd resin

3.7.1 Acid value (AV)

Acid value was measured by ASTM D 1639-90. 1ml of sample was taken and then mix with 4ml of diethyl ether and ethanol with ratio 1:1. A few drops of phenolphthalein are added and the mixture was then titrated with 0.1M KOH. Acid value can be calculated by using Equation 1 below.

$$\text{Acid value} = \frac{Volume\ of\ KOH\ used\ (ml) \times\ 0.1 \times 56}{resin\ sample\ (g)} \tag{3.5}$$

3.7.2 Average degree of polymerisation

The extent of the reaction, P and average degree of polymerization, DP were calculated based on the acid value obtained by using the following equations (Bobalek & Chiang,1964):

$$P = (C_o - C_t)/C_o \tag{3.6}$$

$$DP = (1 - P)^{-1} \tag{3.7}$$

Where C_o was the initial acid value

C_t was the acid value at time t.

3.7.3 Fourier Transform Infrared (FTIR)

Chemical nano structures of alkyd resin are being investigated. Structural information on the samples was attained using an FTIR Spectrometer (Spectrum 100 model,Perkin Elmer brand) equipped with an attenuated total reflectance (ATR) device in the wave number range 500–4500 cm^{-1} and resolution 4 cm^{-1}. The FTIR spectra will be taken in transmittance mode (Ong et al.,2015).

3.7.4 Nuclear magnetic resonance analysis (NMR)

^{13}C NMR. Spectra were obtained by Bruker, Advance III with operating frequency of 500 MHz at the central laboratory in Universiti Malaysia Pahang, Malaysia. Spectra were recorded at concentrations of 10–20% (w/v) (50–100 mg of sample in 0.5 mL of acetone-d) using 5 mm NMR tubes at the controlled temperatures of 21 ± 0.1^{o}C in the broadband proton decoupling mode. Full ^{13}C NMR spectra were obtained with the following acquisition parameters: 16 K data points, spectral width 200 ppm, acquisition time 1.1s, relaxation delay 1s, pulse width 45^{o} and 512 scans. High resolution carbonyl spectra were recorded with 16 K data points, spectral width 10 ppm, acquisition time 12–20s, relaxation delay 5s and pulse width $45–90^{o}$. Free induction decays (FIDs) were transformed by zero filling up to 32 K data points to yield a digital resolution of 0.05–0.08 Hz per point. All FIDs, prior to Fourier transformation (FT), were filtered using an exponential multiplication (0.2-0.4 Hz line broadening) for sensitivity enhancement. The peak intensities of the high resolution ^{13}C NMR carbonyl spectra were accurately quantified using the Topspin (Bruker) curve resolution program.

^{1}H NMR. The spectra of the synthesized alkyd resins were recorded on a Bruker, Advance III, 500 MHz spectrometer. Samples (20 mL) were placed in 5 mm NMR tubes and dissolved in acetone-d (0.7 mL) and DMSO-d_6 (20 mL).

3.7.5 Antimicrobial test

The antimicrobial activity of the MgO catalysed (0.01wt%, 0.02wt%, 0.04wt%, 0.06wt%) alkyd resin samples was determined by the Kirby–Bauer method. A number of microorganisms, such as Escherichia coli (ATCC 8739), Pseudomonas aeruginosa (ATCC 9027), Staphylococcus aureus (ATCC6538) and Salmonella sp. (ATCC 14028) were used in this experiment. The cultures were maintained in a nutrient broth and subcultured at regular intervals. The samples were prepared (10 mg mL^{-1}) using 0.5% DMSO. The microbial cultures in nutrient agar plates were inoculated using the spread plate technique and a cork borer was used to make a hole in the agar. The samples (10 mg mL^{-1}) were loaded in the hole and incubated at 33^{o}C for 18-24 h. A blank sample was maintained separately as a control. The diameter of the zone of inhibition after 24 hours of incubation was measured.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Preparation and characterisation of MgO sol

Synthesis of MgO nano sol was performed by dissolving $Mg(CH_3COO)_2.4H_2O$ in 100g glycerol at room temperature. Hydrazine was then added and the solution was then stirred continuously on a magnetic plate for 12 hours at room temperature. MgO sol with concentrations of 0.01wt%, 0.02wt%, 0.04wt% and 0.06wt% were prepared. The MgO sol was in cloudy white colour as shown in Figure 4.1. The crystallite size of MgO nanoparticles was determined from X-ray diffraction techniques.

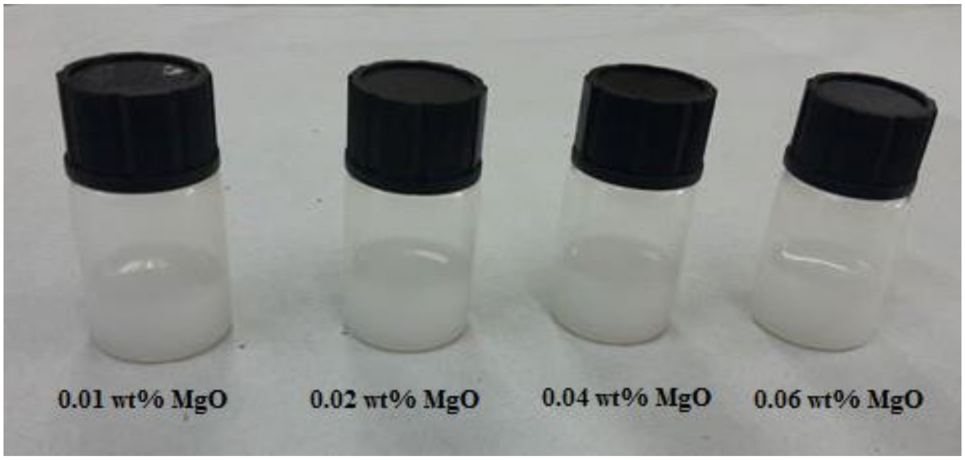


Figure 4.1 : MgO nano sol at different concentration

4.1.1 X-ray diffraction technique (XRD)

The X-ray diffraction pattern of the MgO is shown in Figure 4.2.

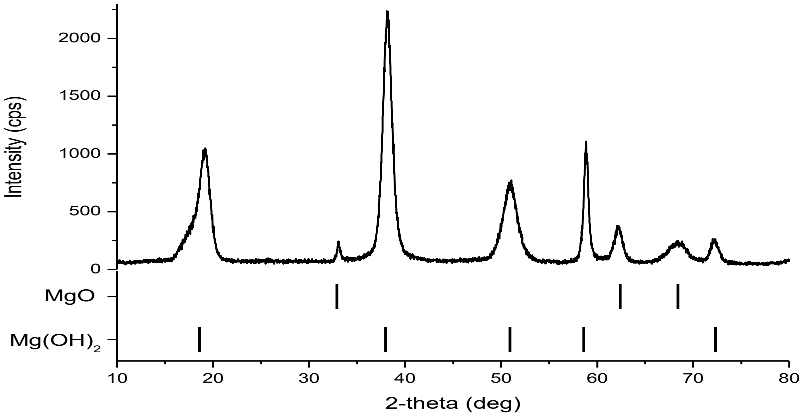


Figure 4.2 : XRD of Magnesium Oxide

The diffraction peaks indicated that the sample is crystalline in nature. As illustrated in Figure 4.2, significant XRD peaks of MgO can be observed at $2\theta = 32.96$, 62.10 and 68.40. As for the XRD peak of $Mg(OH)_2$, it was found at $2\theta = 18.97$, 38.10, 50.85, 58.87 and 72.16 respectively. The d values and intensity of peaks in the XRD pattern agreed with the International Centre for Diffraction Data (ICDD) of both MgO and $Mg(OH)_2$. The most intense peak of MgO and $Mg(OH)_2$ was observed to be at $2\theta = 62.10^o$ and 38.10 respectively. The calculation showed that the approximate crystallized size of MgO and $Mg(OH)_2$ is 78 nm and 77nm respectively. The broad XRD peaks obtained indicated the small particle size of MgO and $Mg(OH)_2$ (RSoniya & Nair,2003). $Mg(OH)_2$ is produced along through hydration of MgO due to the presence of water in the magnesium oxide precursor, Magnesium acetate tetrahydrate salt ($Mg(CH_3COO)_2.4H_2O$). Magnesium acetate increases the rate of hydration of MgO to $Mg(OH)_2$ (Filippou et al.,1999; van der Merwe et al.,2004).

4.2 Preparation and characterisation of MgO incorporated alkyd resin

Synthesis of alkyd resin involved the alcoholysis of palm oil with glycerol followed by the polyesterification with phthalic anhydride. The monoglyceride formation was then determined by methanol solubility test. Acid value was recorded to supervise the reaction progress. The end point was found when acid value reached equilibrium. The synthesised alkyd resin was then confirmed by FTIR, ^{1}H NMR and ^{13}C NMR. The antimicrobial activity of MgO incorporated alkyd resin against microorganisms was tested via the Kirby–Bauer method.

4.2.1 Effect of different catalytic systems on Alcoholysis

In order to investigate the effect of different concentration of MgO catalysed system on alcoholysis, methanol solubility test was carried out to determine the end point of alcoholysis and HPLC analysis to analyse the formation of monoglyceride quantitatively.

4.2.1.1 Methanol solubility test

Methanol solubility test was used to determine the end point of alcoholysis. The time required for conventional NaOH catalysed system (AR-1) and each MgO catalysed system (0.01wt%, 0.02wt%, 0.04wt% and 0.06wt% was denoted by AR-2, AR-3, AR-4 and AR-5 respectively) to reach the end point was shown in Figure 4.3.

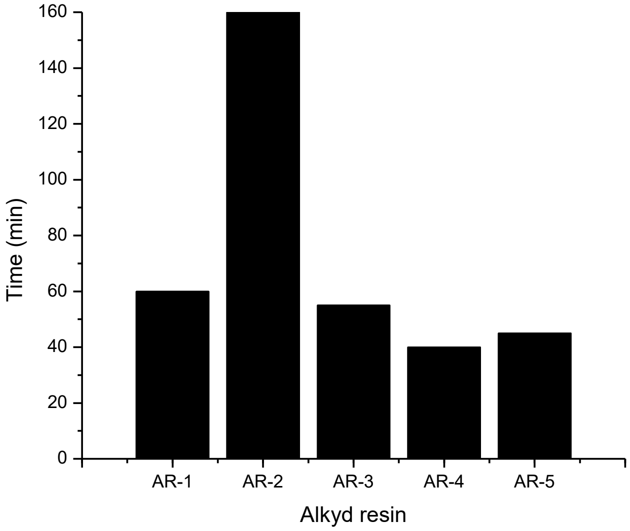


Figure 4.3 : Effect of different catalytic systems on alcoholysis at 240°C

From Figure 4.3, it was presented that reaction time consumed by alcoholysis was the shortest in 0.04wt% MgO catalysed system (40 minutes). According to Ferretti et al.

(2012), the strong base sites of MgO attracted proton from the OH groups of the glycerol molecules by forming glyceroxide and proton for primary and secondary hydroxyls. The Mg^{2+} cations helped to stabilise negatively charged reaction immediately and activate the triglyceride molecules and polarise C=O bond in order for the glyceroxide anion to attack positively charged carbonyl carbon of triglycerides. Due to the reason that MgO was a strong base catalyst, hence it was effectively used for monoglycerides formation.

4.2.1.2 HPLC analysis

Quantitative analyses of the alcoholysis products were conducted using an Agilent 1200 Series HPLC system. Figure 4.4 – 4.6 showed the effect of different MgO catalysed systems on selectivity, TG conversion and MG yield respectively. The relationship of the TG conversion with the selectivity was illustrated in Figure 4.7.

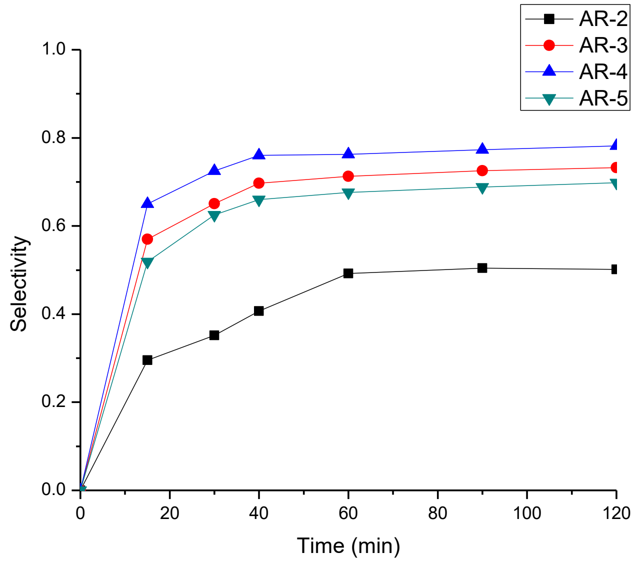


Figure 4.4 : Effect of different MgO catalysed systems on selectivity of MG at 240^{o}C

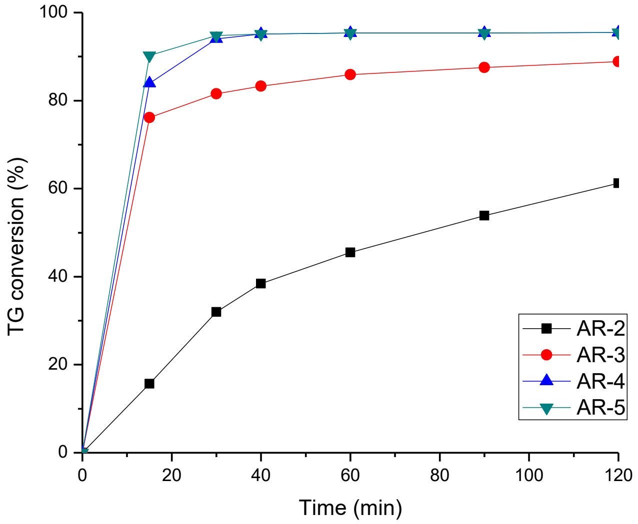


Figure 4.5 : Effect of different MgO catalyzed systems on TG conversion at 240^{o}C

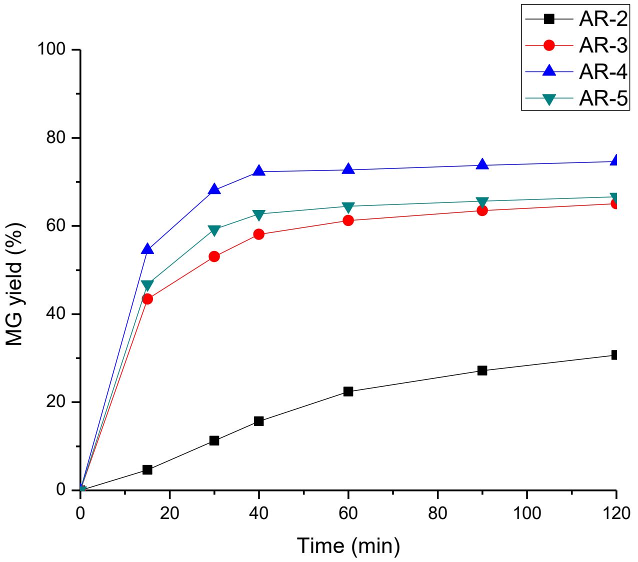


Figure 4.6 : Effect of different MgO catalysed systems on MG yield at 240^{o}C

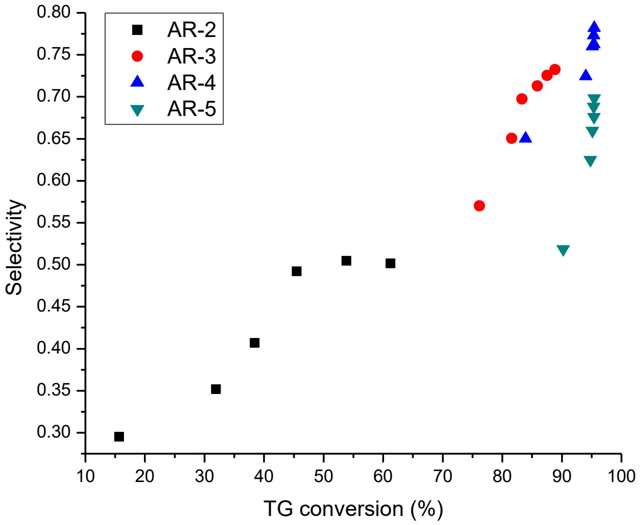


Figure 4.7 : Selectivity versus TG conversion at 240^{o}C

Figure 4.4 indicated the selectivity of MG at each catalyzed systems. It was observed that selectivity of each catalyzed systems increased as reaction time goes. 0.04wt% MgO catalyzed system showed significantly higher selectivity of MG compared to 0.06wt% MgO catalyzed system. Increase of MgO concentration did not result in higher selectivity of MgO, showing that 0.04wt% MgO is the most favorable catalyzed system in elevating the formation of monoglyceride.

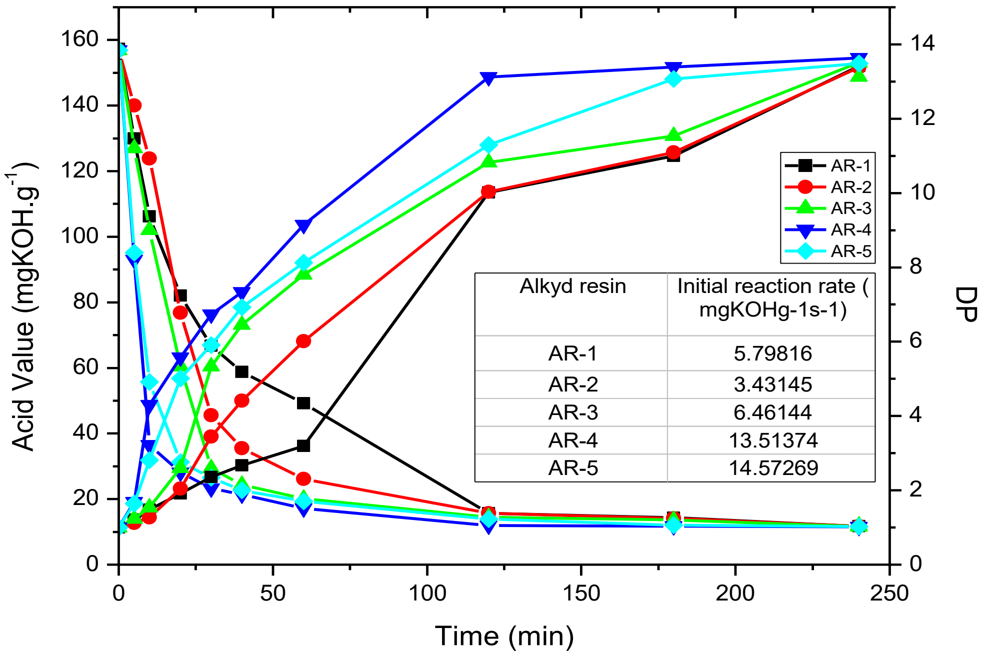
Figure 4.5 illustrated that the TG conversion reached equilibrium in 40 minutes of reaction time for 0.02wt%, 0.04wt% and 0.06wt% except for 0.01wt% MgO catalyzed system. It can also be observed that 0.04wt% MgO catalyzed system achieved a maximum TG conversion of ~95% faster than 0.06wt% MgO catalyzed system .

It was obviously depicted in Figure 4.6 that MG yield increased with increasing TG conversion as reaction time goes. During glycerolysis of palm oils at high temperature (240^{o}C) employing inorganic alkaline base catalyst (MgO) under a nitrogen gas atmosphere, the major product constituent in final equilibrium state was MG, along with traces of DG and occasionally unconverted TG was present too. Increasing amount of MgO catalyst promoted more TG to be converted and higher yield of MG. 0.04wt% of MgO catalysed glycerolysis showed the most positive outstanding result where the reaction reached equilibrium state in a very short time (40 min) and MG yield about ~75%. Further increase concentration of MgO catalyst did not affect the system significantly as we can see from figure that the yield of MG in 0.06wt% MgO catalysed system was lower than that of 0.04wt% MgO catalysed system.

As shown in Figure 4.7, 0.04wt% MgO catalysed system showed the higher selectivity of MG can be obtained at high conversion of TG than that of 0.06wt% MgO catalysed system. This obviously depicted that 0.04wt% MgO was the optimum catalyst concentration which speed up the alcoholysis reaction and more TG was converted.

4.2.2 Formation of alkyd resin

When the end point of alcoholysis was confirmed, reaction mixture was cooled to 140°C. Certain amount of phthalic anhydride was then added into the reaction mixture to start the polyesterification process.



Alkyd resin	Initial reaction rate (mgKOHg-1s-1)
AR-1	5.79816
AR-2	3.43145
AR-3	6.46144
AR-4	13.51374
AR-5	14.57269

Figure 4.8 : Plot of acid value and DP value against reaction time for different catalytic systems during polyesterification at 240°C. Table of initial reaction rates was shown inside the figure.

Figure 4.8 indicates that acid value decreased as the reaction went on. During the early stage of the reaction, the decrease in acid value is more rapidly than the later stage of the reaction. A similar variation in acid value was reported by Menkiti and Onukwuli (2011) and Bora et al. (2014b). The change pattern in acid value during both reactions was explained based on the desperate reactivity of primary and secondary hydroxyl groups of glycerol with carboxyl groups of phthalic anhydride (Goldsmith,1948). A primary hydroxyl group reacts faster than a secondary hydroxyl group, hence it is undeniable that the decrease in acid value at the early stages of the reaction corresponds to the period when primary hydroxyl groups react and the later stage represents the period when secondary hydroxyl groups react (Aigbodion & Okieimen,2001). The decrease in acid value is most rapid for 0.04wt% MgO catalysed alkyd resin compared to 0.01wt% and 0.02wt% MgO catalysed system. Thus, the rate of decrease in acid value can be said to depend on the amount of catalyst used. However, higher catalyst concentration did not influence the system significantly which we can see that 0.06wt% MgO catalysed system did not have much different trend of acid value from 0.04wt% MgO catalysed system. During the period where decrease in acid value is less rapid, it probably symbolised the beginning of formation of three dimensional network as a result of crosslinking of alkyd chains (Aigbodion & Okieimen,1996) and also increased viscosity of the reaction medium. The variation in the average degree of polymerization (DP) with reaction time is also shown in Figure 2. The increasing DP of the alkyd chains results in increasing viscosity of the reaction medium (Oladipo et al.,2013). The initial rates for each MgO catalysed systems can be determined by a three point method and are shown in the table inserted in Figure 2. It can be seen that the initial rate for 0.04 wt% and 0.06 wt% MgO catalysed system were almost close which were 13.5137 and 14.5726 mgKOHg^{-1}s^{-1} respectively. However, 0.04wt% MgO catalysed reaction reached equilibrium faster than 0.06 wt% MgO catalysed reaction. It was also noticed that 0.02,0.04 and 0.06wt% MgO catalysed reaction was much more effective than the conventional NaOH catalysed reaction.

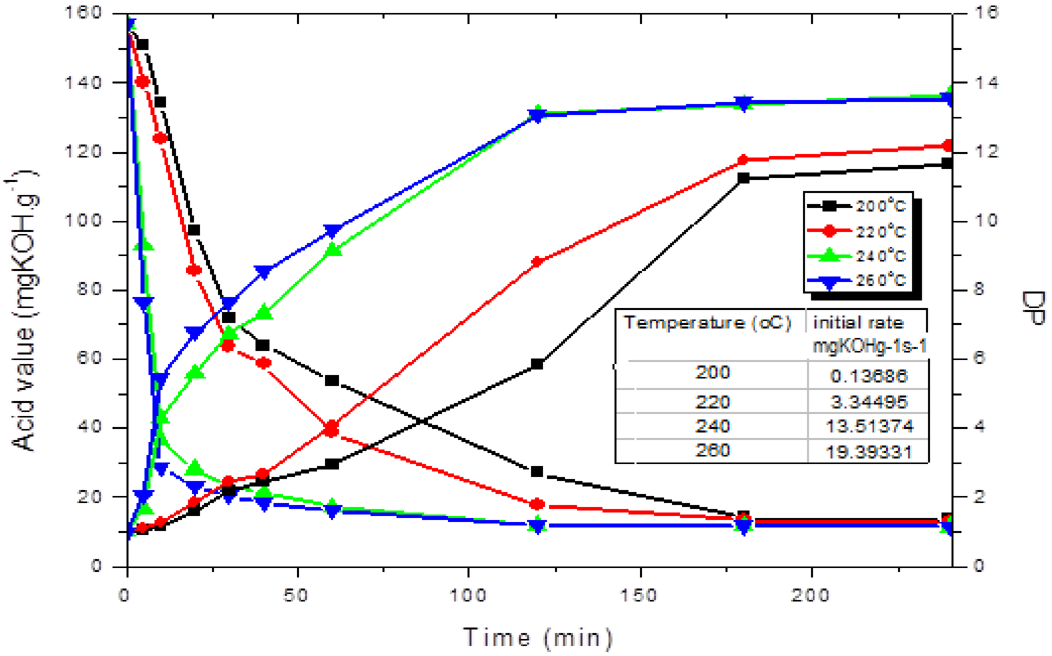


Figure 4.9 : Effect of temperature on 0.04wt% MgO catalysed system

Effect of temperature on 0.04wt% MgO catalysed system was investigated and presented in Figure 4.9. It was observed that temperature variation affect the reaction quite significantly during the early stage of reaction. The initial rates for 200, 220, 240 and 260^{o}C were 0.1368, 3.3449, 13.5137 and 19.3933 mgKOHg^{-1}s^{-1} respectively. The trend of initial rate was increasing with temperature. It can also be found that 0.04wt% MgO catalysed system at 240 and 260^{o}C achieved equilibrium at almost the same time. Therefore, in this case, 240^{o}C was chosen to be the optimum temperature to shorten the reaction period.

4.2.2.1 FTIR analysis

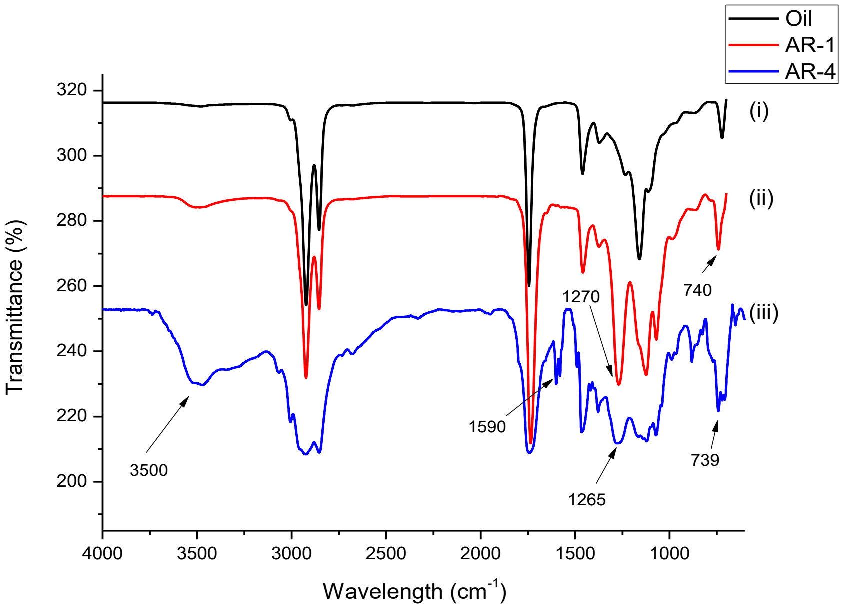


Figure 4.10 : FTIR spectra of oil, NaOH catalysed alkyd resin and MgO incorporated alkyd resin

The FTIR spectra of oil, NaOH catalysed alkyd resin and MgO incorporated alkyd resin are shown in Figure 4.10. In the FTIR spectrum of the oil, the broad absorption bands at 3640-3100cm^{-1} were corresponding to the O-H stretching vibration (Assanvo et al.,2015). The oil spectrum also showed a strong absorption within the range of 2820-2990 cm^{-1} due to aliphatic C-H stretching vibration (Bora et al.,2014a). The peak at 1744 cm^{-1} was attributed to the C=O stretching vibration ester group in triglyceride molecule (Bora et al.,2014b). C-H bending vibration was found within 1446-1470 cm^{-1}. Also, peak at 1160 cm^{-1} was corresponding to C-O-C stretching vibration of ester and that at 722 cm^{-1} was due to the methylene rocking vibration (Boruah et al.,2012).

The FTIR spectra of alkyd resins showed the presence of important linkages such as ester group and other characteristic peaks. Alkyd resin showed a peak at 1734 cm^{-1} whereas palm oil showed a peak at 1744 cm^{-1} for C=O stretching. The aromatic C=C stretching frequency was observed to be at 1590 cm^{-1} (Chiplunkar & Pratap,2016). A new characteristic peak of ester group was found in the spectrum of alkyd resins within the range of 1262-1276 cm^{-1}. In addition, the characteristic peak at 739 cm^{-1} was attributed to C–H bending of the aromatic ring contributed by phthalate units which indicated the formation of alkyd resin via polyesterification process (Ong et al.,2015).

4.2.2.2 NMR analysis

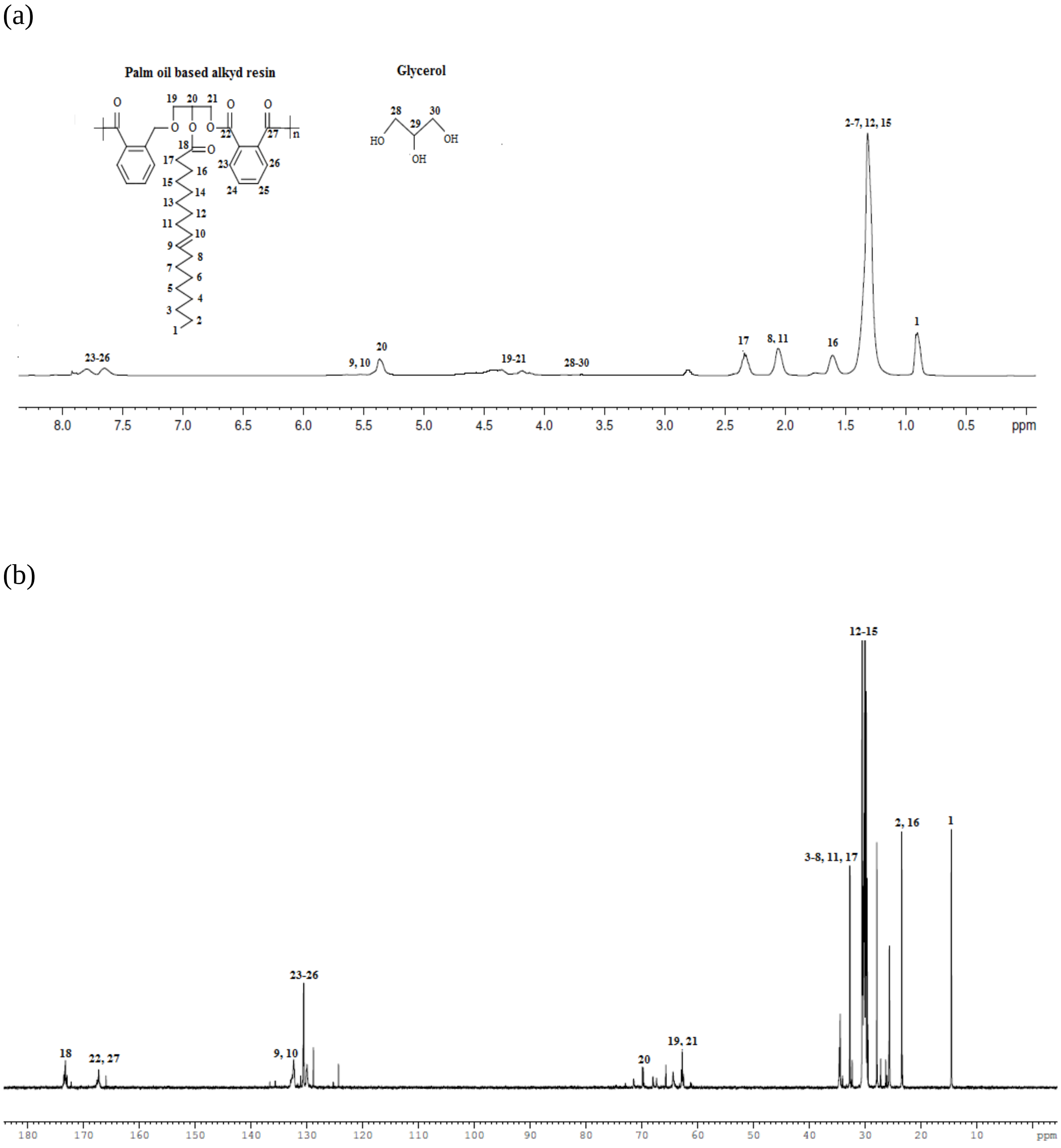


Figure 4.11 : (a) ^{1}H NMR and (b) ^{13}C NMR spectra of MgO catalysed alkyd resin

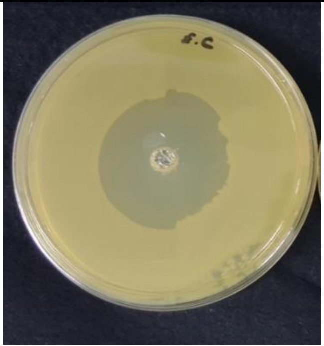
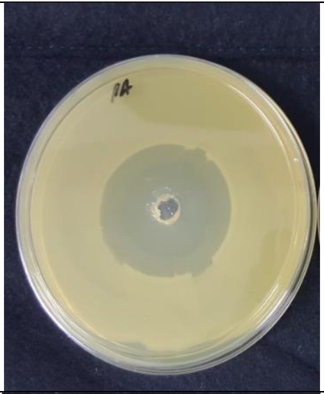
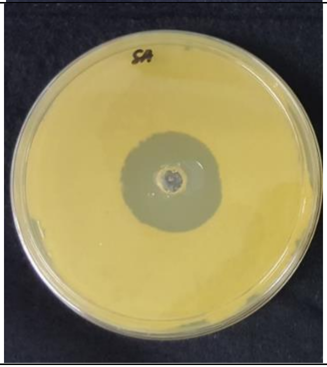
^{1}H NMR and ^{13}C NMR spectra of MgO catalysed alkyd resin are shown in Figure 4.11. Protons of terminal methyl group of the fatty acid chain were observed at 0.90 ppm. Peak at 1.31 ppm was seen for the protons of all the internal CH_2 groups present in the fatty acid chain whereas peak at 1.60 ppm was seen due to protons of CH_2 group attached next to the terminal methyl group. Characteristic peaks for protons of unsaturated carbons were found at 5.30–5.36 ppm (Boruah et al.,2012). The methylene (–CH_2–) protons next to hydroxyl groups in glycerol were seen at 3.60–3.85 ppm. Downfield shift of –CH_2– groups in the glyceride unit (4.12–4.35 ppm) was observed and this may be caused by the reaction of hydroxyls with PA where more electron were withdrawn from the ester to be presented (Ong et al.,2015). The peaks at 7.65–7.90 ppm were attributed to the deshielding effect by the anhydride group possessing aromatic ring which was absent in the ^{1}H NMR spectrum of the oil.

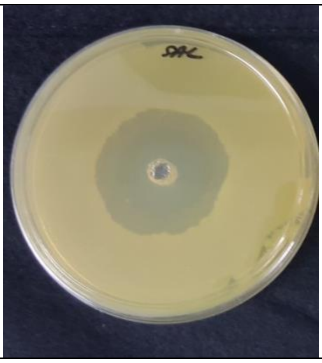
In ^{13}C NMR spectra, an obvious difference between the carbonyl ester of the pendent of oleate/palmitate and the phthalate ester can be observed at 172.00–173.00 ppm and 165–167 ppm respectively. It was also observed that the appearance of smaller peaks at 61.00–72.00 ppm corresponds to the methylene groups (–CH_2–) of the glyceride (Assanvo et al.,2015).

4.2.2.3 Antimicrobial study

The antimicrobial activity of 0.04wt% MgO incorporated alkyd resin against microorganisms was tested based on zone of inhibition as presented in Table 1.

Table 4.1 : Antimicrobial activity of MgO incorporated alkyd resin

Challenge Microorganism	Zone of inhabitation of MgO incorporated alkyd resin	**Average Diameter zone of inhibitation**
Escherichia coli		41.5mm
Pseudomonas aeruginosa		39mm
Staphylococcus aureus		30mm

Salmonella sp.		39.5mm

Gram negative (Escherichia coli, Pseudomonas aeruginosa, Salmonella sp.) and Gram positive (Staphylococcus aureus) microorganisms were selected for the test. The zones of inhibition of the alkyd resin were measured and recorded after 24h of incubation at 33 ^{o}C. It was found that the zone of inhabitation was 41.5 mm for Escherichia coli, 39 mm for Pseudomonas aeruginosa, 30 mm for Staphylococcus aureus and 39.5 mm for Salmonella sp. MgO incorporated alkyd resin showed good antimicrobial activity. The high surface area of MgO corresponded to the high potential number of reactive groups on the particle surface, which are expected to show high antibacterial activity (Pal et al.,2007). In general, MgO nanoparticles show a better antimicrobial activity towards gram-positive bacteria than towards gram-negative bacteria. This may be due to the difference in cell membrane structure of bacteria. The cell wall of gram-positive bacteria (*E. coli*, Pseudomonas aeruginosa, Salmonella sp.) mainly consist of thin layers of lipid A, lipopolysaccharide, and peptidoglycan, while on the other hands, gram-negative bacteria, *S. aureus* consists of a peptidoglycan layer (Tang & Lv,2014). Thus, the outer membrane of Gram-negative bacteria acts as a permeability barrier, so that the absorption of ions into the cell is reduced. (Espitia et al.,2012). As a result, E. coli, Pseudomonas aeruginosa and Salmonella sp are more resistant to MgO nanoparticles compared to S. aureus.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

From this study, it can be concluded that palm oil based alkyd resins was successfully synthesized over colloidal MgO nanoparticles.

- The well dispersion of MgO nanoparticles in the reaction mixture formed a stable suspension which had successfully elevated the rate of reaction of both alcoholysis and polyesterification compared to the conventional NaOH catalyzed system.
- 0.04wt% MgO catalyzed system was chosen to be the optimum catalytic system where alcoholysis completed at 40 minutes and proceeded with polyesterification.
- The formation of alkyd resin was confirmed through FTIR, ^{1}H NMR and ^{13}C NMR. These analysis clearly showed the formation of ester linkages which proved that alkyd resin was formed.
- Colloidal MgO nanoparticles was reported for alkyd resin preparation with dual role: catalyst and antimicrobial agent which added value to the alkyd resin synthesised.

5.2 Recommendation

Substituting the conventional non-renewable resources with easily available and environmental friendly materials is always a challenge for contemporary science. The novelty of this research work is synthesising MgO incorporated alkyd resin which is environmental friendly by using the renewable glycerol and a very small amount of MgO. More importantly, the MgO incorporated is able to reduce the reaction time and at the same time, be the antimicrobial agent to fight against microorganisms. This kind of MgO incorporated alkyd resins are of interest to the coating industry. Hence, further investigation on the physical properties of the alkyd resins in terms of viscosity, drying time and solubility and also the mechanical properties of the alkyd resins in terms of hardness, adhesion and impact strength.

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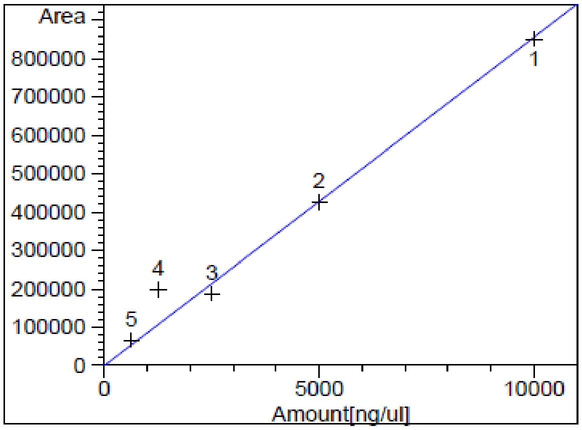
APPENDIX

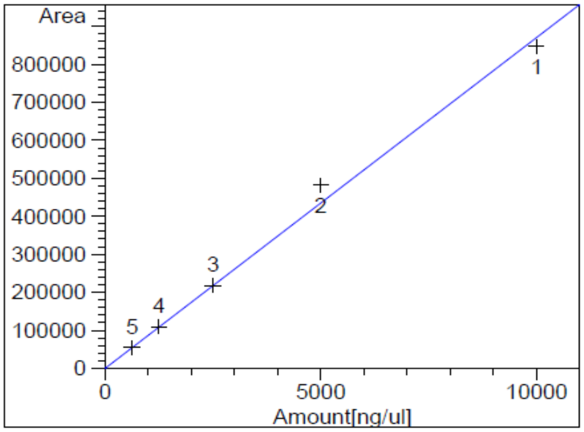
HPLC DATA

MG Standard curve



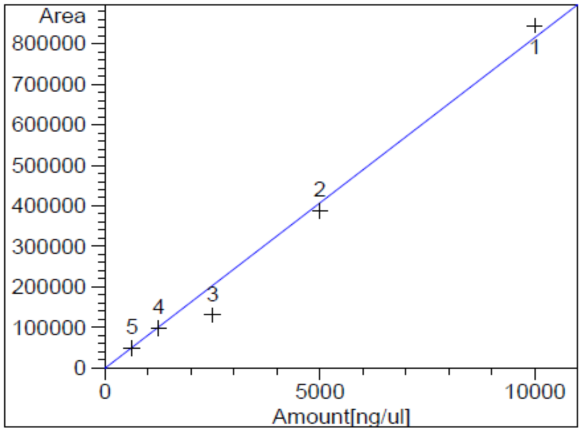
```
MG RID at exp. RT: 3.510
RID1 A, Refractive Index Signal
Correlation:             0.99533
Residual Std. Dev.: 47929.61320
Formula: y = mx
      m:      85.63756
      x: Amount
      y: Area
```

DG Standard curve



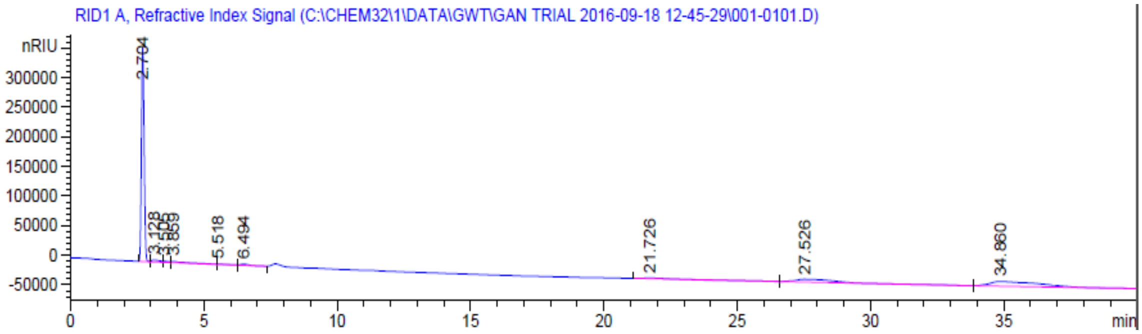
```
DG RID at exp. RT: 7.066
RID1 A, Refractive Index Signal
Correlation:             0.99862
Residual Std. Dev.: 26388.66445
Formula: y = mx
      m:      87.08164
      x: Amount
      y: Area
```

TG Standard curve



```
TG RID at exp. RT: 30.495
RID1 A, Refractive Index Signal
Correlation:             0.99632
Residual Std. Dev.: 40474.40415
Formula: y = mx
      m:      81.55626
      x: Amount
      y: Area
```

Chromatogram for Oil sample



Chromatogram for alkyd resin sample